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Photochemical Reactions of Enamino Ketones[1)]

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Photochemical reactions of *N*-aryl enamino ketones including one enone system and one divinylamine system in the molecule were examined. Photochemical behaviours of *N*-aryl enamino ketones differed for the tertiary and secondary amines involved. While 5,5-dimethyl-3-(*N*-methylanilino)cyclohex-2-en-1-one gave an oxidative cyclization product, 3-anilino-5,5-dimethyl-cyclohex-2-en-1-one gave two major products and a minor one. One of the major products was characterized as 3,3-dimethyl-5-hydroxy-3,4-dihydro-1-benzazocines by their elemental analyses and spectroscopic properties. The compounds showed 6π system pseudo aromaticity in their NMR spectra. The temperature-dependent NMR signals for *gem*-dimethyl protons were due to the flapping of the 8-membered ring. The reduction product with diborane was identified as 1,2,3,4,5,6-hexahydro-1-benzazocine by comparison with an authentic sample. The other major product was a ketene adduct and the minor product, a lactone.

N-Aryl enamino ketones involve both a conjugated enone and a divinylamine system in the molecules. Molecular rearrangement reactions of conjugated enones such as cyclohexenones are known as those of cyclohexadienones.[2)] Divinylamines are isoelectronic with pentadienyl anion. The former was reported to give similar cyclization products.[3)] Linschitz and Grellmann[4)] obtained carbazole derivatives on irradiation of *N*-substituted diphenylamines. Chapman and his co-workers[5)] reported on the nonoxidative photocyclization of *N*-methylaniline enamines to give *trans*-hexahydrocarbazoles. However, all the reactions were of *N*-substituted tertiary amines and we could find no report of photoreactions of *N*-unsubstituted secondary enamines, except for that of diphenylamine which is converted into carbazole with a considerable number of side reactions.[4)] Enamino ketones including these two functional groups are also of importance as intermediates in organic syntheses,[6)] and various investigations have been reported.[7-10)] Photoreactions

1) Preliminary report: K. Yamada, T. Konakahara, S. Ishihara, H. Kanamori, T. Itoh, K. Kimura, and H. Iida, *Tetrahedron Lett.*, **1972**, 2513.

2) W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., "Advances in Photochemistry," John Wiley & Sons, New York, London (1963).

3) A. Schönberg, G. O. Schenk, O. A. Neumüller, "Preparative Organic Photochemistry," 2nd Edn., Springer-Verlag New York Inc. (1968), p. 138.

4) a) K.-H. Grellmann, G. M. Sherman, and H. Linschitz, *J. Amer. Chem. Soc.*, **85**, 1881 (1963); H. Linschitz and K.-H. Grellmann, *ibid.*, **86**, 303 (1964); b) Groen *et al.* reported photocyclization of phenylthioethenes to give a "normal" and an "abnormal" product in low yields (S. H. Groen, R. M. Kellog, J. Buter, and H. Wynberg, *J. Org. Chem.*, **33**, 2218 (1968)).

5) O. L. Chapman, G. L. Eian, *J. Amer. Chem. Soc.*, **90**, 5329 (1968); O. L. Chapman, G. L. Eian, A. Bloom, and J. Clardy, *ibid.*, **93**, 2918 (1971).

6) a) M. Regitz and H. Schwall, *Ann. Chem.*, **728**, 99 (1969); b) R. J. Friary, R. W. Frank, J. F. Tobin, *Chem. Commun.*, **1970**, 283, c) A. G. Cook, "Enamines: Synthesis, Structure, and Reactions," Marcel Dekker, New York and London (1969).

7) For example: A. I. Meyers, A. H. Reine, and R. Gault, *J. Org. Chem.*, **34**, 698 (1969); and references cited therein.

8) a) J. Freimanis, I. Mazeika, *Tero. Eksp. Khim.*, **4**, 601 (1968); *Chem. Abstr.*, **71**, 2865a (1969); b) J. Freimanis, *Zh. Org. Khim.*, 1067 (1967); *Chem. Abstr.*, **68**, 68348d (1968); c) J. Freimanis, J. Stradins, and I. Kravis, *Zh. Obshch. Chim.*, **39**, 631 (1969); *Chem. Abstr.*, **71**, 35474a (1969).

9) C. Kashima, M. Yamamoto, and N. Sugiyama, *J. Chem. Soc., C*, **1969**, 111.

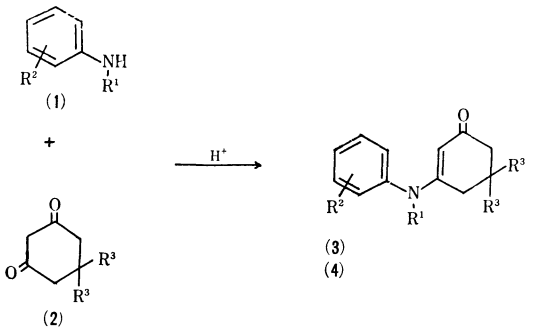
10) J. V. Greenhill, *J. Chem. Soc., B*, **1969**, 299.

of this type of compound, however, have been investigated only for the photocycloaddition of lycopodine derivatives with allene[11a] or methyl methacrylate,[11b] the photodimerization of 1-methylthymine,[12] photoreduction of kynuric acid with sodium sulfite,[13] and the photoisomerization of 1,2-diphenyl-6-methyl-2,3-dihydro-4-pyridone.[14]

In this paper we wish to report photocyclization reactions of *N*-aryl enamino ketones.[1] Irradiation of 3-(*N*-methylanilino)-5,5-dimethylcyclohex-2-en-1-one in nitrogen-saturated ether gave 2,3-dihydro-2,2,9-trimethylcarbazol-4(1*H*)-one in good yields. No corresponding product was obtained on irradiation of an *N*-unsubstituted 3-anilinccyclohex-2-en-1-one derivative in benzene solution. This compound gave two major and one minor products. One of the major products was characterized as 3,3-dimethyl-5-hydroxy-3,4-dihydro-1-benzazocine by its spectroscopic properties. The reactions of five *N*-unsubstituted enamino ketones (Scheme I) were investigated. The enamino ketones were prepared by the condensation of cyclohexane-1,3-diones with the corresponding anilines in the presence of a trace amount of concentrated sulfuric acid or *p*-toluenesulfonic acid in toluene (see Experimental).

Results and Discussion

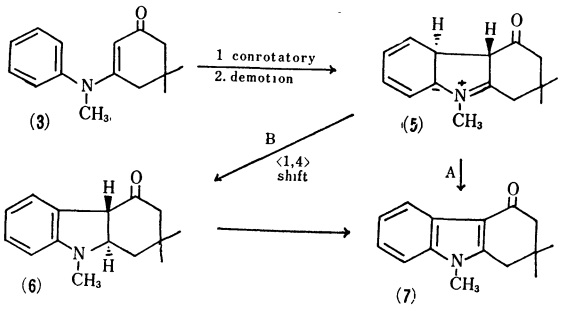
Preparation of Enamino Ketones. The enamino ketones (**3** and **4**) were prepared from aniline derivatives (**1**) and 5,5-dimethylcyclohexane-1,3-dione or cyclohexane-1,3-dione (**2**) in the presence of sulfuric acid or *p*-toluenesulfonic acid by azeotropic distillation employing a Dean-Stark trap. The enamino ketones (**4c** and **4b**) were prepared by methylation of the hydroxyl derivatives with diazomethane. Ketones (**3** and **4**) are illustrated in Scheme 1 (for the yields and physical data see Experimental). Their spectral data are in line with the expected structures.



(**3**) $R^1=CH_3$, $R^2=H$, $R^3=CH_3$
(**4**) **a**, $R^1=R^2=H$, $R^3=CH_3$
b, $R^1=H$, $R^2=3'$-Cl, $R^3=CH_3$
c, $R^1=H$, $R^2=4'$-OCH_3, $R^3=CH_3$
d, $R^1=H$, $R^2=3'$-OCH_3, $R^3=CH_3$
e, $R^1=R^2=R^3=H$

Scheme 1.

Irradiation of 3-(N-Methylanilino)-5,5-dimethylcyclohex-2-en-1-one. Irradiation of 3-(*N*-methylanilino)-5,5-dimethylcyclohex-2-en-1-one (**3**) in ether (5.5×10^{-3} M) with a 450-W Pyrex-jacketed immersion lamp (>3000 Å) under nitrogen gave a major product together with a minor one. The major product (mp 137—138 °C, yield, 38%) isolated after the evaporation of ether and crystallization from *n*-hexane–benzene (4 : 1), was identified as 2,3-dihydro-2,2,9-trimethylcarbazol-4(1*H*)-one (**7**) by comparison of spectroscopic properties with a known sample.[15] A benzene solution of **3** was also irradiated to give the same product. Attempted isolation of the minor product by column chromatography on silica gel was not successful. The photoproduct, which may be a nonoxidative hexahydrocarbazole intermediate, could not be identified or isolated, since it was unstable under these conditions. The oxidative photochemical cyclization can be considered as an electrocyclic reaction of a divinylamine. Its excited-state (probably n,π^* triplet[16]) closure should take a conrotatory course according to the Woodward-Hoffmann rule.[5,17] The initially formed dipolar ion intermediate (**5**) analogous to the observed one in oxidative photocyclization of diphenylamine,[4] seemed to give a final product through two possible reaction paths (Scheme 2).



Scheme 2.

Path A gives the final product directly by oxidation with the residual air in the flask or elimination of two hydrogen atoms due to enolization; path B involves a *trans*-hexahydrocarbazole intermediate (**6**) formed by a thermal, suprafacial<1,4>sigmatropic shift of a hydrogen atom.

In order to examine the molecular orbital implication of this reaction, the bond orders (p_{rs}), frontier densities (f_r), and superdelocalizabilities (S_r) were

11) a) K. Wiesner, I. Jirkovsky, M. Fishman, and C. A. J. Williams. *Tetrahedron Lett.*, **1967**, 1523; b) Z. Koblicova and K. Wiesner, *ibid.*, **1967**, 2563, and analogous reaction was reported by Cantrell (T. S. Cantrell, *Tetrahedron*, **27**, 1227 (1971)).

12) N. J. Turro, G. S. Hammond, J. N. Pitts, and D. Valentine, "Annual Survey of Photochemistry," Vol. 1, Wiley-Interscience, New York, London, Sydony and Toronto (1969), p. 147.

13) T. Tokuyama, S. Senoh, T. Sakan, K. S. Brown, Jr., and B. Witkop, *J. Amer. Chem. Soc.*, **89**, 1017 (1969).

14) C. Kashima, M. Yamamoto, Y. Sato, and N. Sugiyama, This Bulletin, **42**, 3596 (1969).

15) W. Sucrow, E. Wiese, *Chem. Ber.*, **103**, 1767 (1970).

16) The photoreaction of enamino ketone (**3**) carried out with a low-pressure mercury arc lamp, filtered with a quartz plate (2537 Å), gave the same photoproducts as those obtained with a high-pressure mercury arc lamp but in a lower yield (**7**, 13%). Benzene was employed as the solvent, and the minor product was not isolated.

17) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, GmbH, Academic Press Inc., New York (1970).

calculated for 3-(*N*-methylanilino)-5,5-dimethylcyclohex-2-en-1-one (**3**), and the values compared with experimental results. The usual parameters[18] were used in the calculations. The bond orders in the ground state and in the first excited state between C–3 and C–7 are calculated as follows:

	G	n,π^*	π,π^*
P_{37}	0.0861	0.0785	−0.0540

S_r values for radical reaction are also illustrated in Fig. 1. Since the P_{37} value for the n,π^* excited state is larger than that of π,π^*, the photoreaction occurs more favorably through the former state. This is in good agreement with experimental facts.[16] The S_r and f_r values for radical reaction at C–3 and C–7 indicate that these positions are more reactive than the others.

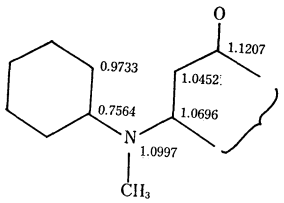


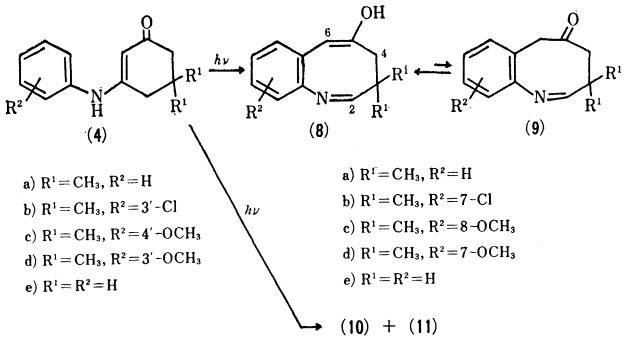
Fig. 1.

$S_r^{(R)}$ values of the enamino ketone (**3**)

Irradiation of 3-Anilino-5,5-dimethylcyclohex-2-en-1-one. For the irradiation of 3-anilino-5,5-dimethylcyclohex-2-en-1-ones (**4**), a benzene solution was employed because of lower solubility of enamine ketones (**4**) in ether. The solution of **4** was irradiated for 0.5 to 2 hours under the same conditions as for **3** to give two major products (**8** and **10**) and a minor one (**11**) (Scheme 3). Yields of **8a**—**e** are summarized in Table 1. In the case of (**4b**) the tlc R_f values (silica gel, benzene–ethyl acetate 9 : 1) were 0.81, 0.68, and 0.54, respectively. One of the two major products with a R_f value 0.68, **8b**, was characterized as 7-chloro-3,3-dimethyl-5-hydroxy-3,4-dihydro-1-benzazocine by its elemental analysis and physical properties. Elemental analysis and high resolution mass spectrum indicate the molecular formula $C_{13}H_{14}NOCl$, formed by elimination of methylene group from the starting material (**4b**). The molecular formula involves one oxygen atom, but the IR spectrum showed a carbonyl band at 1698 cm^{-1} and a hydroxy-absorption at 3324 cm^{-1}. This coexistence of the carbonyl and a hydroxy-absorption indicates the presence of a keto-enol equilibrium (Scheme 3). Measurements of IR spectra of **8b** in various solvents showed a remarkable change in the ratio $D(\nu_{OH})/D(\nu_{C=O})$ of the absorbance for the two absorption bands (Table 2). This indicates that solvation in polar solvents stabilizes the enol form giving rise to an increase of the ratio $D(\nu_{OH})/D(\nu_{C=O})$. This is also supported by the fact that only absorption due to enol form at 3170 cm^{-1} and 1198 cm^{-1} was observed in tetrahydrofuran solution highly diluted with carbon tetrachloride.

TABLE 1. SUMMARY OF YIELDS OF (**8**)

Compound	Conversion (%)	Yield (%)
8a	25	14
8b	19	12
8c	25	20
8d	90	17
8e	4	3



Scheme 3.

TABLE 2. SUMMARY OF IR SPECTRAL DATA OF **8b** IN VARIOUS SOLVENTS

Solvent	ν_{OH} (cm^{-1})	$\nu_{C=O}$ (cm^{-1})	$\nu_{C=N}$ (cm^{-1})	ν_{C-O} (cm^{-1})	$D(\nu_{OH})/D(\nu_{C=O})$
KBr	3324	1698	1630	1200	0.4
CCl_4	3200	1713	1640	1200	1.0
Dioxane	3175	1713	1632	1198	2.0
THF[a]	3170	1713	1632	1198	2.7
CCl_4[b]	3170	—	—	1198	—

a) THF: tetrahydrofuran.
b) THF solution **8b** was highly diluted with CCl_4. Only the absorption bands at 3170 (strong) and 1198 cm^{-1} (medium) were observed.

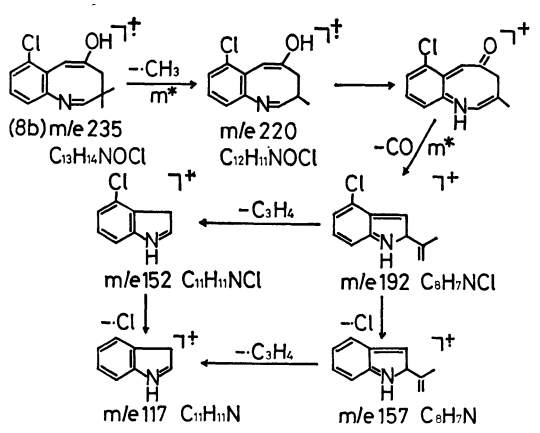
The absorption bands at 1382, 1367, and 1215 cm^{-1} indicate the presence of *gem*-dimethyl group. This was further supported in the NMR by the presence of a signal at $\delta(CCl_4, TMS)$ 1.28 (singlet, 6H) and by the absence of a signal assignable to a methine proton in the range δ 2—5 (Table 3). The mass spectrum showed a fragment ion peak ($C_{12}H_{11}NOCl$, 220.0400, base) formed by elimination of methyl radical from the molecular ion ($C_{13}H_{14}NOCl$, 235.0743) with a "flat-topped metastable" ion (m^*=206), indicating the presence of a *gem*-dimethyl group (Scheme 4-1).[18,19] A broad NMR signal at δ 6.18 (1H) exchangeable with deuterium oxide and a singlet-like signal at δ 6.98 (1H) were assigned to the enolic hydroxyl proton at C–5 and vinyl proton at C–6, respectively. An aryl substitution of the vinyl group shifts the *gem*-proton signal downfield to the range δ 6—8.5 compared with that of alkyl substituted one (δ *ca.* 5.5) because of deshielding by the ring. The IR spectra of **8a** and **8e** (753 and 694 cm^{-1}; 753 and 692 cm^{-1}) and their NMR spectra indicate the presence of an *ortho*-

18) a) L. E. Orgel, T. L. Cottrel, W. Dick, and Sutton, *Trans. Faraday Soc.*, **47**, 113 (1951); b) A. Streitwieser, Jr. and P. M. Nair, "Conference of Hyperconjugation," Pergamon Press, London (1959).
19) F. W. McLafferty, "Mass Spectrometry of Organic Ions," Academic Press, New York, London (1963), p. 641.

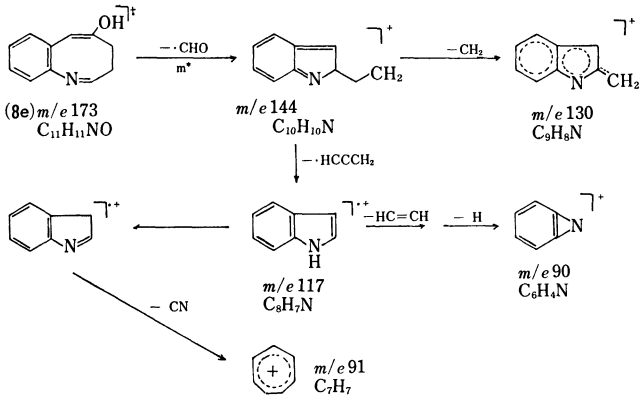
Table 3. Summary of NMR spectral data of (**8**)[a]

Compd.	Position										
	2	3	4	5-OH[c]	6	7	8	9	10	R^1	R^2
8a[b]	6.56 (s, 1H)	—	2.33 (s, 2H)	6.17 (bs, 1H)	7.10 (s, 1H)	7.37 (m, 1H)	6.99[f] (t, d, 2H)		7.37 (m, 1H)	1.28 (s, 6H)	—
8b	6.37 (s, 1H)	—	2.24 (s, 2H)	6.22 (bs, 1H)	6.98 (s-l[e], 1H)	—	6.8[g] (d, d, 1H) or 6.82[h] (d, d, 1H)	7.13[i] (d, d, 1H)	6.82[h] (d, d, 1H) or 6.8[g] (d, d, 1H)	1.82 (s, 6H)	—
8c	6.19 (s, 1H)	—	2.22 (s, 2H)	5.82 (bs, 1H)	6.77 or 6.85 (s-l, 1H)	6.85 or 6.77 (s-l, 1H)	—	6.92[j] (d, d, 1H)	6.72[k] (d, 1H)	1.25 (s, 6H)	3.71 (s, 3H)
8d[b]	6.52 (s, 1H)	—	2.30 (s, 2H)	6.11 (bs, 1H)	6.57 (s-l, 1H)	—	6.61[l] or 6.47 (d, d, 1H)	7.20[m] (t, 1H)	6.47[l] or 6.61 (d, d, 1H)	1.28 (s, 6H)	3.79 (s, 3H)
	6.59[d,n] (t, 1H)	2.62[d,o] (t, d, 2H)	2.37[p] (t, 2H)	6.18 (bs, 1H)	7.02 (s, 1H)	7.18 (m, 1H)	6.80 (m, 2H)		7.18 (m, 1H)	—	—

a) Values (100 MHz in CCl_4), b) In $CDCl_3$, c) Disappeared with the addition of D_2O, d) Demonstrated by double resonance, e) s-l; singlet-like, f) $J_{ortho}=7.5$, $J_{meta}=2.4$ Hz, g) $J_{ortho}=7$, $J_{meta}=ca.$ 7.5 Hz, h) $J_{ortho}=8.7$, $J_{meta}=ca.$ 2.5 Hz, i) $J_{ortho}=8.7$, $J_{ortho}=7$ Hz, j) $J_{9,10}=8$, $J_{7,9}=3$ Hz, k) $J_{9,10}=8$ Hz, l) $J_{8,9}=8$, $J_{8,10}=3$ Hz, m) $J_{8,9}=J_{9,10}=8$ Hz, n) $J_{2,3}=3.0$ Hz, o) $J_{3,4}=4.5$, $J_{2,3}=3.0$ Hz, p) $J_{3,4}=4.5$ Hz.



Scheme 4-1.



Scheme 4-2.

disubstituted phenylene group. The latter showed AA'BB' patterns. The spectroscopic data showed 1,2,3-trisubstitution of **8b** and **8d**, and those of **8c** 1,2,4-trisubstitution (see Experimental and Table 3). A strong C–N stretching absorption at 1295 cm^{-1} and a C=N stretching absorption at 1630 cm^{-1} in the IR spectrum of **8b** suggested the presence of an anil system. This was also supported by an NMR signal at δ 6.37 (singlet, 1H) (see Tables 2 and 3). The singlet signal indicated that the carbon adjacent to the anil group was quaternary. The corresponding signal of **8e** at δ 6.59 was a one-proton triplet (J=3.0 Hz), coupled with a two-proton triplet signal at δ 2.62 (J=4.5 and 3.0 Hz) for the methylene protons. The coupling was demonstrated by the double resonance. A two-proton triplet at δ 2.3 (J=4.5 Hz) of **8e**, coupled with the methylene described above, corresponded to a two-proton singlet at δ 2.24 of **8b**.[20,21]

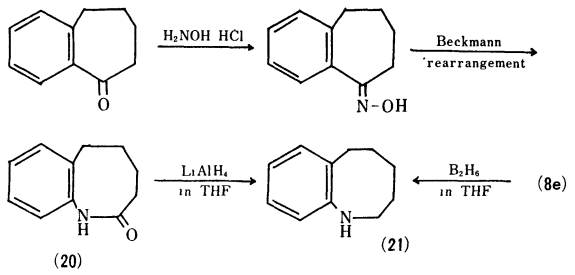
Structure **8** including a dihydroazocine ring, can now be written. Its UV spectrum showed more reasonable absorption maxima (λ_{max} (EtOH) 257 (ε 15800) and 305.5 nm (7010)) for the chromophores compared with those of the related compounds (styrene, λ_{max} (EtOH) 244 (ε 12000) and 282 nm (500); *ortho*-aminostyrene, λ_{max} 240 (ε 10000) and 332 nm (1600); diethylketone-anil, λ_{max} 250 (ε 12000) and 300 nm (2000); 2-methoxyazocine, λ_{max} (isooctane) 214 (ε 8750) and 305 nm (350)).

The mass spectrum of **8b** showed three intense peaks (except isotopic peaks due to ^{37}Cl) at *m/e* 235 (molecular ion $M^{+\cdot}$ peak, 40.5% of base), 220 (base), and 192 (40.2% of base) with some weak peaks (Scheme 4-1). The empirical formula of each fragment ion was determined by means of high-resolution mass spectrometry (see Experimental).

The structure was confirmed by the fact that reduction of **8e** with diborane in tetrahydrofuran gave a product identical with authentic 1,2,3,4,5,6-hexahydro-1-benzazocine (**21**), which was prepared from benzo-2-cycloheptenone oxime (Scheme 5).

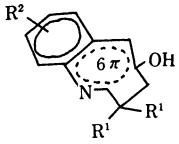
20) No signals assignable to ring-juncture hydrogens for one of the tautomeric isomers, 3,4-dihydro-3,3-dimethylcyclopent[*b*]-indolin-1(2*H*)-one, were found, which were found at δ 3.5 (multiplet) in the spectrum of 1*b*,4-dimethyl derivative.[21]

21) The NMR spectral data were kindly supplied by Prof. Dr. Yoshio Ban (Hokkaido University).



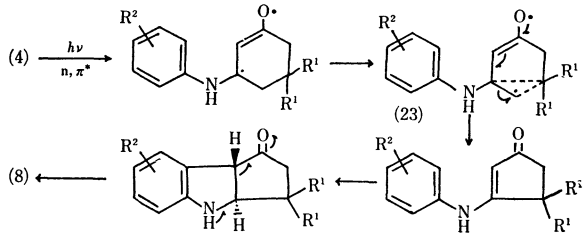
Scheme 5.

Eu(dpm)$_3$-induced shifts in the NMR were used for obtaining information on the conformation of **8b**. The shift-values ($\Delta Eu=\delta_{Eu}-\delta_0$) for the *gem*-dimethyl were 0.93 and 1.01 ppm (in CCl_4) and 1.16 ppm for methylene. The former methyl signal was assignable as *endo*, and the latter as *exo* (Formula **22**). The temperature-dependent NMR signal for the *gem*-dimethyl of **8b** may be considered to be due to the 8-membered ring-flapping of **22**: half height width $b_{1/2}$ 1.25 Hz at 36 °C; 1.75 Hz at −10 °C; 3.65 Hz at −20 °C; 4.90 Hz at −30 °C. The stability of the compounds, the downfield-shifts of signals for protons at 2- and 6-positions, and the stability of the enol-form can be



(**22**)

attributed to the 6π system pseudo aromaticity. The spectra (UV, IR, NMR, and mass) of other derivatives prepared from (**4a**—**e**) were in accord with the structures (**8a**—**e**). A possible reaction path is illustrated in Scheme VI. The higher yield of **4a**—**d** than of **4e** is considered to be due to the stabilization of the radical or charge at the *tertiary* center of (**23a**—**d**, $R^1=CH_3$).



Scheme 6.

Irradiation of hydroxyl derivatives of the enamino ketone (**4**, $R^1=CH_3$, $R^2=3'$ -and 4'-OH) in benzene gave rise to less destruction of the starting material, isolation of traces of similar photoproducts not being possible.

The other major product (**10**) was ketene adduct and the minor one (**11**) a lactone (see Experimental).

Experimental

All melting points and boiling points are uncorrected. Melting points were measured with a Yanagimoto micro melting point apparatus. Ultraviolet spectra were recorded on a Hitachi EPS-3T spectrophotometer. Infrared spectra were recorded on Model IR-G and IR-S (Japan spectroscopic Co., Ltd.) spectrometers. NMR spectra were recorded with JNM 4H-100, Hitachi H-60 and Varian HA-100D high resolution spectrometers for solutions in deuteriochloroform, carbon tetrachloride, or methanol-d_4. The temperature-dependent NMR spectra were measured on a Varian A-60D in a deuteriochloroform solution at −30, −20, −10, and 36 °C. Chemical shifts are reported in δ (internal tetramethylsilane). The mass spectra were obtained with Hitachi RMU-6E (for normal mass spectra), JMS-OlSG (Japan Electron Optics Lab., for high resolution mass spectra), and CEC11OB (for high resolution mass spectra) mass spectrometers at 70 eV. Elemental analyses were performed at the Institute of Physical and Chemical Research.

*Preparation of Enamino Ketones (**3**) and (**4a**).* 5,5-Dimethyl-3-(*N*-methylanilino)cyclohex-2-en-1-one (**3**) and 3-anilino-5,5-dimethylcyclohex-2-en-1-one (**4a**) were prepared from 5,5-dimethylcyclohexane-1,3-dione[22] and anilines (*N*-methylaniline and aniline) in the presence of sulfuric acid by azeotropic distillation with toluene; **3**: mp 80 °C (lit,[9] 81 °C), $M^{+\cdot}$ 229; **3a**: mp 184—185 °C (lit,[9] 181 °C).

*3-(3'-Chloroanilino)-5,5-dimethylcyclohex-2-en-1-one (**4b**).* *m*-Chloroaniline (1.96 g, 0.015 mol), 5,5-dimethylcyclohexane-1,3-dione (2.14 g, 0.015 mol) and toluene (300 ml) were refluxed in the presence of sulfuric acid in a flask equipped with a Dean-Stark trap for 6 hr. The reaction mixture was treated by the usual method to give 3.34 g (87.0%) of the pure enamino ketone: mp 153 °C (from benzene); UV λ_{max}(EtOH) 230 (ε 8790), 315 nm (24200); IR (KBr) 3100, 1590, 780, and 715 cm^{-1}; NMR ($CDCl_3$, 60 MHz) 6.84—7.35 (m, 5, aromatic and N-H), 5.52 (s, 1, vinyl), 2.32 (s, 2, methylene-4), 2.18 (s, 1, methylene-6), and 1.08 (s, 6); mass spectrum (70 eV) *m/e* (rel. intensity) 251 (27), 249 (81; M^+), 234 (21), 232 (34), 221 (10), 206 (14), 195 (34), 194 (42), 193 (100), 192 (95), 178 (9), 167 (12), 166 (22), 165 (24), 164 (43), 152 (10), 130 (44), 127 (11), 126 (12), 111 (17), 76 (12), 68(28).

Found: C, 67.42; H, 6.60%. Calcd for $C_{15}H_{16}NOCl$: C, 67.32; H, 6.47%.

*5,5-Dimethyl-3-(4'-hydroxyanilino)cyclohex-2-en-1-one (**4**, $R^1=H$, $R^2=4'$-OH, $R^3=CH_3$).* *p*-Aminophenol (1.0 g, 0.01 mol), 5,5-dimethylcyclohexane-1,3-dione (1.4 g, 0.01 mol), and toluene (200 ml) were heated for 4 hr under the same conditions as for **4b**. The resulting solid product was filtered, and washed with cold water. Recrystallization from ethanol gave 0.88 g (37%) of the enamino ketone; mp 227—230 °C; UV λ_{max}(EtOH) 304 nm (ε 17100), mass spectrum *m/e* 231 (M^+).

*5,5-Dimethyl-3-(4'-methoxyanilino)cyclohex-2-en-1-one (**4c**).* To a solution diazomethane[23] in 500 ml of ether, generated from nitrosomethylurea (6.2 g, 0.06 mol), was added 5,5-dimethyl-3-(4'-hydroxyanilino)cyclohex-2-en-1-one (4.10 g, 0.018 mol) in 100 ml of ethanol, allowed to stand overnight in an ice-box. Tlc indicated the presence of the starting material and the product (silica gel with benzene–ethyl acetate 1 : 1, R_f value 0.7 and 0.6, respectively). This was recrystallized from ethyl acetate to give 1.17 g (34%) of the pure enamino ketone (colorless needles): mp 194 °C (lit,[24] 189—190 °C); UV λ_{max} (EtOH) 314 nm (ε 19700); IR (KBr) 3370, 3150, 1610, and 1550 cm^{-1}; NMR methanol-d_4, 100 MHz) δ 7.08 and 6.89 (AA'MM' pattern,

22) R. L. Shriner and H. R. Todd, "Organic Syntheses," Coll. Vol. II, (1943), p. 200.
23) F. Arndt, *ibid.*, p. 165.
24) M. Regitz and H. Schwall, *Ann. Chem.*, **728**, 99 (1969).

4, $J_{AM}=J_{A'M'}=8$ Hz, aromatic), 5.28 (s, 1, vinyl), 3.75 (s, 3, $-OCH_3$), 2.38 (s, 2, methylene-4), 2.16 (s, 2, methylene-6), and 1.08 (s, 6, *gem*-dimethyl); instead of the N–H proton signal, increase of the OH signal (δ 4.75) of methanol was observed; mass spectrum (70 eV) *m/e* (rel. intensity) 246 (20), 245 (100), 230 (10), 228 (26), 217 (13), 202 (12), 190 (16), 189 (88), 175 (10), 174 (71), 160 (10), 146 (12), 123 (12), 122 (23), 108 (11).

*5,5-Dimethyl-3-(3'-hydroxyanilino)cyclohex-2-en-1-one (**4**, $R^1=H$, $R^2=3'$-OH, $R^3=CH_3$).* Prepared from 5,5-dimethylcyclohexane-1,3-dione (1.4 g, 0.01 mol) and *m*-aminophenol (1.0 g, 0.01 mol) as yellow prisms (from ethanol, 41%): mp 246 °C; UV λ_{max} (EtOH) 314 nm (ε 25500); mass spectrum (70 eV) *m/e* 231 (M^+).

Found: C, 72.28; H, 7.42; N, 5.97%. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06%.

*5,5-Dimethyl-3-(3'-methoxyanilino)cyclohex-2-en-1-one (**4d**).* Prepared by methylation of 5,5-dimethyl-3-(3'-hydroxyanilino)cyclohex-2-en-1-one (**2**, $R^1=H$, $R^2=3'$-OH, $R^3=CH_3$) with diazomethane as light yellow needles (from benzene, 73.2%): mp 118 °C; UV λ_{max} (EtOH) 314 nm (ε 20400), λ_{max} (acidic EtOH) 301 nm (ε 17700); IR (KBr) 3425, 3245, 1605, and 1583 cm^{-1}; NMR ($CDCl_3$, 100 MHz) 7.2 (m, 1, aromatic proton-2'), 7.1 (broad, 1, N–H), 6.68 (m, 3, aromatic), 5.57 (s, 1, vinyl), 3.72 (s, 3, $-OCH_3$), 2.32 (s, 2, methylene-4), 2.15 (s, 2, methylene-6), and 1.05 (s, 6, *gem*-dimethyl); mass spectrum (70 eV) *m/e* (rel. intensity) 245 (98, M^+), 228 (49), 217 (9), 202 (13), 189 (83), 174 (17), 160 (100), 146 (28), 130 (27), 122 (10), 117 (11), 107 (11) 92 (18), 83 (14), 77 (25).

Found: C, 73.67; H, 7.97; N, 5.52%. Calcd for $C_{15}H_{19}NO_2$: C, 73.47; H, 7.76; N, 5.71%.

*3-Anilinocyclohex-2-en-1-one (**4e**).* Aniline (4.3 g, 0.046 mol), cyclohexane-1,3-dione (5 g, 0.045 mol) and toluene (600 ml) were heated for 5 hr under the same conditions as for **4b**. The product was recrystallized from benzene–ethyl acetate to give 6.36 g (76%) of the pure enamino ketone (**4e**) (colorless prisms): mp 182 °C (lit,[25] 179—181 °C); UV λ_{max} (EtOH) 225 (ε 6650) and 309 nm (18700); IR (KBr) 3245, 1590, 1570, 1530, 750, and 706 cm^{-1}; NMR ($CDCl_3$, 100 MHz) 7.0—7.7 (m, 6, aromatic and N–H), 5.53 (s, 1, vinyl), 2.49 (t, 2, $J_{4,5}=6$ Hz, methylene-4), 2.3 (t, 2, $J_{6,5}=6$ Hz, methylene-6), and 1.96 (p, 2, $J_{5,4}=J_{5,6}=6$ Hz, methylene-5), mass spectrum (70 eV) *m/e* (rel. intensity) 188 (13), 187 (77, M^+), 186 (18), 170 (26), 160(13), 159 (100), 158 (50), 144 (14), 131 (22), 130 (54), 117 (9), 93 (23), 92 (35), 85 (11), 77 (36).

Irradiation of Enamino Ketones. All n,π^* irradiations were carried out in a flask equipped with a Pyrex-jacketed immersion lamp at its center. An Ushio Type UM-452 450-W mercury lamp was used as the light source. π,π^* Irradiations were also carried out in the same manner with a quartz-jacketed immersion lamp (Ushio Type ULI-8BQ 80-W). For the sake of complete dissolution the enamino ketones were agitated in ether or benzene for 30 min with a magnetic stirring bar. Agitation and bubbling of dry nitrogen were continued during the course of preparation of the solution and irradiation. The progress of reaction was monitored by tlc.

*Irradiation of 5,5-Dimethyl-3-(N-methylanilino)cyclohex-2-en-1-one (**3**) in Ether with High Pressure Mercury Arc Lamp.* A solution of enamino ketone (**3**) (500 mg, 2.18 mmol) was irradiated in 750 ml of ether (5.5×10^{-3} M) for 4 hr. Tlc (silica gel) revealed a decrease in the amount of starting material and the presence of one major product and one minor one. Evaporation of the solvent *in vacuo* at room temperature left an oily residue. The product soluble in *n*-hexane was separated to give 75 mg of 2,3-dihydro-2,2,9-trimethylcarbazol-4(1*H*)-one (**7**) (conversion 40%,[24] yield 38%). Recrystallization from *n*-hexane–benzene (4 : 1) gave 41 mg of light-yellow needles: mp 137—138 °C; mass spectrum (70 eV) *m/e* (rel. intensity) 227 (86, M^+), 171 (100, $M-C_4H_8$), 143 (52, $M-C_4H_8-CO$)), 128 (10, C_9H_6N), 115 (15, C_8H_5N).

Isolation of the minor product by column chromatography on silica gel was not possible.

*Irradiation of 5,5-Dimethyl-3-(N-methylanilino)cyclohex-2-en-1-one (**3**) in Benzene with High Pressure Mercury Arc Lamp.* A solution of enamino ketone (**3**) (200 mg, 0.87 mmol) was irradiated in 20 ml of benzene (4.4×10^{-2} M) for 8 hr. Tlc (silica gel) of the product mixture showed the presence of same two products as in the case of irradiation in ether.

*Irradiation of 5,5-Dimethyl-3-(N-methylanilino)cyclohex-2-en-1-one (**3**) in Benzene with Low Pressure Mercury Arc Lamp.* A solution of enamino ketone (**3**) (200 mg, 0.87 mmol) was irradiated in 20 ml of benzene (4.4×10^{-2} M) for 16 hr at *ca.* 10 °C with a low pressure mercury arc lamp. Tlc (silica gel) of the product mixture showed the presence of the same two products as in the case of irradiation with high pressure mercury arc lamp. Column chromatography on silica gel (0.05—0.20 mm, E. Merck) in *n*-hexane containing increasing amount of benzene gave 25 mg of the carbazole (**7**) (13%).

*Irradiation of 3-Anilino-5,5-dimethylcyclohex-2-en-1-one (**4a**).* Four grams of enamino ketone (**4a**) was divided into five 800 mg portions, and each portion was dissolved in 2 l of benzene (2.3×10^{-1} M). After irradiation for 2 hr, the solvent was evaporated to 10 ml *in vacuo* below 30 °C. The resulting light-brown crystals and the starting material (compared with standard material by tlc) were separated by decantation and the mother liquor was evaporated to give 160 mg of the photoproducts. They were composed of 3,3-dimethyl-5-hydroxy-3,4-dihydro-1-benzazocine (**8a**) (one of the two major products), ketene adduct (**10a**), lactone (**11a**) (minor product), and polymerized products (tlc analysis on silica gel; R_f values 0.73, 0.83, 0.69, and 0.0, respectively; benzene–ethyl acetate 4 : 1). The combined mother liquor of five portions (820 mg) were chromatographed over silica gel eluted with *n*-hexane–benzene. The first band gave **10a** recrystallized from *n*-hexane as light-yellow crystals, 11%): mp 177—178 °C, UV λ_{max} (EtOH) 271.5 nm (ε 45600); IR (KBr) 3360, 1630, 1600, 1530, 1500, 750, and 700 cm^{-1}; NMR ($CDCl_3$, 100 MHz) 7.24 (m, 10), 6.10—6.70 (m, 3), 2.35 (q, 1), 1.35 (d, 3), and 1.32 (s, 3); mass spectrum (70 eV, high resolution) *m/e* 304 ($C_{20}H_{20}N_2O$ (M^+, obsd. 304.1575 mu, error from calculated value -0.0030 mu), 289 $C_{19}H_{17}N_2O$ ($M-CH_3$. 289.1339, -0.0029), 261 $C_{18}H_{17}N_2$ ($M-CH_3+CO$), 261.1391, -0.0017), 212 $C_{14}H_{14}NO$ ($M-(CH_3+C_5H_3N)$, 212.1075, -0.0015), 197 $C_{13}H_{11}NO$ ($M-(CH_3+C_5H_3N+CH_3)$, 197.0841, 0.0013), 184 ($C_{13}H_{14}N$ ($M-(CH_3+CO+C_5H_3N)$, 184.1124, $+0.0045$), 169 ($C_{11}H_7NO$ ($M-(CH_3+C_5H_3N+CH_3+C_2H_4)$, 169.0528, -0.0079), 155 $C_{11}H_{12}$ ($M-(CH_3+CO+C_5H_3N+C_2H_2N)$, 144.0940, -0.0056), 118 C_9H_{10} ($M-(CH_3+CO+C_5H_3N+C_2H_2N+C_2H_2)$, 118.0748, -0.0037).

The second band gave 3,3-dimethyl-5-hydroxy-3,4-dihydro-1-benzazocine (**8a**): mp 70—73 °C (light-yellow needles from *n*-hexane), UV λ_{max} (EtOH) 229 (ε 10400) (Sh), 252.5 16200), 306 (4800, sh), and 315 nm (5100); IR (KBr) 3320 (OH), 1708 (C=O), 1630 (C=N), 1385, 1365, 1297 (Ar–N), 1215, 1182, 753, and 694 cm^{-1}; NMR: summarized

25) 300 mg of the starting material was recovered from the residue (insoluble to *n*-hexane).

in Table 3; mass spectrum (70 eV) *m/e* 201 (M^+), 186 (M–CH_3), 158 (M–(CH_3+CO)), 118 (M–(CH_3+CO+C_3H_4)), 77 (C_6H_5).

Found: C, 77.58; H, 7.51; N, 6.96%. Calcd for $C_{13}H_{15}NO$: C, 77.61; H, 7.46; N, 6.97%'

The third band gave a trace of **11a**: mp 100—101 °C (colorless); UV λ_{max} (EtOH) 270.5 nm (ε 27100); mass spectrum (70 eV) *m/e* 229 (M^+).

*Irradiation of 3-(3'-Chloroanilino)-5,5-dimethylcyclohex-2-en-1-one (**4b**).* Enamino ketone (**4b**) (2.11 g, 8.6 mmol) was divided in to three portions, each portion being dissolved in 2 l of benzene. In one case, 702.55 mg was dissolved in 2 l of benzene (1.4×10^{-3} M). The solution was irradiated for 30 min and then concentrated to 10 ml *in vacuo* below 30 °C. Removal of the starting material by the same method as that for **4a** left an oily product. Column chromatography of the combined oily products (409 mg) on silica gel (30 g) in *n*-hexane containing an increasing amount of benzene gave 42 mg of **10b** (24%), 21 mg, of **8b**, and 16 mg of **11b** (9% isolated). **10b**: mp 156 °C (yellow needles from *n*-hexene); UV λ_{max} (EtOH) 274.6 (ε 41960) and 349.5 nm (510): IR (KBr) 3340, 1630, 1599, 1525, 1485, 783, and 700 cm^{-1}; NMR ($CDCl_3$, 60 MHz) 7.22 (s, 2), 6.76—7.15 (m, 6), 6.3—6.7 (broad, 3), and 1.37 (s, 6); mass spectrum (70 eV, high resolution) *m/e* 372 $C_{20}H_{18}N_2OCl_2$ (M^+, obsd. 372.0732 mu, error −0.0065), 357 $C_{19}H_{15}N_2OCl_2$ (M−CH_3, 357.0519, −0.0041), 322 ($C_{19}H_{15}N_2OCl$ (M−(CH_3+Cl), 322.0838, −0.0036), 246 $C_{14}H_{13}NOCl$ (M−(CH_3+Cl+C_5H_2N), 246.0667. −0.0019), 231 $C_{13}H_{10}NOCl$ ((*m/e* 246)–CH_3, 231.0467, +0.0016), 218 ($C_{13}H_{13}NCl$ ((*m/e* 246)–CO, 218.0689, −0.0049), 211 $C_{14}H_{13}NO$ ((*m/e* 246)−Cl, 211.0976, −0.0023), 182 $C_{13}H_{12}N$ ((*m/e* 246) NO ((*m/e* 246)−Cl, 211.0976, −0.0023), 182 $C_{13}H_{12}N$ ((*m/e* 211)–CHO, 182.0920, −0.0051), 167 $C_{12}H_9N$ (167.0692, −0.0046), 152 $C_{11}H_6N$ (152.0576, +0.0076).

7-Chloro-3,3-dimethyl-5-hydroxy-3,4-dihydro-1-benzazocine (**8b**) was obtained from the second band: mp 104.5—105 °C (colorless needles from *n*-hexane); UV λ_{max} (EtOH) 257 (ε 15800) and 305.5 nm (7010); IR (KBr) 3324 (strong, OH), 1698 (strong, C=O), 1630 (strong, C=N), 1382, 1367, 1295 (strong, Ar–N), 1215, 1200, and 830 cm^{-1} (strong), and also see Table II; NMR; summarized in Table 3; mass spectrum (70 eV, high resolution) *m/e* 235 $C_{13}H_{14}NOCl$ (M^+, obs. 235.0743, error −0.0021), 220 $C_{12}H_{11}NOCl$ (220.0400, −0.0129), 192 $C_{11}H_{11}NCl$ (192.0434, −0.0146), 157 $C_{11}H_{11}N$ (152.0227, −0.0040), 117 C_8H_7N (117.0570, −0.0009), observed metastable peaks: 235→220 *m**=206 (calcd 206.0) "flat-topped", 220→192 *m**=168 (calcd 167.6) "flat-topped" (Scheme 4–1).

Found: C, 66.41; H, 6.17%. Calcd for $C_{13}H_{14}NOCl$: C, 66.38; H, 5.96%.

The third band gave **11b**: mp 98 °C (from *n*-hexane); UV λ_{max} (EtOH) 274 nm (ε 20000); NMR ($CDCl_3$, 60 MHz) 6.17—7.22(m, 6), 2.26 (broad d, 2), and 1.24 (t, 6); mass spectrum 70 eV) *m/e* 263 (M^+).

Found: C, 63.73; H, 5.40%. Calcd for $C_{14}H_{14}NO_2Cl$: C, 63.75; H, 5.31%.

*Irradiation of 5,5-Dimethyl-3-(4'-methoxyanilino)cyclohex-2-en-1-one (**4c**).* Four grams of enamino ketone (**4c**) were divided into ten portions. Each portion (400 mg) was added to 2 l. of benzene (0.82×10^{-3} M). The solution was irradiated for 4 hr at room temperature and evaporated to 10 ml. This was treated in the same way as for **4a**. 990 mg of the photoproducts were obtained from the combined mother liquor. Column chromatography on silica gel (45 g) in *n*-hexane containing an increasing amount of benzene gave 16.0 mg of 3,3-dimethyl-5-hydroxy-8-methoxy-3,4-dihydro-1-benzazocine (**8c**). This was recrystallized from *n*-hexane for analysis: mp 93—94 °C (light-yellow needles); UV λ_{max} (EtOH) 252 (ε 11700) and 316 nm (2900); IR (KBr) 3350 (strong, OH), 1705 (C=O), 1630 (C=N), 1390, 1369, 1300 (Ar–N), and 1180 cm^{-1}; NMR; summarized in Table 3; mass spectrum (70 eV) *m/e* (rel. intensity) 232 (11), 231 (65, M^+), 217 (17), 216 (100), 189 (6), 188 (38), 173 (5).

Found: C, 72.64; H, 7.44; N, 6.01%. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06%.

*Irradiation of 5,5-Dimethyl-3-(3'-methoxyanilino)cyclohex-2-en-1-one (**4d**).* Enamino ketone (**4d**) (1.26 g, 5.1 mmol) was added to 2 l of benzene (2.6×10^{-3} M). The solution was irradiated for 4 hr at room temperature and evaporated to 10 ml. After separation of the starting material, the products (1.12 g) were chromatographed on silica gel (50 g) in *n*-hexane containing an increasing amount of benzene to give 12.5 mg of 3,3-dimethyl-5-hydroxy-7-methoxy-3,4-dihydro-1-benzazocine (**8d**) (17%). This was recrystallized from petroleum ether for analysis: mp 84 °C (colorless needles); UV λ_{max} (EtOH) 215 (ε 19000), 252 (10700), and 299.5 nm (3700); IR (KBr) 3340 (strong, OH), 1706 (C=O), 1634 (C=N), 1381, 1365, 1300 (Ar–N), 1218 and 1200 cm^{-1}; NMR; summarized in Table 3; mass spectrum (70 eV) *m/e* (rel intensity) 232 (8), 231 (45, M^+), 217 (17), 216 (100), 189 (7), 188 (45), 173 (5), 148 (6), 77 (11).

Found: C, 72.83; H, 7.56%. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41%.

*Irradiation of 3-Anilinocyclohex-2-en-1-one (**4e**).* Enamino ketone (**4e**) (5.41 g, 29 mmol) was divided into ten portions, and each portion was irradiated for 2 hr in 2 l of benzene (1.45×10^{-3} M). From the combined reaction mixture was recovered 5.20 g of the starting material. A mixture of the photoproducts (210 mg, conversion 3.9%) was chromatographed on silica gel (35 g) in *n*-hexane containing an increasing amount of benzene. Only the second band was isolated to give 5-hydroxy-3,4-dihydro-1-benzazocine (**8e**) (6.25 mg, 3%); mp 101—102.5 °C (yellow needles from *n*-hexane); UV λ_{max} (EtOH) 227 (ε 6700, sh), 254 (11000), 302 (3100, sh), and 313 nm (3400); IR (KBr) 3330 (strong, OH), 1697 (strong, CO=), 1635 (strong, C=N), 1282 (Ar–NO, 753, and 692 cm^{-1}; NMR; summarized in Table 3; mass spectrum (70 eV, high resolution) *m/e* 173 $C_{11}H_{11}NO$ (M^+, obsd. 173.0844 mu. error +0.003 mu), 144 $C_{10}H_{10}N$ (144.0797 −0.0016), 130 C_9H_8N (130.0646, −0.0011), 117 (C_8H_7N (117.0609, +0.0030), 91 C_7H_7 (91.0528, −0.0020), 90 C_6H_4N (90.0429, +0.0085) (see Scheme IV-2).

Cinnamylidenemalonic Acid. This was quantitatively prepared from cinnamaldehyde and malonic acid according to the procedure of Stuart:[27] mp 208—209 °C (decomp., yellow needles, lit, 208 °C decomp.); UV λ_{max} (EtOH) 236 (ε 3900) and 330 nm (14800).

δ-Phenylvaleric Acid. This was obtained by reduction of cinnamylidenemalonic acid with the Raney nickel followed by decarboxylation according to the reported procedure;[28] yield 80%: mp 57.0—58.8 °C(lit,[29] 58—59 °C); UV λ_{max} (EtOH) 238 (ε 72), 244 (95), 249 (136), 254.2 (183), 255.5 (181), 259.8 (213), 261.9 (215), 264.9 (165), and 268.7 nm (171).

Benzo-2-cycloheptenone. The cyclization procedure[26] in phosphoric acid–phosphorus pentoxide was employed. Yield 79%, bp 123—124 °C/6 mmHg (lit,[26] 90∼93 °C/1 mmHg);

26) R. C. Gilmore and W. J. Horton, *J. Amer. Chem. Soc.*, **73**, 1411 (1951).
27) C. M. Stuart, *J. Chem. Soc.*, **49**, 365 (1886).
28) J. W. Cook, R. Philip, and A. R. Somerville, *J. Chem. Soc.*, **1948**, 164.

UV λ_{max} (EtOH) 246.5 (ε 9050), 286.5 (1430), and 328 nm (90); NMR (CCl_4, 100 MHz) 7.05—7.65 (m, 4, aromatic), (t, 2, J=6 Hz, methylene-5), 2.62 (t, 2, J=6 Hz, methylene-2), 1.7—1.95 (m, 4, methylene-3 and -4); mass spectrum (70 eV) *m/e* 160 (M^+).

*1,2,3,4,5,6-Hexahydro-2-oxo-1-benzazocine (**20**).* This was prepared from benzo-2-cycloheptenone oxime (mp 110.5—111 °C from petroleum ether; lit,[30] 108—109 °C) by the Beckmann rearrangement in glacial acetic acid–sulfuric acid according to the procedure in literature;[31] yield 83%; mp 157.5~157.7 °C (colorless needles from benzene, lit, 151—153 °C); UV λ_{max} (EtOH) 229.7 (ε 7580), 268.5 (690), and 275 nm (580); IR (KBr) 3175 (associated N–H), 3050, 1660, and 760 cm^{-1}; NMR (CCl_4, 100 MHz) 9.77 (broad s, 1, N–H), 7.13 (s, 4, aromatic), 2.7 (m, 2, methylene-6), 2.08 (m, 2, methylene-3), 1.7—1.9 (m, 4, methylene-4 and -5); mass spectrum (70 eV) *m/e* 175 (M^+).

*1,2,3,4,5,6-Hexahydro-1-benzazocine (**21**).* Tetrahydrofuran was freshly distilled from lithium aluminum hydride under nitrogen after distillation from metallic sodium. The second distillation of tetrahydrofuran and reduction were carried out in a flask connected to a vacuum-line replaced with dry nitrogen. To a stirred ice-cold suspension of lithium aluminum hydride (400 mg, 11 mmol, excess) in 30 ml of freshly distilled dry tetrahydrofuran was slowly added 527 mg (3 mmol) of the lactam in 35 ml of freshly distilled dry tetrahydrofuran under stirring with a magnetic stirring bar. The mixture was refluxed for 8 hr on a water bath, cooled in an ice bath and treated carefully with saturated sodium sulfate aqueous solution (4 ml). After liberation of hydrogen gas, white precipitate appeared. The tetrahydrofuran solution was separated from the insoluble part, was boiled with additional tetrahydrofuran (20 ml). The combined extract was evaporated. Tlc of the resulting oily product showed the presence of one major and one minor product. The major product was isolated by column chromatography on silica gel to give 406 mg (2.52 mmol) of the benzazocine (**21**) (84%). Rechromatography for analysis gave 337 mg (yellow oil). Boiling point was not measured (lit,[32] 130—150 °C/15 mmHg): UV λ_{max} (EtOH) 230 (ε 2050), 261 (960), and 304 nm (180); IR (neat) 3405 (weak), 3320 (weak), 1603, 1580, 1495, and 742 cm^{-1}; NMR (CCl_4, 100 MHz) 7.03 (d, d, 1, J_{ortho}=7, J_{meta}=2 Hz, H–7), 6.87 (m, 2, H–8 and –9), 6.71 (m, 1, H–10), 3.15 (broad, s, 2, methylene-2), 3.09 (s, 1, NH, exchangeable with deuterium oxide), 2.83 (t, 2, J=6 Hz, methylene-6), and 1.35—1.92 broad m, 6, methylene-3, -4, and -5); mass spectrum (70 eV) *m/e* (rel intensity) 161 (100, M^+), 146 (25), 144 (32), 133 (24), 132 (68), 130 (22), 129 (20), 120 (31), 118 (81), 117 (24), 106 (33), 91 (33), 77 (28).

Table 4. Summary of tlc analysis data

	Ratio of benzene : ethyl acetate		
	2 : 1	3 : 1	6 : 1
Reduction product	0.39	0.34	0.21
1,2,3,4,5,6-hexahydro-1-benzazocine (**21**)	0.40	0.34	0.22

*Reduction of 3,4-Dihydro-5-hydroxy-1-benzazocine (**8e**) with Diborane.* Diborane was generated from borohydride and boron trifluoride etherate according to the procedure in literature.[33] Diglyme and tetrahydrofuran were freshly distilled from metallic sodium and dried with sodium wire. Diborane was passed into a four-necked flask, the reactor, by applying a slight flow of dry nitrogen through the generator. Dry tetrahydrofuran (45 ml) was placed in the reactor to prepare a solution of diborane. The reactor was equipped with a reflux condenser, thermometer, gas dispersion tube to inlet diborane and a pressure-equalizing dropping funnel involving a solution of 20 mg of 3,4-dihydro-5-hydroxy-1-benzazocine (**8e**) in 40 ml of tetrahydrofuran. This solution was slowly added to a stirred, ice-cold diborane solution at 3° C for 45 min. The resulting mixture was then heated under reflux for 2 hr, cooled in an ice bath and carefully treated with 30 ml of 3 M hydrochloric acid. The mixture was refluxed again for 1 hr. The solvent was evaporated *in vacuo*, and the residue was made alkaline with 10% sodium carbonate aqueous solution followed by extraction with benzene (three times). The combined extract was evaporated *in vacuo* to dryness. The data of tlc analysis are summarized in Table 4.

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29) A. Baeyer and O. R. Jackson, *Ber.*, **13**, 122 (1880).
30) F. S. Kipping and A. E. Hunter, *J. Chem. Soc.*, **79**, 607 (1901).
31) D. H. Jones, G. F. Stephenson, G. W. Spray, and W. R. Wragg, *J. Chem. Soc., C*, **1969**, 2176.
32) H. König and R. Huisgen, *Chem. Ber.*, **92**, 429 (1959).
33) G. Zweiffl and H. C. Brown, "Organic Reactions," Vol. 13, John Wiley & Sons, Inc., New York, London (1963), p. 27.