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PHOTOCHEMICAL REACTION OF ENAMINO KETONES

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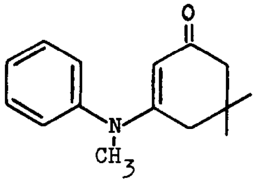
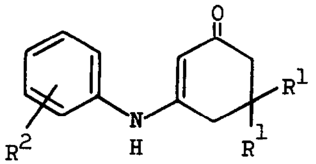
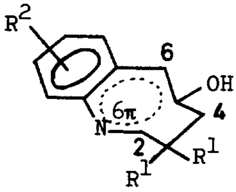
The photochemical cyclisation of enamines has been the subject of several recent investigations, but these studies have involved N-methyl enamines (tertiary amines).[1,2] We wish now to report the photochemical synthesis of 5-hydroxy-3,4-dihydro-1-benzazocines (IVa ~ e) from enamino ketones (IIa ~ e) together with the normal photocyclisation of N-methyl one (I) (secondary amine).

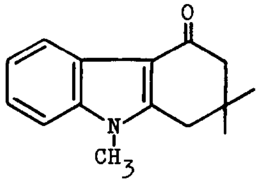
5,5-Dimethyl-3-(N-methylanilino)cyclohex-2-en-1-one (I) in an ether solution (5.5×10^{-3}M) was irradiated with a Pyrex-jacketed immersion lamp (>3000A) under dry nitrogen; this gave 2,3-dihydro-2,2,9-trimethylcarbazol-4(1H)-one (III) (mp 137-138°), which, recently synthesized in another way,[3] was identified by comparison of spectroscopic properties with a known sample. On the other hand, substituted 3-anilino-5,5-dimethylcyclohex-2-en-1-ones (IIa ~ e) in benzene solutions ($1 \sim 2.5 \times 10^{-3}$M) were irradiated under the same conditions as those of (I) to furnish products (IVa ~ e), which were isolated by silica gel chromatography. Yields were summarized in Table 1. In this case, however, no corresponding tetrahydrocarbazole derivatives were obtained. The products (IVa ~ e) were identified as 5-hydroxy-3,4-dihydro-1-benzazocines by their spectro-



(I)







(III)

(IIa) $R^1=CH_3$, $R^2=H$

(IIb) $R^1=CH_3$, $R^2=3'-Cl$

(IIc) $R^1=CH_3$, $R^2=4'-OCH_3$

(IId) $R^1=CH_3$, $R^2=3'-OCH_3$

(IIe) $R^1=R^2=H$

(IVa) $R^1=CH_3$, $R^2=H$

(IVb) $R^1=CH_3$, $R^2=7-Cl$

(IVc) $R^1=CH_3$, $R^2=8-OCH_3$

(IVd) $R^1=CH_3$, $R^2=7-OCH_3$

(IVe) $R^1=R^2=H$

Table 1. Summary of yields and physical properties of (IV).

Compds.	Conversion (%)	Yield (%)	mp (°C)	uv λ_{max}^{EtOH} nm (ε x 10^{-4})
IVa	25	14	70 - 73	252.5 (1.62), 315 (0.51)
IVb	19	12	104.5-105	257 (1.58), 305.5 (0.70)
IVc	25	20	93 - 94	252 (1.17), 316 (0.29)
IVd	90	17	84	252 (1.07), 299.5 (0.37)
IVe	4	3	101 -102.5	254 (1.10), 313 (0.34)

scopic properties (Tables 1 and 2). Elemental analysis and high resolution mass spectrum of (IVb) indicated the molecular formula $C_{13}H_{14}NOCl$. The uv (Table 1) and ir spectrum suggested the presence of anil system ($\nu_{C=N}$ 1630 and ν_{C-N} 1295 cm^{-1}). The coexistence of a carbonyl band (1698 cm^{-1}) and a hydroxy-absorption (3324 cm^{-1}) indicates a formation of a keto-enol equilibrium. A remarkable change in the ratio ($D(\nu_{OH})/D(\nu_{C=O})$) of the absorbance for these two absorption bands in carbon tetrachloride and in tetrahydrofuran (from 1.0 to 2.7), indicated that solvation in polar solvents stabilized the enol form resulting in an increase of the ratio. This was also supported by the fact that only the absorption due to enol form at 3170 and 1198 cm^{-1} was observed in tetrahydrofuran solution, highly diluted with carbon tetrachloride. The nmr (Table 2) and ir spectra of these products indicated the presence of a 8-membered dihydro-

Table 2. Summary of nmr spectral data of (IV).

Position / Compds.	2	3	4	5-OH*2	6	R1	R2
IVa*1	6.56 (s,1H)	-	2.33 (s,2H)	6.17 (bs,1H)	7.10 (s,1H)	1.28 (s,6H)	-
IVb	6.37 (s,1H)	-	2.24 (s,2H)	6.22 (bs,1H)	6.98 (s-1,1H)*4	1.82 (s,6H)	-
IVc	6.19 (s,1H)	-	2.22 (s,2H)	5.82 (bs,1H)	6.77 or 6.85 (s-1,1H)	1.25 (s,6H)	3.71 (s,3H)
IVd	6.52 (s,1H)	-	2.30 (s,2H)	6.11 (bs,1H)	6.57 (s-1,1H)	1.28 (s,6H)	3.79 (s,3H)
IVe	6.59*3 (t,1H)	2.63*3 (t,d,2H)	2.37 (t,2H)	6.18 (bs,1H)	7.02 (s,1H)	-	-

δ ppm from tetramethylsilane (100 MHz in CCl_4)
*1; in $CDCl_3$, *2; disappeared by the addition of D_2O,
*3; demonstrated by double resonance, *4; s-1: singlet-like,

azocine ring. Especially, the gem-dimethyl signals of (IVa ~ d) were temperature-dependent. At room temperature, the signal of (IVb) showed a sharp singlet at δ 1.3 ppm, while at -30° remarkable broadening was observed, which may be considered due to the ring-flapping. Furthermore, no signals assignable to a ring-juncture methine proton in a 2,3-trimethyleneindoline system were found in nmr spectra of (IVa ~ e).

The structure (IV) was confirmed by the fact that reduction of (IVe) with diborane in tetrahydrofuran gave the product which was identical to authentic 1,2,3,4,5,6-hexahydro-1-benzazocine (V).[4] The stability of these photoproducts (IVa ~ e), the downfield-shifts of signals for protons at 2- and 6-positions (Table 2), and the stability of enol-form were explained due to the 6π system pseudo aromaticity.

References

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4) The compound (V) was prepared from 1,2,3,4,5,6-hexahydro-2-oxo-1-benzazocine[5] by reduction with lithium aluminum hydride in tetrahydrofuran: uv λ_{max}(EtOH) 230 (ε 2,050), 261 (960), and 304 nm (180); nmr (CCl_4, 100 MHz) δ 7.03 (dd, 1, 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), 2.83 (t, 2, methylene-6), 1.35~1.92 (broad m, 6, methylene-3, -4, and -5); mass spectrum (70 eV) m/e 161 ($M^{+\cdot}$, base).

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