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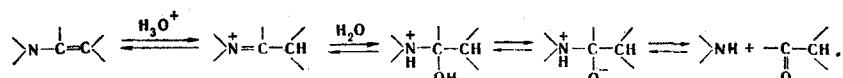
ENAMINES.

6.* HYDROLYSIS OF CYCLIC ENAMINO KETONES OF THE PYRROLIDINE, PIPERIDINE, AND HEXAHYDROAZEPINE SERIES

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The kinetics and mechanism of the hydrolysis of various enamines have been studied in fairly great detail [2-4], and according to the current ideas, the hydrolysis process takes place in accordance with the following scheme:



At the same time, it has been shown that the rate-limiting step varies as a function of the ambient pH [2-4] and the degree of conjugation between the lone pair of the nitrogen atom and the enamine carbon-carbon double bond [5, 6].

In contrast to the enamines, no systematic investigations of the hydrolysis of enamine ketones have previously been carried out, while in a number of cases, the hydrolysis of enamine ketones is a convenient method for obtaining the corresponding dicarbonyl compounds. Therefore, the study of the features of the hydrolysis of enamine ketones is of definite interest not only in the theoretical respect, but also in the practical respect. In accordance with this goal, the present work was an investigation of the hydrolysis of enamino ketones [in the examples of 1-methyl-2-(2'-benzoylmethylene)pyrrolidine (Ia) [7], -piperidine (Ib) [8], and -hexahydroazepine (Ic) [9]] and of the dependence of the rate of this process on the conditions selected (pH, temperature) and the size of the saturated azaheterocycle. Polarography was selected as the instrumental method, since the half-wave potentials of the original enamino ketones and of their hydrolysis products of type II differ significantly over a broad pH range. As an example, Table 1 presents the values of $E_{1/2}$ for enamino ketones of type I and of the corresponding β -diketones of type II in an acetate buffer solution with pH 4.6.

In moderately acidic media (pH 1-6) the rate of hydrolysis is usually limited by the rate of the addition of water to the immonium cation [2-4]. Thus, already from general considerations it follows that the six-membered enamino ketone (Ib) should undergo hydrolysis most readily. In fact, in this case, in the rate-limiting step there is an sp^2 - sp^3 change in the configuration of the $C_{(2)}$ atom of the ring, which, according to the concept of an I strain [10, 11], is most advantageous for a six-membered ring and least advantageous for a five-membered ring. At the same time, as we see from the scheme presented, the hydrolysis of enamino ketones is a reversible process, and its rate should be determined by the ratio between the rate of constants of the forward and reverse reactions. For this reason, it is necessary to take into account the factors which influence

*For report 5 see [1].

TABLE 1. Half-Wave Potentials (V, s.c.e.) of Enamino Ketones of Type I and β -Diketones of Type II in a 1 M Acetate Buffer

Compound	Ia	Ib	Ic	IIb	IIc
$E_{1/2}$	-1.05; -1.27	-0.99; -1.25	-0.98; -1.25	-1.12; -1.20	-1.12; -1.21

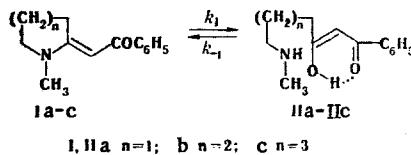
TABLE 2. Rate Constants and Activation Parameters for the Hydrolysis of Ic in a 0.1 M Acetate Buffer*

$t, ^\circ\text{C}$	$k \cdot 10^4 \text{ sec}^{-1}$
25	1.39 ± 0.07
40	3.74 ± 0.17
50	7.8 ± 2.3
60	16.47 ± 0.38
70	29.8 ± 3.7

* $\Delta H^\ddagger = 55.7 \pm 5.4 \text{ kJ/mole}$
 $(13.3 \pm 1.3 \text{ kcal/mole})$. $\Delta S^\ddagger = -132 \pm 17 \text{ J/mole} \cdot \text{deg}$ ($-31.5 \pm 4.1 \text{ cal/mole} \cdot \text{deg}$).

not only the rate of the hydrolysis of enamino ketones, but also the rate of the reverse reaction (II \rightarrow I). It is known [12] that the probability of a cyclization reaction decreases with increasing size of the chain closed and accordingly with increasing size of the ring formed, i.e., along the series 5 > 6 > 7. Thus, the probability of the formation of enamino ketones of type I upon the cyclization of diketones of type II should decrease along the series Ia > Ib > Ic. The results obtained are in good agreement with the arguments advanced.

When enamino ketone Ic was heated (50°C) in 0.1 N HCl, a decrease in the height of the reduction waves of this compound was observed along with the appearance and enhancement of the reduction waves of hydrolysis product IIc. The latter compound (IIc) was isolated by a preparative method and characterized by elemental analysis and spectral data. The rate constant of the hydrolysis of enamino ketone Ic under these conditions is equal to $(2.98 \pm 0.18) \cdot 10^{-4} \text{ sec}^{-1}$.



As in the investigation of the hydrolysis of enamines [13], in the case of enamino ketone Ic, a distinct "bell-shaped" dependence of k_1 on the ambient pH with a maximum at $\text{pH} \sim 4$ was observed.

Table 2 presents the rate constants for the hydrolysis of enamino ketone Ic as a function of the temperature (0.1 M acetate buffer) and the activation parameters of the process. Our attention is turned to the low (large negative) value of the entropy of activation, which points out the significantly greater ordering of the activated complex in comparison to the original state.

While enamino ketone Ic was hydrolyzed quantitatively, and after the completion of the process only reduction waves of the reaction product IIc were recorded on the polarogram, in the case of the six-membered enamino ketone Ib in 0.1 N HCl, the reduction wave of the original compound diminished only to a certain level. Subsequently, the ratio between the heights of the reduction waves of Ib and IIb was not dependent on the time, i.e., the establishment of the equilibrium Ib \rightleftharpoons IIb could be observed with the aid of polarography. This is evidence of a significant increase in the rate of reverse reaction in accordance with the aforementioned increase in the probability of cyclization when a six-membered ring is formed in comparison to the case of a seven-membered ring. However, the rate of the forward reaction (hydrolysis) for the six-membered enamino ketone Ib is significantly higher than that for the seven-membered enamino ketone Ic. A calculation shows that at 50°C

TABLE 3. Equilibrium Constants, Standard Free Energies, and Constants of the Forward Reaction in the Process Ib \rightleftharpoons IIb at 50°C in Mixed Solvents Containing 10% Aqueous 1 N HCl and 90% Component B (by volume)

B	Glycerol	H ₂ O	1:1 Ethanol-glycerol	Ethanol	DMFA
K_{eq} ΔG^{\ddagger} , kcal/mole (323°K, 1 atm) $k_1 \cdot 10^3$ sec ⁻¹	0 - - 0.90	0.55 ± 0.08 0.38 - 0.90	0.60 ± 0.16 0.33 - 0.19	1.72 ± 0.05 -0.35 - 3.0	3.50 ± 0.75 -0.80 - 2.3

in 0.1 N HCl the value of k_1 for Ib is 9×10^{-4} sec⁻¹, which is approximately twice as great as the corresponding value for Ic (see above). Thus, the I strain has a significant influence on the rate of the hydrolysis of cyclic enamino ketones.

Finally, we were not able to observe the hydrolysis of the five-membered enamino ketone Ia under these conditions. In this case, both factors, viz., the ease of cyclization and the energy disadvantage of the sp^2 - sp^3 change in configuration, act in the same direction. As a result, compound Ia is fairly stable under these conditions.

A more detailed study of the Ib \rightleftharpoons IIb equilibrium reveals (Table 3) that the values of K_{eq} depend on the nature of the solvent used. In glycerol the equilibrium is shifted toward the cyclic enamino ketone, in water the concentrations of the cyclic (Ib and open (IIb) forms are approximately equal, and in ethanol and especially in dimethylformamide diketone IIb predominates at equilibrium. This type of variation of K_{eq} is possible due to the decrease in the ability of the solvent to disrupt the chelate structure characteristics of β -diketones. The presence of such an intramolecular hydrogen bond stabilizes the open form of IIb and causes a shift of the Ib \rightleftharpoons IIb equilibrium to the right.

In order to try to shift the Ib \rightleftharpoons IIb toward β -diketone IIb and to find the conditions for the occurrence of the process Ia \rightarrow IIa, enamino ketones Ia and Ib were boiled in a 0.1 M acetate buffer solution. Unlike enamino ketone Ic, which is rapidly hydrolyzed to β -diketone IIc under these conditions (the latter remains unchanged even during prolonged boiling), enamino ketone Ib produced an equilibrium mixture, and no reduction waves of β -diketone IIa were noted in the case of the five-membered enamino ketone Ia. In both cases (Ia and Ib), a decrease in height and then the disappearance of the reduction waves of the original compounds were observed. The reaction product was isolated by a preparative method, and with the aid of thin-layer chromatography and IR, UV, and mass spectroscopy it was shown that benzoic acid acid forms quantitatively under these conditions, i.e., the process corresponds to the acid hydrolysis of β -diketones (we again stress, however, that β -diketone IIc is stable under these conditions). In the case of enamino ketones Ia and Ib, the process probably proceeds through a C-protonated form according to an ordinary scheme of acid hydrolysis. The rate constants of this process for enamino ketones Ia and Ib are equal to $(1.63 \pm 0.37) \cdot 10^{-4}$ sec⁻¹ and $(6.2 \pm 1.9) \cdot 10^{-4}$ sec⁻¹ (at 100°C), respectively.

When compounds Ia-Ic were heated in 0.1 N NaOH, we observed a decrease in the heights of the reduction waves of the enamino ketones and an increase in the height of the wave with $E_{1/2} = -1.65$ V, which corresponds to the reduction of acetophenone. The formation of acetophenone under these conditions was also confirmed with the aid of mass spectrometry.* The question of whether the original enamino ketones undergo ketone splitting or whether this process is preceded by a hydrolysis step arises. The study of the comparative behavior of enamino ketone Ic and diketone IIc revealed that when the latter is heated in alkali, it decomposes to acetophenone significantly more rapidly, i.e., the half-life $\tau_{1/2}$ for IIc at 55°C is less than 1 min, while $\tau_{1/2}$ for Ic is 11.4 \pm 0.1 h.

Thus, the data in Table 4 make it possible to compare the rate of hydrolysis of enamino ketones in an alkaline medium. These data allow us to conclude that in the case in which the hydrolysis is followed by an irreversible process, viz., "ketone" splitting, it is possible to characterize the hydrolysis process for a five-membered enamino ketone, i.e., a process which could not be observed or characterized under other conditions.

It is interesting to note that the variation in the free energies of activation of this process as a function of the size of the ring is due completely to the differences in the enthalpies of activation, while the entropy of activation is not dependent on the ring size, i.e., the differences in the ordering of the transition and initial states

*With the aid of special experiments it was shown that the formation of acetophenone is quantitative.

TABLE 4. Rate Constants k and Activation Parameters for the "Ketone" Splitting of Enamino Ketones in 0.1 N NaOH

$t, ^\circ\text{C}$	Ib	Ic	Ia
	$k \cdot 10^4 \text{ sec}^{-1}$	$k \cdot 10^4 \text{ sec}^{-1}$	$k \cdot 10^4 \text{ sec}^{-1}$
25	1.1; 0.9	—	—
35	2.3; 2.07; 2.29	—	—
45	4.88; 5.04; 4.88	0.97; 0.90	—
55	9.1; 9.22; 9.47	1.6; 1.8	—
60	—	—	0.118; 0.106
65	—	3.6; 4.5; 3.7	—
70	—	5.4; 4.6; 6.0	0.25; 0.16
75	—	—	0.361; 0.324
$\Delta H^\ddagger, \text{ kJ/mole}$ (kcal/mole)	54.6 ± 3.4 (13.04 ± 0.82)	60 ± 7 (14.4 ± 1.6)	69 ± 13 (16.4 ± 3.1)
$\Delta S^\ddagger, \text{ J/mole} \cdot \text{deg}$ (cal/mole · deg)	-137 ± 11 (-32.8 ± 2.6)	-133 ± 21 (-31.7 ± 4.9)	-134 ± 38 (-32 ± 9)

are identical for all the enamino ketones investigated. From Table 4 it is also seen that in alkaline media the six-membered enamino ketone is hydrolyzed with the greatest rate and the five-membered is hydrolyzed with the lowest rate.

Finally, the last stage of our work was a study of the cyclization of β -diketone IIc to enamino ketone Ic. As we see from the foregoing data, cyclization of hydrolysis product IIc could not be observed in protogenic media. For this reason, we investigated the closing of the seven-membered ring in aprotic organic solvents with different polarities, viz., toluene and dimethylformamide (DMFA). The rate constants and activation parameters of the cyclization process are presented in Table 5. As we see from the results presented, the rate of the cyclization reaction is somewhat higher in DMFA. Our attention is turned to the fact that the enthalpy of activation of the cyclization process is significantly lower in the polar solvent (DMFA) than in toluene. However, this difference in the values of ΔH^\ddagger does not cause great changes in the rate constants of the reactions, since a significantly lower (larger negative value) entropy of activation is observed in DMFA. Therefore, the stabilization of the activated complex by delocalization of the charges (in it) owing to the solvation of the ionic centers by the polar solvent is almost completely compensated by the increase in the steric requirements for the formation of the transition state due to the participation of the solvent in it. The latter situation is also manifested as a decrease in the entropy of activation by ~ 8 cal/mole · deg.

Thus, significant differences in the rates of hydrolysis of the enamino ketones as a function of the size of the saturated azaheterocycle have been established. In moderately acidic media the seven-membered enamino ketone Ic is hydrolyzed practically irreversibly to β -diketone IIb, the six-membered ring is characterized by the establishment of the equilibrium enamino ketone Ib \rightleftharpoons hydrolysis product IIb, and the hydrolysis of the five-membered enamino ketone Ia could not be observed. When heated in an acetate buffer solution, enamino ketones Ia and Ib undergo acid hydrolysis. Interestingly enough, β -diketone IIc, which forms from Ic, is completely stable under these conditions. Finally, heating in the presence of sodium hydroxide results in the ketone splitting of all the compounds investigated, Ia-Ic. In all the media the rate of the hydrolysis of the enamino ketones decreases as a function of the size of the ring along the series 6 > 7 > 5, which is in good agreement with the concept of an I strain.

From the data it also follows that polarography is a convenient and effective method for studying various chemical conversions of enamino ketones, including the hydrolysis processes of "acid" and "ketone" splitting, as well as the processes of cyclization (to enamino ketones) of the corresponding carbonyl compounds.

EXPERIMENTAL

The kinetic measurements and polarography were carried out in a thermostated cell, and the assigned temperature was held by an ultrathermostat with an accuracy of $\pm 0.1^\circ\text{C}$. The polarograms were recorded according to a three-electrode scheme with the aid of a PAR-170 "electrochemical system." A dropping mercury electrode with a PAR-172 device for forced departure of a drop was used. A saturated calomel electrode (s.c.e.) served as the reference electrode. All the solutions except those indicated contained 10% ethanol by volume. In the solutions undergoing polarography the concentration of the depolarizers was between 0.3 and 3.0 mmole/liter. The fairly fast reactions at temperatures below 60°C were carried out directly in the polarographic cell. In this case, polarograms were recorded after definite time intervals, or the kinetic curve, i.e., the decrease in the current with time at a constant potential corresponding to the plateau of the limiting current

TABLE 5. Rate Constants k and Activation Parameters for the Cyclization Process IIc \rightarrow Ic in Aprotic Solvents

$t, ^\circ\text{C}$	Toluene	DMFA
	$k \cdot 10^3 \text{ sec}^{-1}$	$k \cdot 10^3 \text{ sec}^{-1}$
70	—	0.427 ± 0.075
80	0.522 ± 0.046	0.70 ± 0.13
90	0.962 ± 0.086	1.15 ± 0.37
100	1.67 ± 0.12	1.73 ± 0.64
110	2.87 ± 0.45	—
$\Delta H^\ddagger, \text{ kJ/mole}$ (kcal/mole)	60.7 ± 1.9 (14.49 ± 0.45)	47.0 ± 3.7 (11.22 ± 0.89)
$\Delta S^\ddagger, \text{ J/mole} \cdot \text{deg}$ (cal/mole \cdot deg)	-157 ± 5 (-37.4 ± 1.2)	-193 ± 10 (-46.0 ± 2.5)

of the enamino ketone of type I, was traced. The slow reactions, as well as the reactions at temperatures above 60°C , were studied by collecting samples, the polarography being carried out at a standard temperature of 25°C . The reactions were studied over the course of one to two periods of half-conversion, and two or three repeated measurements were carried out. The rate constant was calculated from a first-order equation, all the experimental points being considered equally accurate. In order to measure the equilibrium constant of the process $\text{Ib} \rightleftharpoons \text{IIb}$, the decrease in the limiting current of Ib with time to a certain constant value i_{eq} , which corresponds to the equilibrium concentration, was recorded on the polarograph. The equilibrium constant was calculated as the ratio $K_{\text{eq}} = (i_0 - i_{\text{eq}})/i_{\text{eq}}$, and the quantity $(i_0 - i_{\text{eq}})$ was found from the equation [14]

$$\ln(i_0 - i_{\text{eq}}) = \ln(i_0 - i_{\text{eq}}) - (k_1 + k_{-1}) \cdot t.$$

Table 3 presents the mean values of the equilibrium constants from a series of three to seven repeated measurements. The activation parameters were calculated from Eyring's equation

$$\ln \frac{k}{T} = 23.76 + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{R} \cdot \frac{1}{T}.$$

Each point was assigned a statistical weight, which was equal or proportional to the value of p/s^2 , where p is the number of repeated measurements at the particular point, and s^2 is the variance of the quantity $(\ln k/T)$, which was evaluated from the repeated measurements. If repeated measurements were not carried out (the data from Tables 2 and 5), a weight proportional to the quantity $(\ln n/s^2)$, where n is the number of experimental points used to calculate the rate constant, and s^2 is the variance for the rate constant, was used in the calculation of the activation parameters.

ϵ -Methylaminocapronylacetophenone Hydrochloride (Enol) (IIc). A 2.2-g portion (9.6 mmole) of Ic in 150 ml of 0.1 N HCl was boiled (10 h, polarographic monitoring), the mixture was evaporated in a vacuum, and IIc was obtained. The yield was 2.6 g (95%), and the mp was $118\text{--}119^\circ\text{C}$ (from ethanol). UV spectrum (in 0.1 N NaOH), λ_{max} (log ϵ): 238 (3.90), 325 nm (4.20). PMR spectrum (in CDCl_3): 1.64 (5, 6, 7- CH_2), 2.43 (4- CH_2), 2.69 (N-CH_2), 2.94 (8- CH_2), 6.17 (2-CH), 7.40-7.90 ppm (Ph), M^+ 247. Found: C, 63.60; H, 7.72; N, 4.73; Cl, 12.42%; M 283.80. Calculated for $\text{C}_{15}\text{H}_{21}\text{NO}_2 \cdot \text{HCl}$: C, 63.44; H, 7.81; N, 4.93; Cl, 12.48%.

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LUMINESCENCE AND MASS-SPECTROMETRIC
INVESTIGATION OF INDOLYLQUINOLINES
AND INDOLYLACRIDINES

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The quantum-chemical calculations in [1] show that the nitrogen atom in the pyridine ring is simultaneously a σ and a π acceptor of electrons, while the pyrrole nitrogen atom is a π donor and a σ acceptor, its strong π -donor properties more than compensating the σ -acceptor effect. The presence in one system of interacting π -electron-donor and π -electron-acceptor nuclei should result in significant intramolecular interactions, which increase the electron density in the region of the internuclear bond. The order of this bond, which is equal to ~ 0.4 , indicates that it has a significant double-bond character [2].

With the aid of mass spectrometry it has previously been established that the molecular ion (M^+) in indolylquinolines [2] has conjugation between hetaryl nuclei. Criteria which make it possible to evaluate the conjugation in M^+ are enumerated in [3-5]. This fact has also been noted in the ground state for other bisheterocycles [6, 7].

The conjugation in compounds with such a structure is due to the nearly coplanar orientation of the rings, since the magnitude of the mesomeric effect ($\pm M$) is significantly dependent on the rotation angle of the conjugated groups relative to one another [8].

The energies of the barrier to internal rotation in bisheterocycles, which have been calculated or determined experimentally, are 3 to 12 kcal/mole [9, 10]. Such energy values suggest the real existence of stable conformers; however, their isolation is possible only at low temperatures.

The purpose of the present investigation was to determine the energy of the singlet transition (E_S) and the fluorescence quantum yield (φ_f) of a number of indolylquinolines and indolylacridines. In these compounds the π -donor and π -acceptor heterocyclic rings are joined to one another by a simple C-C bond. A relationship between the value of E_S and the planarity (or conjugation) of the molecule is known [11]: The smaller is the angle of rotation between the planes of the rings comprising the original molecule, the lower is the value of E_S . An increase in the conjugation in the compounds investigated should cause an increase in the fluorescence quantum yield, since the probability of intersystem crossing decreases [12]. In this case, a comparison of the values of E_S and φ_f obtained independently by investigating the luminescence spectra and the mass spectrometric data characterizing the conjugation in the systems under investigation is of definite interest.

We studied the following compounds: ^{*} 2-(indol-3-yl)quinoline (I), 4-(indol-3-yl)quinoline (II), 4-(1-methylindol-3-yl)quinoline (III), 2-(1-methylindol-3-yl)quinoline (IV), 2-(2-methylindol-3-yl)quinoline (V), 2-(indol-3-yl)-7-methylquinoline (VI), 2-(indol-3-yl)-8-methylquinoline (VII), 1-benzoyl-1,2-dihydro-2-(indol-3-yl)quinoline (VIII), 9-(indol-3-yl)-acridine (IX), 9-(1-methylindol-3-yl)acridine (X), and 9-(2-methylindol-3-yl)acridine (XI). The values of E_S and φ_f and some mass-spectrometric characteristics for the compounds just listed are presented in Table 1.

According to this table, compounds I-IV, VI, and VII, in which π -electron conjugation between the rings is possible, fluoresce well in polar solvents under conditions for the existence of these molecules in a nearly

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