PROTONATION OF α-ENAMINES OF LACTAMS

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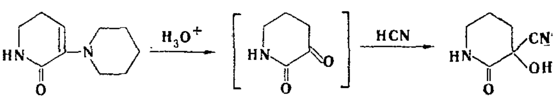
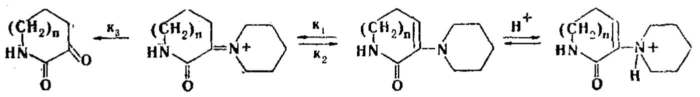
The substantial differences in the physicochemical properties and chemical behavior of α-enamines of valerolactams (I) and caprolactams (II) are caused by the different degree of conjugation of the p-electrons of nitrogen with the C = C bond; this determines the difference in the site of protonation of these compounds [1]. In the present paper, it is shown that a rather rapid conversion of the immonium cation (II_CH^+ is the C-protonated form) to 3-oxocaprolactam (III) is observed during polarography of enamines I, II in dimethylformamide (DMF) containing CF_3COOH. The wave of the reduction of the protonated form of enamine I cannot be fixed under these conditions, since this compound is protonated at the nitrogen atom [1]. The facilitation of the reduction of enamines during their protonation should be substantially less than during C-protonation, and the wave of reduction of the piperidinium cation (I_NH^+) should be concealed by the base-electrolyte discharge current. Moreover, presence of an unstable (similar to II_CH^+) C-protonated form (I_CH^+) also cannot be detected, but one does observe the appearance and growth with time of a wave that can be assigned to the reduction of 3-oxovalerolactam (IV). A similar pattern is also observed in CH_3COOH solutions: when II is introduced (just as in DMF + CF_3COOH), there are two waves on the polarogram, and the first drops rapidly with time, while the overall current remains constant. The first wave corresponds to reduction of the cation (II_CH^+) ($E_{1/2}$ = −0.76 V),* while the second corresponds to reduction of lactam III ($E_{1/2}$ = −0.96 V). In the case of enamine I, $E_{1/2}$ of the wave of the reduction of I_NH^+ is −1.40 V, and one observes the development and slow growth of a new wave with $E_{1/2}$ = −0.88 V, which apparently corresponds to the reduction of lactam IV. Thus under the indicated conditions enamine I may be hydrolyzed to lactam IV; this is confirmed by the synthesis of the previously inaccessible [1] cyanohydrin IV (V) (in 45% yield with mp 161.5-162.5°C). Found: C 51.2; H 5.8; N 20.1%. $C_6H_8N_2O_2$. Calculated: C 51.4; H 5.7; N 20.0%, by the action of NaCN on enamine I in aqueous CH_3COOH with polarographic control of the stage of formation of lactam IV:



I IV V

The data obtained attest to slow conversion of the N-protonated form (I_NH^+) to the thermodynamically more stable immonium cation (I_CH^+), which then undergoes rapid hydrolysis.



III n=2
IV n=1

I_CH+n=1
II_CH+n=2

I n=1
II n=2

I_NH+n=1
II_NH+n=2

Thus when the preferred C-protonation of enamines is established, the rate of hydrolysis is determined by both K_1 and K_2 and K_3. On the other hand, one cannot observe the development of a cation of the I_CH^+

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* Polarography in CH_3COOH was carried out with 0.5 M CH_3COONa as the base electrolyte; the $E_{1/2}$ values are presented relative to an Ag electrode in the same medium.

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type for enamines of low basicity (N-protonation), and the rate of formation of the corresponding ketone (for example, IV) is determined by the rate of C-protonation. Even under those conditions in which N-protonation has been reliably established, conversion to the C-protonated form may be realized under certain conditions, and this opens up prospects for the preparation of various α-substituted lactams.

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