washed on the filter with dry ether, and dried in vacuum over calcium chloride. Yield 0.18 g (75%), mp 260°C (with decomposition). IR spectrum (KBr): 3307 (NH), 3320-2100 cm⁻¹ (NH₃⁺). Found, %: C 68.0, H 6.3, Cl 14.2, N 11.2. C₁₄H₁₄N₂.HCl. Calculated, %: C 68.1, H 6.1, Cl 14.3, N 11.3.

LITERATURE CITED

SYNTHESIS OF 1-SUBSTITUTED 1,2,3,9a-TETRAHYDRO-9H-
imidazo[1,2-a]INDOL-2-ONES

A. A. Shachkus and Yu. A. Degutis

UDC 547.752'785.5.07:543.422

1-R-9,9,9a-Trimethyl-1,2,3,9a-tetrahydro-9H-imidazo[1,2-a]indol-2-ones and the corresponding 2-methylene-2,3-dihydroindoles were obtained by the reaction of 2,3,3-trimethyl-3H-indole with a number of N-substituted chloroacetic acid amides and subsequent reaction of the resulting quaternary salts with bases. The kinetics of intramolecular cyclization of 1-(N-alkylcarbamoyl)ethyl)-2-methylene-2,3-dihydroindoles under the influence of acetic acid were studied. Under the influence of strong protic acids 1-R-imidazo[1,2-a]indol-2-ones undergo decyclization and are converted to 3H-indolium salts.

As we have already reported [1], the reaction of 2,3,3-trimethyl-3H-indole (I) with α-chloroacetamide with subsequent treatment of 1-carbamoylmethyl-3H-indolium chloride (IIa) with bases leads to the formation of imidazo[1,2-a]indol-2-one (IIia) or the corresponding 2-methylene-2,3-dihydroindole (IVa). It seemed of interest to us to study the alkylation of I with N-substituted chloroacetamides and to determine the effect of substituents attached to the nitrogen atom of the carbamoyl group on the formation of the imidazolidine ring.

The reaction of 3H-indole I with chloroacetic acid alkyl-, cyclohexyl-, allyl-, and benzylamides yielded salts IIb-h, which, without isolation, were subjected to the action of potassium hydroxide at 40°C; this procedure gave mixtures of imidazo[1,2-a]indol-2-ones (IIib-h) and methylene bases IVb-h. The degree of conversion of 1-(N-benzylcarbamoylmethyl)-3H-indolium chloride (IIh) to the corresponding imidazo[1,2-a]indol-2-one under the indicated conditions reaches 90%, as compared with 3-5% in the case of 1-(N-cyclohexylcarbamoylmethyl)-3H-indolium chloride (IIf). For the separation of IIa and IV ether or benzene solutions of the mixtures were treated with 2-3% hydrochloric acid; IIb-h remain primarily in the organic solvent, while methylene bases IVb-h pass into the acidic layer in the form of indolium salts IIb-h. Perchlorates IIa-k crystallize out when the calculated amount of perchloric acid is added to ethanol solutions of imidazo[1,2-a]indolones IIb-d.

Opening of the imidazolidine ring of 1-methyl-imidazo[1,2-a]indol-2-one (IIb) by strong protic acids is confirmed by the fact that in the PMR spectrum of a solution in C₂H₅COOH, instead of a singlet of the CONHCH₃ group, one observes a doublet at 2.65 ppm with a spin-spin coupling constant (SSCC) of 4.7 Hz, which is peculiar to the methyl protons of the CONHCH₃...
group of the cation of salt IIb. Methylene bases IVb-h are primarily formed in the neutralization of cooled (to 0°C) solutions of IIIb-h in hydrochloric acid or perchlorates IIIi-k with sodium carbonate. Individual 1- (N-alkylcarbamoylmethyl)-2,3-dihydroindoles IVb-f were obtained by this method.

An investigation of the reaction of 1- (N-tert-butylcarbamoylmethyl)- and 1-(N-phenylcarbamoylmethyl)-3H-indolium chlorides (IIl, m) with potassium hydroxide at 40°C showed that the formation of an imidazolidine ring does not occur and that the final products are methylene bases IVi,j.

Like the compound with a primary amide group (IVa), N-substituted 1-carbamoylmethyl-2,3-dihydroindoles IVb-h undergo cyclization to imidazo[1,2-a]indol-2-ones (IIIb-h) under the influence of weak carboxylic acids such as acetic or propionic acid. We studied the kinetics of the conversion of IVb-e to imidazo[1,2-a]indol-2-ones (IIIa-e) in a 5% solution of acetic acid in deuteroacetone. The kinetics were investigated by the usual PMR spectroscopic methods [2]. Under the indicated conditions the cyclization is described by a first-order reaction equation [3]. The rate constants (K_{eff}) obtained are presented in Table 1. It is apparent from these data that the rate of cyclization depends substantially on the nature of the substituents attached to the nitrogen atom of the carbamoyl group. The significant increase in the rate of formation of IIIb as compared with the rate of formation of IIIa is explained by the increased nucleophilicity of the amide nitrogen atom under the influence of the electron-donor methyl radical. However, in the case of further lengthening of the alkyl chain the effect of the developing frontal strains in the transition state in the formation of the imidazolidine ring leads to a significant decrease in the rate constants, and cyclization of 1-(N-cyclohexylcarbamoylmethyl)-, 1-(N-tert-butylcarbamoylmethyl)-, and 1-(N-phenylcarbamoylmethyl)-2,3-dihydroindoles (IVf,i,j), under the influence of carboxylic acids does not occur.

The structures of the synthesized compounds were confirmed by the results of spectral studies. The IR spectra of IIIb-h in the 1685-1700 cm\(^{-1}\) region contain an absorption band

<table>
<thead>
<tr>
<th>Compound</th>
<th>K_{eff} -10^6, sec(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>IVa</td>
<td>0.895</td>
</tr>
<tr>
<td>IVb</td>
<td>1.750</td>
</tr>
<tr>
<td>IVc</td>
<td>0.892</td>
</tr>
<tr>
<td>IVd</td>
<td>0.794</td>
</tr>
<tr>
<td>IVe</td>
<td>0.682</td>
</tr>
</tbody>
</table>

*The starting concentration of IVa-e was 0.31 M.*