SYNTHESIS OF DERIVATIVES OF 1-OXO-1H-2, 3, 4, 5-TETRAHYDROAZEPINO[3, 4-b]INDOLE AND ITS 9-AZA ANALOG FROM CAPROLACTAM

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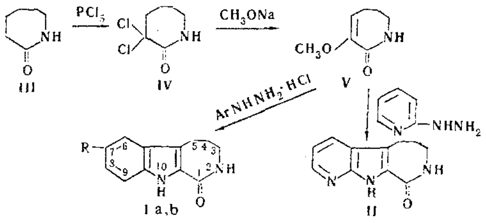
Derivatives of 1-oxo-1H-2, 3, 4, 5-tetrahydroazepino[3, 4-b]indole (**Ia, b**) [1] and 1-oxo-1H-2, 3, 4, 5-tetrahydro-9-azaazepino[3, 4-b]-indole (**II**) are of interest as key compounds for the synthesis of 1- and 2-substituted derivatives of **I** and **II** and also of various condensed heterocyclic systems including indole and azaindole rings. In addition, **I** and **II** may be the starting materials for the preparation of 3-(γ-aminopropyl) derivatives of the indoles [1] and 7-azaindoles.

The methods of obtaining **I** from indol-3-ylbutyric ester [2] and 1-oxo-1, 2, 3, 4-tetrahydrocarbazole [3] published in the literature are complex and can hardly be used for the synthesis of **II**.

We have developed a method for obtaining **I** [1] and **II** from caprolactam (**III**) in the following way:



Ia R=H; Ib R=OCH$_3$

According to this scheme, **III** is converted via α, α-dichlorocaprolactam **IV** [4] into 3-methoxy-2-oxo-2H-1, 5, 6, 7-tetrahydroazepine (**V**) [5]. When **V** is heated (4 hr) with a small excess of phenylhydrazine hydrochloride in ethanolic sulfuric acid solution, i.e., under the conditions generally used for the conversion of carbonyl compounds into indoles by the Fischer reaction [6], **Ia** is obtained. Found, %: C 71.87; H 5.97; N 13.90. Calculated for $C_{12}H_{12}N_2O$, %: C 72.00; H 6.00; N 14.00. Yield 75%, mp 225–227° C (from ethanol, 1 : 20). According to the literature [3], mp 224–227° C. The generality of this reaction for the synthesis of tetrahydroazepino[3, 4-b]indoles substituted in the benzene ring and of tetrahydro-9-azaazepino[3, 4-b]indoles has been shown by the condensation of **V** with p-methoxyphenylhydrazine hydrochloride (**VI**) and with pyrid-2-ylhydrazine (**VII**). Thus, in analogy with the production of **Ia**, the reaction of **V** and **VI** gives **Ib**. Found, %: C 67.81; H 5.90; N 12.01. Calculated for $C_{13}H_{14}N_2O_2$, %: C 67.82; H 6.08; N 12.17. Yield 60.9%, mp 190–191° C (from ethanol). When **V** was fused (230–240° C, 7 min) with a 10% excess of **VII** and 3 mole of zinc chloride, **II** was obtained. Found, %: C 65.94; H 5.50; N 20.88. Calculated for $C_{11}H_{11}N_3O$, %: C 65.65; H 5.51; N 20.89. Yield 66.9%, mp 300° C (decomp., from ethanol). The IR spectra of compounds **I–II** have absorption bands at 1630–1650 cm^{-1} (amide carbonyl) and 3200–3290 cm^{-1} (NH group). The UV spectrum of **II** (in ethanol) has three absorption maxima: λ_{max}, nm (log ε): 222 (4.15); 235 (4.07); 300 (4.11).

REFERENCES

1. R. G. Glushkov and O. Yu. Magidson, USSR patent no. 221708; Byull. izobr., no. 22, 1968.
2. R. Jackson and R. Manske, J. Am. Chem. Soc., **52**, 5030, 1930.
3. H. Tueber, D. Cornelius, and U. Wolcke, Ann., **696**, 116, 1966.
4. W. Francis, J. Thornton, J. Werner, and T. Hopkins, J. Am. Chem. Soc., **80**, 6238, 1958.
5. C. M. Brenner and M. A. Stevens, Swiss patent no. 384579, 1965; 24N532P, 1966.
6. N. N. Suvorov, V. P. Mamaev, and V. M. Rodionov, Reactions and Methods of Investigating Organic Compounds, Collection 9 [in Russian], Goskhimizdat, Moscow, p. 7, 1959.

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THE QUESTION OF THE MECHANISM OF CHLORINATION IN THE HERZ REACTION

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In agreement with statements by Weinberg [1, 2], Huestis [3], by the action of thionyl chloride on o-aminothiophenol obtained benzo-1, 3, 2-thiazathionium chloride (**I**) which, according to their results, does not contain a chlorine atom in the benzene nucleus. The proof of the structure of the products obtained was based on an analysis of the derivatives obtained by the hydrolysis and further transformations of **I**. The results obtained were interpreted by the authors as a proof of the fact that chlorination in the Herz reaction takes place by an electrophilic mechanism with the formation of **I** according to the scheme proposed by Gompper [4]. We have established that the action of