ordinary organic solvents. IR spectrum: 1710 (CO), 1640 (C=C), and 1530 cm⁻¹ (NO₂). Found: C 44.4; H 4.1; Cl 16.4; N 12.9%. C₈H₈N₂O₃ HCl. Calculated: C 44.3; H 4.1; Cl 16.4; N 12.9%. Base IX was obtained as light-yellow crystals with mp 74-75 deg C (from heptane). The product was soluble in ordinary organic solvents but insoluble in water. IR spectrum: 1710 (CO), 1600 (C=C, C=N), and 1510 cm⁻¹ (NO₂). PMR spectrum: 9.21 s (2-H), 4.18 s (PyCH₂), 2.32 s (CH₃), 8.67 d (6-H), and 4.35 d ppm (5-H). Mass spectrum: M^+ 180. Found: C 53.2; H 4.4; N 15.5%. C₈H₈N₂O₃. Calculated: C 53.3; H 4.4; N 15.5%.

<u>2-Methyl-6-azaindole (X)</u>. A solution of 0.6 g (2.8 mmole) of the hydrochloride of IX in 100 ml of ethanol was hydrogenated in the presence of 0.4 g of 6% palladium oxide on carbon at room temperature and an excess hydrogen pressure of 20-30 cm (water column), after which the catalyst was separated, and the filtrate was vacuum evaporated to dryness. The residue (0.47 g) was recrystallized from absolute ethanol to give 0.38 g (81%) of the hydrochloride of X with mp 231-232 deg C. The white crystals were soluble in water and alcohols but insoluble in other ordinary organic solvents. Found: C 57.1; H 5.2; Cl 21.0; N 16.7%. $C_8H_8N_2 \cdot HCl$. Calculated: C 57.0; H 5.3; Cl 21.1; N 16.6%. Base X [5] had mp 183-183.5 deg C. PMR spectrum: 6.13 s (3-H), 11.21 s (NH), 2.44 s (CH₃), 8.56 d (7-H, J=1 Hz), and 7.30 d ppm (4-H, J=5.5 Hz).

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CHEMISTRY OF HETEROCYCLIC N-OXIDES AND RELATED

COMPOUNDS

VIII.* DEHYDROGENATION OF PIPERIDINES BY PYRIDINE N-IMINE DERIVATIVES

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The dehydrogenation of anabasine, piperidine, and isoanabasine N-imine hydrochlorides by pyridine N-imine hydrochloride and the dehydrogenation of anabasine pyridinia-p-toluene-sulfonamidate were studied. The corresponding pyridines and products of reductive deimination were obtained.

We have demonstrated the possibility of the application of pyridine N-imine hydrochlorides as homogeneous dehydrogenating agents for the dehydrogenation of the completely saturated heterocyclic ring of anabasine [2]. In the present research we extended the limits of applicability of the method by studying the thermal transformation of anabasine N-imine hydrochloride (I), the dehydrogenation of piperidine (II) and isoanabasine (III) hydrochlorides by pyridine N-imine hydrochloride (IV), and the dehydrogenation of anabasine (V) by pyridinia-p-toluenesulfonamidate (VI).

*See [1] for communication VII.

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N-Imine derivatives IV and VI were obtained by the methods described in [2]. Since the anabasine molecule contains a secondary amino group that is capable of undergoing amination with O-hydroxylamine-sulfonic acid [3], the method of acyl protection of the piperidine ring was used for the synthesis of starting I; for this anabasine was converted to N-benzoylanabasine [4], and the latter was aminated to give the N-benzoyl derivative of N-iminoanabasine (VII), which was subjected to acid hydrolysis.

The structure of the synthesized I was confirmed by deimination with nitrous acid [5], as a result of which anabasine was obtained.

The dehydrogenation of hydrochloride I is achieved by thermolysis (at 220-235 deg C), during which a dehydrogenation product -2,3'-dipyridyl - and a product of reductive deimination - anabasine - are formed.



Dehydrogenation of piperidines II and III occurs under similar conditions under the influence of imine IV.



In contrast to the dehydrogenation of dihydropyridine [2], the reactions with hexahydropyridines I-III are accompanied by resinification, and the dehydrogenation products are formed in lower yields.

Results close to the results of dehydrogenation of piperidines by means of N-oxides of pyridine bases [6] were obtained in the case of dehydrogenation of anabasine with sulfonamidate VI.

EXPERIMENTAL

Monitoring of the reactions and isolation of the reaction products was accomplished by paper chromatography (on "rapid" brand paper) in butanol-hydrochloric acid-water (50:7:14) (system A) and butanol-acetic acid-water (50:7:14) (system B) with development with Dragendorf's reagent and by thin-layer chromatography (TLC) on activity II aluminum oxide in chloroform-benzene-alcohol (22:8:2) (system C) with development by iodine vapors. The reaction products were identified by mixed-melting-point determinations with authentic samples.

<u>N'-Imino-N-benzoylanabasine Hydrochloride (VII)</u>. A 10-g (80 mmole) sample of previously neutralized (with 5 N KOH) O-hydroxylaminesulfonic acid was added in portions with vigorous stirring at 70-75 deg C to a suspension of 2.65 g (10 mmole) of N-benzoylanabasine (VIII) in 15 ml of water, during which the pH was maintained at seven by the addition of potassium acetate. At the end of the reaction the mixture was cooled and extracted with chloroform to separate the unchanged VIII. The mother liquor was acidified with hydrochloric acid, an equivalent amount of barium chloride was added, and the mixture was filtered. The filtrate was evaporated, and the dry residue was extracted with absolute ethanol. The alcohol solution was decolorized with activated charcoal and worked up to give 2.45 g (70%) of VII with mp 140 deg C and R_f 0.72 (system A). Found: Cl 11.25%. C₁₇H₁₉N₃O'HCl. Calculated: Cl 11.21%. The picrate had mp 150-153 deg C. Found: N 16.45%. C₁₇H₁₉N₃O₇. Calculated: N 16.47%.

<u>N'-Iminoanabasine Dihydrochloride (I)</u>. A 2.45-g (9 mmole) of VII was refluxed in 20% hydrochloric acid for 15 h, after which the mixture was extracted with ether to isolate the benzoic acid [0.57 g (70%)]. The residue was evaporated to dryness, and the dry residue was treated with alcohol to give I in the form of a hygroscopic oil, with R_f 0.3 (system A) that did not crystallize on prolonged standing. Found: Cl 28.41% $C_{10}H_{15}N_3 \cdot$ 2HCl. Calculated: 28.40% Dipicrate (amorphous powder), mp 82 deg C. Found: N 19.60% $C_{10}H_{15}N_3 \cdot 2C_6H_3N_3O_7 \cdot$ Calculated: N 19.84%

Deimination of N'-Iminoanabasine Hydrochloride (I). A 0.25-g (1 mmole) sample of I was dissolved in 0.3 ml of hydrochloric acid, 3 ml of water was added, and the mixture was cooled to 0 deg C. A solution of 0.08 g (1.1 mole) of sodium nitrite in 0.6 ml of water was added dropwise with stirring. When nitrogen evolution

ceased, the mixture was made alkaline to pH 8 and extracted with ether. The solvent was removed from the extract by distillation to give 0.14 g (87%) of anabasine with R_f 0.56 (system B). Traces of N-nitrosoanabasine with R_f 0.9 (system B) were detected in the reaction mixture.

<u>Dehydrogenation of N'-Iminoanabasine Hydrochloride (I).</u> A 0.5-g (2 mmole) sample of I was heated at 220-235 deg C for 8 h, after which the mixture was dissolved in water, and the solution was made alkaline to pH 4-5 and extracted with chloroform. Workup of the extract gave 0.03 g (23%) of 2,3'-dipyridyl (IX) with R_f 0.9 (system B). The mother liquor was made alkaline to pH 8 and extracted with chloroform. Workup of the extract gave 0.19 g (60%) of anabasine (V) with R_f 0.57 (system B).

Dehydrogenation of Piperidine Hydrochloride (II) by Pyridine N-Imine Hydrochloride (IV). A mixture of 0.62 g (5 mmole) of II and 2 g (15 mmole) of salt IV was heated at 205-215 deg C for 2 h, after which it was dissolved in water. The aqueous solution was acidified to pH 3-4 and extracted with ether. Hydrogen chloride was bubbled into the ether solution, after which the solvent was removed by distillation to give 0.8 g (34%) of pyridine hydrochloride (X) with R_f 0.28 (system A). The mother liquor was evaporated to a small volume and subjected to chromatography on silica gel in system A to give starting II and IV in 72 and 46% yields, respectively. Ammonia was detected by means of Nessler's reagent.

Dehydrogenation of Isoanabasine Hydrochloride (III) by Pyridine N-Imine Hydrochloride (IV). A mixture of 0.59 g (25 mmole) of hydrochloride III and 1 g (7.5 mmole) of hydrochloride IV was heated at 210-215 deg C for 3 h, after which it was dissolved in water, and the solution was extracted with ether. Workup of the extract gave 0.07 g (18%) of IX with R_f 0.9 (system C). Dry hydrogen chloride was bubbled into the ether solution, and the mixture was worked up to give 0.13 g (15%) of X. Workup of the aqueous solution at pH 8 gave 0.23 g of unchanged III with R_f 0.5 (system B).

Dehydrogenation of Anabasine (V) by Pyridinia-p-toluenesulfonamidate (XI). A mixture of 0.4 g (2.5 mmole) of V and 1.86 g (7.5 mmole) of amidate was heated in a distillation flask at 190-200 deg C for 30 min. The distillate consisted of 0.43 g (74%) of X with R_f 0.28 (system A). The reaction mixture was dissolved in chloroform, and the solution was decolorized with aluminum oxide. The solvent was removed by distillation, and the residue was dissolved in water. The aqueous solution was acidified to pH 3 and extracted with ether. Workup of the extract gave 0.98 g (76%) of p-toluenesulfonamide with R_f 0.3 (system C) and mp 136 deg C. The mother liquor was extracted (at pH 5) with chloroform, and the extract was worked up to give 0.3 g of IX, which was purified in the form of the hydrobromide. The yield of product with R_f 0.9 (system B) was 0.17 g (44%).

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