DIMERIZATION OF N-METHYLANABASINE IN THE PRESENCE OF RANEY NICKEL

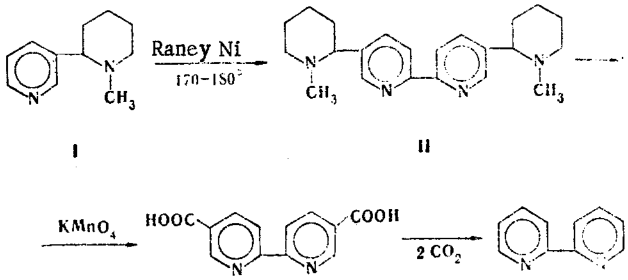
A. A. Ziyaev, O. S. Otroshchenko,
A. S. Sadykov, Kh. D. Khalilova,
and G. A. Tolkacheva

UDC 542.952.6:547.828

N-Methylanabasine undergoes dimerization in the presence of Raney nickel at 170-180°C to give 5,5'-bis(1-methyl-2-piperidyl)-2,2'-dipyridyl. Oxidation of the latter gives 6,6'-bis(nicotinic acid).

We have previously shown [1] that N-methylanabasine (I) reacts with sodium metal to give a dimer in which the pyridine rings are connected in the 4 and 4' positions. In the present research we studied the direction of dimerization of I under the influence of Raney nickel under conditions similar to those described in [2, 3] for pyridine.

In contrast to pyridine, dimerization of N-methylanabasine is not observed at 20-115°C, and 5,5'-bis(1-methyl-2-piperidyl)-2,2'-dipyridyl (II) is formed in only 10-12% yield only at 170-180°C.



I II III IV

The structure of II was confirmed by the UV, IR, and PMR spectral data and also by subsequent transformations of this compound. Thus its oxidation by potassium permanganate gave 6,6'-bis(nicotinic acid) (III), the decarboxylation of which leads to 2,2'-dipyridyl (IV).

Thus the presence of a substituent such as N-methyl-2-piperidyl in the pyridine ring does not affect the direction of dimerization [2, 3] but only hinders it.

EXPERIMENTAL

The UV spectrum of a 10^{-3} mole/liter solution of the compound in alcohol was recorded with an SF-4A spectrophotometer. The IR spectrum of a potassium bromide pellet of the compound was recorded with a UR-10 spectrometer. The PMR spectrum of a CCl_4 solution was obtained with a Hitachi H-60 spectrometer with tetramethylsilane as the internal standard.

5,5'-Bis(1-methyl-2-piperidyl)-2,2'-dipyridyl (II). A 50 g (0.3 mole) sample of N-methylanabasine (I) and 5 g of Raney nickel were added to a three-necked flask equipped with a stirrer, reflux condenser, and a thermometer, and the mixture was heated at 170-180°C for 12 h. At the end of the reaction, the catalyst was removed by filtration, and unchanged I was removed by distillation at 138-140°C (12 mm). The residue was extracted with petroleum ether, and the solvent was removed from the extract by distillation to give 18 g of a viscous yellow oil, which was separated with a column filled with activity II aluminum oxide (elution with ether). Monitoring was accomplished by means of paper chromatography in a

---

V. I. Lenin Tashkent State University, Tashkent 700095. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1224-1225, September, 1978. Original article submitted October 26, 1977.

0009-3122/78/1409-0988$07.50

butanol–acetic acid–water system (4:1:5). The eluates with R_f 0.4 were combined, and the solvent was removed by distillation to give 16.1 g (60%) of 5,5'-bis(1-methyl-2-piperidyl)-2,2'-dipyridyl with mp 150-151°C (from hexanol). IR spectrum: 850 (substituted pyridine CH); 1550, 1620, and 1660 cm^{-1} (C=C and C=N). UV spectrum, λ_{max} (log ε): 237 (3.5) and 290 nm (4.3). PMR spectrum: 8.50 (2H, s, 6-H), 8.43 (2H, d, J = 7.3 Hz, 4-H), 7.74 (2H, d, J = 7.3 Hz, 3-H), 3.0 (2H, d, J = 11 Hz, α-CH_2), 2.9 (2H, m, α-CH), 2.0 (6H, s, N–CH_3), and 1.1-2.2 ppm (β and γ protons of the piperidine ring). Found: C 75.3; H 8.4; N 15.8%. $C_{22}H_{30}N_4$. Calculated: C 75.4; H 8.5; N 16.0%. The dipicrate had mp 224-225°C (from alcohol). Found: C 50.5; H 4.4; N 17.3%. $C_{22}H_{30}N_4 \cdot 2C_6H_3N_3O_7$. Calculated: C 50.4; H 4.4; N 17.3%.

6,6'-Bis(nicotinic acid) (III). An excess amount of a saturated aqueous solution of potassium permanganate was added to an aqueous solution of 3 g of II, and the mixture was allowed to stand for 24 h. The precipitated manganese dioxide was removed by filtration and washed with water, and the filtrate was treated with copper acetate to yield the copper salt of acid III. The latter was washed thoroughly with water, suspended in hot water, and decomposed with hydrogen sulfide. The precipitated copper sulfide was removed by filtration and washed with hot water. The filtrate was evaporated to dryness, and the residue was crystallized from absolute alcohol to give 0.65 g (21.6%) of acid III in the form of pinkish crystals with mp 364-365°C (after sublimation). Found: C 58.9; H 3.2; N 11.4%. $C_{12}H_8N_2O_4$. Calculated: C 59.0; H 3.3; N 11.5%.

2,2'-Dipyridyl. A mixture of 1.5 g of acid III and 4.5 g of copper bronze in 80 ml of benzene was heated in a sealed tube at 240-250°C for 3 h. At the end of the reaction the tube was opened, and the solid material was removed by filtration and washed several times with hot benzene. The solvent was removed from the filtrate by distillation, and the residue was treated with absolute alcohol to extract the 2,2'-dipyridyl (IV). The yield of the product with mp 68.5-69°C (from petroleum ether) and R_f 0.88 [Al_2O_3, acetone–ether–methanol (5:5:3)] was 0.43 g (44%). No melting-point depression was observed for a mixture of this product with a sample of 2,2'-dipyridyl.

LITERATURE CITED

1. A. A. Ziyaev, O. S. Otroshchenko, A. S. Sadykov, and G. A. Tolkacheva, Khim. Geterotsikl. Soedin., No. 2, 364 (1969).
2. G. M. Badger and W. H. F. Sasse, J. Chem. Soc., 616 (1956).
3. G. D. Jackson, W. H. F. Sasse, and C. P. Whittle, Austral. J. Chem., 16, 1 (1963).