BRIEF COMMUNICATIONS

DIMERIZATION OF N-METHYLANABASINE IN THE PRESENCE OF METALLIC SODIUM

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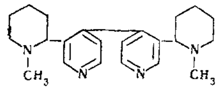
In a study of the dimerization of N-methylanabasine in the presence of metallic sodium under conditions for the dimerization of pyridine, it was found that the reaction does not take place at room temperature while at 50–70° C it leads to the formation of β, β'-di(1-methylpiperid-2-yl)-γ, γ'-bipyridyl. Oxidation of the latter yielded 4, 4'-bipyridyl-5, 5'-dicarboxylic acid, the decarboxylation of which gave γ, γ'-bipyridyl.

Dimerization of pyridine and some other heterocyclic compounds in the presence of various metals has been studied by several authors [1, 2]. This paper gives the results of a study of the dehydrogenation condensation of N-methyl anabasine (I) under the action of metallic sodium. The initial I was obtained by a known procedure [3]. The dimerization of I was studied over a wide range of temperatures—from 20 to 180° C. It was found, in contrast to pyridine, that no dimerization takes place at room temperature. At 50–70° C the reaction leads to the formation of β,β'-di(1-methylpiperid-2-yl)-γ,γ'-bipyridyl (II). A test for the α,α'-bond with the ferrous ion was negative. In contrast to this, at 115–120° C and at 160–180° C dimerization takes place also at the α-carbon atoms of the pyridine ring of N-methylanabasine. An account of this will be given separately.

In order to prove the structure of II, it was oxidized with potassium permanganate, giving 4,4'-bipyridyl-5,5'-dicarboxylic acid (III). The formation of this acid shows that the oxidation destroys the two α-substituted N-methylpiperidine rings. The UV spectrum of the acid and of the base itself has λ_{max} 240 nm, which is characteristic for γ,γ'-bipyridyl. In the IR spectrum of the base II, in the region of nonplanar deformation vibrations there is a band at 853 cm^{-1} corresponding to 1,2,4-substitution in a benzene ring [4].

The decarboxylation of III yielded γ,γ'-bipyridyl, which gave no depression of the melting point in admixture with an authentic sample. Its formation shows that the dimerization of I in the presence of metallic sodium leads to the dimer with a γ,γ'-link, as in the case of pyridine.

On the basis of all that has been said above, the following structural formula is proposed for the dimer II:



EXPERIMENTAL

Dimerization of N-methylanabasine in the presence of metallic sodium. A three-necked flask fitted with a mechanical stirrer, reflux condenser, and thermometer was charged with 66 g (0.380 mole) of I and, with constant stirring, 5 g (0.220 mole) of metallic sodium was added in portions. After the whole of the sodium had been added, the reaction mixture was heated at 50–70° C for 33 hr. The reaction was considered complete when no pieces of sodium were left in the flask. After the end of the reaction, the unchanged I was distilled off in vacuum. The residue was oxidized with a current of air. Then the reaction mixture was decomposed with water and extracted with benzene. After the solvent had been distilled off, the technical product was obtained in the form of a viscous oil. The yield of reaction products was 10.56 g (16%).

β, β'-Di(1-methylpiperid-2-yl)-γ, γ'-bipyridyl (II). Ten grams of the mixture of reaction products was separated in a column filled with alumina of activity II. Elution was carried out with ether. The process was monitored by paper chromatography in the butanol—acetic acid—water (10 : 4 : 5) system. The eluates with R_f 0.55 were combined. Distillation of the solvent yielded 6 g (9% calculated on the initial N-methylanabasine) of II in the form of a dark yellow oil which could not be crystallized. Dipicrate—mp 189–190° C (from ethanol). Found, %: N 17.41, 17.14. Calculated for $C_{22}H_{30}N_4 \cdot 2C_6H_3N_3O_7$, %: N 17.32.

4, 4'-Bipyridyl-5, 5'-dicarboxylic acid (III). A saturated aqueous solution of potassium permanganate was added to an aqueous solution of 1.5 g (0.005 mole) of II until a pink coloration was obtained which did not disappear in the course of a day. The precipitate of manganese oxide was filtered off and washed with water. Addition of copper acetate to the concentrated solution yielded the copper salt of the acid III. This was carefully washed with water, suspended in hot water, and decomposed with hydrogen sulfide. The precipitate of copper sulfate was filtered off and washed with hot water. The filtrate was evaporated to dryness and the residue was recrystallized from absolute ethanol, giving 0.31 g (30%) of the acid III in the form of grayish crystals with mp 240–242° C (subl.). Found, equiv: 123, 122. Calculated for $C_{12}H_{18}N_2O_4$, %: equiv: 122.

γ, γ'-Bipyridyl. A mixture of 0.5 g (0.002 mole) of III and 1.5 g (0.023 mole) of copper bronze in 25 ml of benzene was heated in a sealed tube at 220–230° C for 3 hr. Then the tube was opened, and the mixture was filtered. The benzene was distilled off from the filtrate, and the residue was treated with absolute ethanol to give 0.13 g (40%) of γ, γ'-bipyridyl with mp 110–111° C. Found, %: N 18.26, 18.20. Calculated for $C_{10}H_8N_2$, %: N 18.00. Picrate—mp 254–255° C. A mixture with the picrate of an authentic sample of γ, γ'-bipyridyl melted at 255–256° C.

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