The 4-amino-4'-methoxydiphenyl necessary for the synthesis of spirochromenes IV-VI was obtained from 4-nitrodiphenyl by the following known transformations: Nitration to 4,4'-dinitrodiphenyl [8], partial reduction of the dinitro compound [9], diazotization of the resulting nitro amine and subsequent decomposition of the diazonium salt in the presence of dilute sulfuric acid, treatment of the 4-hydroxy-4-nitrodiphenyl with dimethyl sulfate in alkaline media [8], and reduction of the 4-methoxy-4'-nitrodiphenyl with hydrazine hydrate in isopropyl alcohol [10]. 4-Methoxy-4'-hydrazinodiphenyl (X) was synthesized by the method used to prepare 4-hydrazinodiphenyl [11]. 5-(p-Methoxyphenyl)-2,3,3-trimethylindolinine methodide (XI) was obtained by the method in [12]. The properties of the compounds obtained are presented in Table 2.

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RESEARCH IN THE DIPIPERIDYL SERIES

XIX.* SYNTHESIS OF 4-(4-PIPERIDYL)-1,2,5,6-TETRAHYDROPYRIDINE

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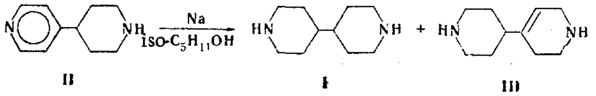
UDC 547.828:542.942.4:543.422.25.4.6'544

Hydrogenation of 4,4'-dipyridyl or 4-(4-piperidyl)pyridine with sodium in isoamyl alcohol gives a mixture of hydro derivatives, from which 4-(4-piperidyl)-1,2,5,6-tetrahydropyridine was isolated.

It has been shown that 4,4'-dipiperidyl (I) and 4-(4-piperidyl)pyridine (II) are formed in the hydrogenation of 4,4'-dipyridyl [2-4].

In a continuation of our earlier research [5] we have investigated the side products of the reaction and have shown that 4-(4-piperidyl)-1,2,5,6-tetrahydropyridine (III) is formed in 42% yield along with I in the hydrogenation of 4,4'-dipyridyl and II with sodium in isoamyl alcohol.



II I III

A one-proton broad signal with Δν 1/2 Hz, which corresponds to an olefinic proton having spin–spin coupling constants on the order of 5-8 Hz from the protons of the methylene group, is observed in the NMR spectra of III at 2.3 ppm (in pyridine) and 5.4 ppm (in $CHCl_3$). This result unambiguously excludes from con-

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*See [1] for the preceding communication.

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sideration a structure with double bonds in the 4−4', 2−3, and 1−2 positions; i.e., the double bond is in the 3−4 position, as is also manifested in the additional splitting of the signals of the axial and equatorial protons of the α-methylene groups at 2.3-3.4 ppm. The signals at 1.65 and 2.23 ppm indicate the presence of two NH groups; this also is confirmed by measurement of the ionization constants (pK_{a1} 10.87 and pK_{a2} 9.78). These data are in agreement with the proposed structure (III).

EXPERIMENTAL METHOD

The IR spectra of KBr pellets of the compounds were recorded with a UR-10 spectrometer at 500-3600 cm^{-1}. The UV spectra of 10^{-4} M alcohol solutions of the compounds were recorded with an SF-4A spectrophotometer. The NMR spectra of chloroform and pyridine solutions were recorded by V. B. Leont'ev with a Hitachi P-20A spectrometer (60 MHz) with tetramethylsilane as the internal standard. Potentiometric titration was carried out with an LPM-60M pH-meter by the standard method. The pK_a values were calculated with allowance for a correction for the concentration of the hydroxide ions [6]. The chromatography of the bases was realized with a column filled with KSK silica gel; the ratio of the diameter of the column to the thickness of the sorbent layer was 1:20, the ratio of the sorbent to the bases was 1:40, and elution was accomplished with petroleum ether−benzene.

The individuality of the compounds was monitored by ascending TLC on a loose layer of activity II aluminum oxide in a methanol−benzene−ammonia−saturated chloroform system (1:5:35) with development by iodine vapors.

Commerical-grade 4,4'-dipyridyl, with mp 113-114° [7], was used in the experiments. 4-(4-Piperidyl)-pyridine was synthesized by the method in [3] and had mp 79-80°.

4-(4-Piperidyl)-1,2,5,6-tetrahydropyridine (III) and 4,4'-Dipiperidyl (I). A) Sodium [15 g (0.87 g-atom)] was supended in 150 ml of refluxing toluene, and 16.2 g (0.1 mole) of II dissolved in 150 ml of isoamyl alcohol was added. After all of the sodium had been converted, 200 ml of water was added to the mixture, and it was refluxed for 30 min. The organic layer was separated, and the bases were extracted twice with isoamyl alcohol. The extract was dried with $MgSO_4$ and vacuum evaporated. The residue was recrystallized from benzene to give 14.8 g (88%) of a mixture of I and III (R_f 0.16 and 0.19).

B) A mixture of I and III (10 g) was introduced into a chromatography column and eluted with 300 ml of eluent (1:1). Eluate A, enriched in I, was obtained; the residual bases were eluted with the eluate (1:2) to give eluate B containing III. The solvent was removed by distillation, and residual A was recrystallized from benzene to give 6.74 g (45%) of I with mp 166-167° [2] and R_f 0.16. NMR spectrum in pyridine: 2.4 ppm (NH). IR spectrum (KBr), cm^{-1}: 3163 and 3430 (two NH groups). Ionization constants, pK_a: 10.99 and 10.23 [8]. Recrystallization of B from ether gave 6.23 g (42%) of III with mp 80-81° and R_f 0.19. IR spectrum (KBr), cm^{-1}: 1630 and 802 (double bond); 3260, 3290 (NH). UV spectrum (in ethanol), λ_{max}: 215 nm. Found: C 71.3; H 11.8; N 16.5%. $C_{10}H_{20}N_2$. Calculated: C 71.4; H 11.9; N 16.8%. The dipicrate had mp 217-218° (from alcohol).

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