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SELECTIVE HYDROGENATION AND DEHYDROCYCLIZATION OF 3-METHYL-4-BENZYL-2,6-DIPHENYLPYRIDINE

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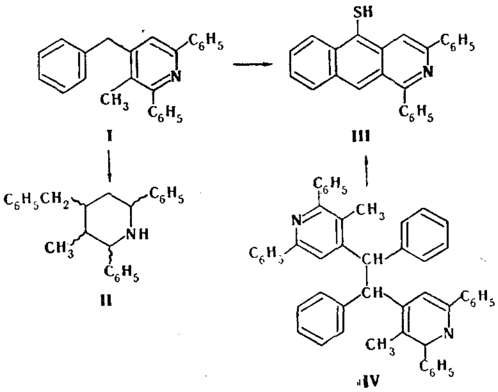
3-Methyl-4-benzyl-2,6-diphenylpiperidine was obtained by hydrogenation of 3-methyl-4-benzyl-2,6-diphenylpyridine in the presence of rhenium heptasulfide; this confirms the common character of the method of selective hydrogenation of aryl(aralkyl)-substituted pyridine bases to give similarly substituted piperidines. Dehydrocyclization of this pyridine base by heating with sulfur leads to 10-mercapto-1,3-diphenyl-2-azaanthracene, which was obtained under the same conditions from 1,2-diphenyl-1,2-bis(3-methyl-2,6-diphenyl-4-pyridyl)ethane.

The selective hydrogenation of arylpyridine bases is of interest as a method for the preparation of similarly substituted piperidines. We have established that the pyridine ring is selectively hydrogenated without involvement of the phenyl ring in the hydrogenation of 2,5-dimethyl-4-phenyl(p-methylbenzyl) pyridines in the presence of rhenium heptasulfide [1]. In the present communication we describe the hydrogenation under the same conditions of the previously synthesized 3-methyl-4-benzyl-2,6-diphenylpyridine (I) [2] to give 3-methyl-4-benzyl-2,6-diphenylpiperidine (II), which was obtained in rather high yield. This example also serves as a confirmation of the common character of the selective hydrogenation of aryl- and aralkylpyridines in the presence of rhenium heptasulfide.



In a study of the catalytic dehydrocyclization of pyridine base I it was established that it is converted to condensed heterocycles, viz., 1,3-diphenyl-2-azaanthracene and 2-phenyl-1-azabenzo[f]fluoranthene [2]. We used a K-16 industrial dehydrogenating catalyst as the catalyst. We attempted to bring about the dehydrocycliza-

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tion of pyridine base I by means of sulfur (300°C). In this case also the reaction leads to the formation of an azaanthracene system. However, 1,3-diphenyl-2-azanthracene itself is not formed in this case; instead, we obtained its thiol derivative, viz., 10-mercapto-1,3-diphenyl-2-azaanthracene (III) (in 33% yield). The same compound was obtained in lower yield (10%) under similar conditions from 1,2-diphenyl-1,2-bis(3-methyl-2,6-diphenyl-4-pyridyl)ethane (IV) – the product of oxidative dimerization of pyridine base I [2]. The corresponding substituted stilbene was not isolated in this case. The principal transformations of IV are evidently cleavage of the C–C bond, dehydrocyclization, and dehydrogenation.

It is important to note that mercapto derivative III is not formed when 1,3-diphenyl-2-azaanthracene is heated with sulfur. On the basis of this it may be assumed that sulfur is incorporated in the dehydrocyclization or dehydrogenation step. It is possible that 1,3-diphenyl-2-azaanthro-10-thione, which as a result of enolization is converted to thiol derivative III, is an intermediate in these transformations.

The IR spectrum of III contains a weak-intensity band of stretching vibrations of an SH group at 2563 cm^{-1}. Its UV spectrum is similar to the spectrum of 1,3-diphenyl-2-azaanthracene, but, in contrast to the latter, the long-wave absorption band does not have a fine structure. The molecular-ion peak with m/z 363, which corresponds to its empirical formula, is the most intense peak in the mass spectrum of III. The intense peaks of the fragment ions with m/z 362 and 330, which correspond to splitting out of H and SH particles by the molecular ion, are characteristic for the dissociative ionization of thiophenols [3].

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The UV spectra of solutions in alcohol were obtained with a Specord UV-vis spectrophotometer. The PMR spectra were recorded with a Tesla BS-487C spectrometer with tetramethylsilane as the internal standard. The mass spectra were measured with an MKh-1303 mass spectrometer. Column chromatography and thin-layer chromatography (TLC) were carried out on Brockmann activity II Al_2O_3.

3-Methyl-4-benzyl-2,6-diphenylpiperidine (II). A glass ampul, open at one end and containing 1 g (2.98 mmole) of I, 0.05 g of rhenium heptasulfide, and 15 ml of benzene, was placed in a 125-ml rotating autoclave, and hydrogenation was carried out at 240°C and an initial hydrogen pressure of 130 atm for 5 h. The catalyst was removed by filtration, the benzene was removed from the filtrate by distillation, and the residue (0.92 g) was crystallized from heptane to give 0.68 g (69%) of III with mp 141-142°C and R_f 0.44 [ethyl acetate–heptane (1:4)]. IR spectrum: 3312 cm^{-1} (NH). PMR spectrum (in $CDCl_3$): 3.70 (1H, q, 6-H), 3.14 (1H, d, 2-H), and 0.83 ppm (3H, d, CH_3). Found: C 88.0; H 8.0; N 4.2%; M 341. $C_{25}H_{27}N$. Calculated %: C 88.0; H 7.9; N 4.1%; M 341.

10-Mercapto-1,3-diphenyl-2-azaanthracene (III). A) A mixture of 3 g (8.9 mmole) of pyridine base I and 0.72 g (0.022 mole) of sulfur was heated in a stream of nitrogen at 300-305°C for 1 h, after which it was extracted with 600 ml of boiling heptane. The heptane was removed from the extract by distillation, and the residue (2.3 g) was chromatographed with a column (h=25 cm, d=2.5 cm, heptane) to give, initially, 0.99 g (33%) of mercaptoazaanthracene III as yellow crystals with mp 167-168°C (from heptane) and R_f 0.69 [ethyl acetate–heptane (1:4)]. UV spectrum (in alcohol), λ_{max} (log ε): 208 (4.51), 255 (4.47), 272 (4.46), and 404 nm (3.94). PMR spectrum (in $CDCl_3$): 7.94 ppm (1H, s, 4-H). Found: C 82.7; H 4.6; N 3.7%; M 363. $C_{25}H_{17}N$. Calculated: C 82.6; H 4.7; N 3.6%; M 363. Subsequent elution gave 0.96 g of starting I.

B) By a similar method, from 0.45 g (6.7 mmole) of diphenyldipyridylethane IV and 0.021 g (0.67 mmole) of sulfur we obtained 0.025 g (10%) of mercaptoanthracene VII with mp 167-168°C. No melting-point depression was observed for a mixture of this product with a sample obtained by method A.

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