CATALYTIC DEHYDROCYCLIZATION OF 3-ISOPROPYL(n-PROPYL)-2,6-DIPHENYLPYRIDINE AND 3-n-PROPYL-2,4,6-TRIPHENYLPYRIDINE

N. S. Prostakov, A. V. Varlamov,
and T. N. Borisova

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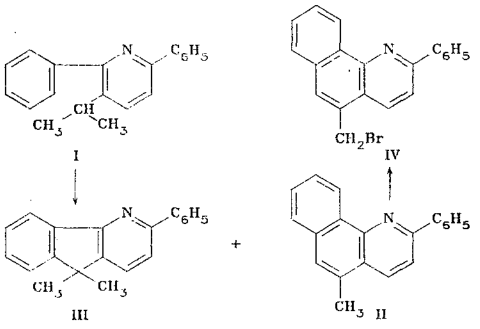
The catalytic dehydrocyclization of 3-isopropyl-2,6-diphenylpyridine proceeds in two directions: conversion to 10-methyl-3-phenyl-4-azaphenanthrene and conversion to 9,9-dimethyl-4-azafluorene. $C_{(9)}$-Unsubstituted 4-azafluorenes were obtained in the dehydrocyclization of pyridine bases that contain a phenyl group in the α position and an n-propyl group in the β position.

The catalytic dehydrocyclization of pyridine bases that contain methyl and aryl substituents in certain positions in the pyridine ring is a preparative method for the synthesis of condensed nitrogen heterocycles. Isomeric (with respect to the position of the nitrogen atom) azafluorenes [1-4], benzo[g]isoquinolines [5, 6], benzoazafluoranthrenes [7, 8], and dihydrosilazaanthracenes [9] have been obtained by this method.

The transformation of substituted pyridine bases that contain alkyl substituents other than methyl groups under catalytic dehydrocyclization conditions has not been studied.

In the present communication we present information on the condensed heterocyclic compounds that are formed during dehydrocyclization on a K-1 catalyst of six pyridine bases that contain phenyl groups in the α(γ) positions and an isopropyl or n-propyl group in the β position.

10-Methyl-3-phenyl-4-azaphenanthrene (II) and 9,9-dimethyl-4-azafluorene (III) were isolated in 13% overall yield from the products of the dehydrocyclization of 3-isopropyl-2,6-diphenylpyridine (I):



Thus the dehydrocyclization of pyridine base I proceeds via splitting out of a hydrogen atom either from the methylidyne or methyl group of the isopropyl grouping. Azaphenanthrene II and azafluorene III are formed in a ratio of 1:0.75, which indicates the approximately equal probabilities of these two dehydrocyclization pathways.

It was established by gas-liquid chromatography (GLC) that the catalyzate contains very small amounts of yet another substance, which we were unable to isolate. However, on the basis of the fact that a molecular-ion peak (M^+) with m/z 255 is observed in the mass spectrum of the products of catalytic transformation of pyridine base I, it may be assumed that this compound is the product of demethylation of azaphenanthrene II, viz., 3-phenyl-4-azaphenanthrene. The UV spectra of azaphenanthrene II and azafluorene III are similar to the spectra of, respectively, phenanthrene [10] and 9-methyl-4-aza-9-fluorenol [11].

10-Bromomethyl-3-phenyl-4-azaphenanthrene (IV) was obtained in the radical bromination of azaphenanthrene II. 3-n-Propyl-2,6-diphenylpyridine (V) and 3-n-propyl-2,4,6-triphenyl-

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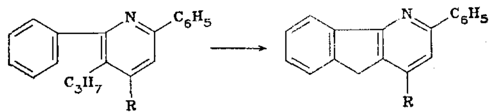
Patrice Lumumba Peoples' Friendship University, Moscow 117923. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 648-650, May, 1984. Original article submitted June 16, 1983.

pyridine (VI) underwent similar dehydrocyclization reactions. $C_{(9)}$-Unsubstituted 4-azafluorenes, viz., 3-phenyl-4-azafluorene (VII) [4] and 1,3-diphenyl-4-azafluorene (VIII) [12], respectively, were isolated from the complex mixtures of reaction products.



V,VI VII,VIII

V,VII R=H; VI,VIII R=C_6H_5

Two possible pathways for the transformation of pyridine bases V and VI to $C_{(9)}$-unsubstituted azafluorenes VII and VIII may be assumed: cleavage of the propyl group under the reaction conditions and subsequent dehydrocyclization; dehydrocyclization with the formation of a 9-ethyl-substituted azafluorene and subsequent splitting out of an ethyl group as a result of hydrogenolysis.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in $CDCl_3$ were recorded with a B5 487C spectrometer (80 MHz) with tetramethylsilane as the internal standard. The UV spectra of solutions in alcohol were recorded with a Specord UV-vis spectrophotometer. The mass spectra were obtained with an MKh-1303 spectrometer at an ionizing-electron energy of 70 eV. Activity II aluminum oxide and elution with chloroform were used to separate the picrates.

10-Methyl-3-phenyl-4-azaphenanthrene (II) and 9,9-Dimethyl-3-phenyl-4-azafluorene (III). A solution of 10 g (36 mmole) of pyridine base I in 50 ml of benzene was passed at a constant rate for 2 h through a contact tube containing 25 ml of K-16 catalyst; the temperature in the catalyst zone was 530-540°C. The benzene was removed from the catalyzate by distillation, and the residue (8.1 g), which, according to GLC data, contained, in addition to starting pyridine base I, three substances with retention times of 2.3, 3.7, and 5.2 min (in a ratio of 0.75:1:0.32), was chromatographed with a column (h = 50 cm, d = 2 cm) packed with aluminum oxide by elution with heptane. We initially isolated 0.3 g of azaphenanthrene II in the form of colorless crystals with mp 136-137°C (from heptane). PMR spectrum: 2.64 ($10-CH_3$), 7.40-8.40 (m, aromatic protons), and 9.40 ppm (m, 5-H). UV spectrum, λ_{max} (log ε): 220 (4.6), 2.42 (5.01), 286 (4.83), 345 (4.18), 362 nm (4.14) Mass spectrum, m/z (%): M^+ 269 (100), 254 (10.3), 192 (7), 191 (15), 190 (29), 164 (35). Found: C 89.2; H 5.7; N 5.0%. $C_{20}H_{15}N$. Calculated: C 89.2; H 5.5; N 5.3%; M 269.

We then isolated 6.0 g of a mixture of substances with mp 85-140°C, which was treated with a solution of 6 g of picric acid in 80 ml of acetone. The precipitated mixture of picrates was subjected to fractional crystallization from a mixture of alcohol with acetone. The initially isolated 1.3 g of the picrate of azafluorene III, with mp 176-178°C, was decomposed on aluminum oxide to give 0.4 g (4%) of colorless crystals of azafluorene III with mp 108-110°C (from heptane). PMR spectrum: 1.64 ($9-CH_3$), 7.43-7.60 (m, aromatic protons), 7.72 (d, 1-H), and 8.19 ppm (m, 5-H). UV spectrum, λ_{max} (log ε): 206 (4.8), 240 (4.6), 270 (4.18), 3.24 nm (4.52). Mass spectrum, m/z (%): M^+ 271 (56), 256 (100), 178 (8), 152 (10). Found: C 88.6; H 6.5; N 5.4%. $C_{20}H_{17}N$. Calculated: C 88.6; H 6.3; N 5.1%; M 271.

We then isolated 1.5 g of the picrate of azaphenanthrene II with mp 166-167°C, from which, after decomposition on aluminum oxide, we obtained 0.6 g of II (mp 136-137°C) for an overall yield of 0.9 g (9%).

At the end of the chromatography we isolated 3.5 g of the picrate of starting pyridine I, with mp 165-166°C, from which we obtained 1.1 g of the base with mp 81-82°C.

10-Bromomethyl-3-phenyl-4-azaphenanthrene (IV). A mixture of 0.15 g (0.6 mmole) of azaphenanthrene II, 0.11 g (0.6 mmole) of N-bromosuccinimide (NBS), and 0.007 g (0.042 mmole) of azobisisobutyronitrile in 15 ml of carbon tetrachloride was refluxed for 2 h, after which the mixture was cooled, and the succinimide was removed by filtration. The filtrate was washed successively with a 4% solution of sodium hydroxide and water, the solvent was removed by distillation, and the residue was crystallized from heptane to give 0.07 g (35%) of yellowish crystals of IV with mp 150-153°C. PMR spectrum: 4.82 ($10-CH_2$), 7.38-8.50 (m, aromatic protons), and 9.35 ppm (m, 5-H). Found: Br 23.0; N 4.3%. $C_{20}H_{14}BrN$. Calculated: Br 22.8; N 4.2%.

3-Phenyl-4-azafluorene (VI). The dehydrocyclization of pyridine base V (10.2 g; 40 ml of benzene, 2 h) was carried out on the same catalyst at 550-560°C. The reaction products (5.2 g) were converted to picrates, from which 1.6 g of the picrate of azafluorene VI, with mp 186-187°C, was isolated by fractional crystallization. Found: N 12.1%. $C_{18}H_{13}N \cdot C_6H_3N_3O_7$. Calculated: N 11.9%. The picrate was decomposed on aluminum oxide to give 0.67 g of 3-phenyl-4-azafluorene (VI) with mp 124-125°C. No melting-point depression was observed for a mixture of this product with a standard sample.

1,3-Diphenyl-4-azafluorene (VIII). Similar treatment of 7.45 g of pyridine base VII gave 5.5 g of catalyzate, which was converted to picrates. Fractional crystallization of the mixture of picrates from acetone gave 0.7 g of the picrate of azafluorene VIII with mp 236-238°C. Decomposition of the picrate on aluminum oxide gave 0.47 g of azafluorene VIII with mp 156-157°C (from heptane). No melting-point depression was observed for a mixture with a standard sample.

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