TRANSFORMATIONS OF PYRIDINE BASES

ON A NICKEL – ALUMINUM CATALYST

V. V. Antonova, T. I. Ovchinnikova,
K. P. Bespalov, T. N. Serova,
V. K. Promonenkov, and B. F. Ustavshchikov

The electronic structures of some pyridine bases are analyzed by means of ^{1}H and ^{13}C NMR spectroscopic data for substituted pyridines and the calculated bond orders in the pyridine ring. The differences in the chemical bonds in the pyridine ring of isomeric methylpyridines and the carbon–carbon bonds between the ring and the methyl groups in these compounds are in agreement with the experimental data on the thermal stability of the simplest pyridine bases and the gas-phase transformation of the isomeric methylpyridines on an industrial nickel–aluminum catalyst. The possibility of obtaining mono- or dialkylpyridines under these conditions, depending on the structure of the starting pyridine bases, is demonstrated.

The peculiarities of the electronic structures of alkylpyridines are responsible for certain transformations in their series. The data presented in Table 1 constitute evidence, for example, for different strengths of the bonds in the pyridine ring of isomeric methylpyridines, as well as the carbon–carbon bonds between the ring and the methyl groups in these compounds. One therefore might have expected differences also in the transformations of isomeric alkylpyridines.

We have investigated the gas-phase transformation of some alkylpyridines on an industrial nickel–aluminum catalyst, which was selected from a number of tested catalytic systems as one that ensures the greatest selectivity of the investigated processes and has a significant period of constant activity and sufficient thermal stability.

Consecutive-parallel reactions involving equilibrium demethylation of the 2-methyl group with the formation from the starting alkylpyridines of, respectively, pyridine or 3-ethylpyridine (reaction 1, Table 2) and alkylation of the starting compounds by methyl radicals primarily in the 2 position of the pyridine ring (reaction 2, Table 2) are characteristic in the case of contact of 2-methyl-substituted alkylpyridines (for example, 2-methyl- and 2-methyl-5-ethylpyridines) on this catalyst. We showed that both reaction 1 and parallel reaction 3 – cleavage of the pyridine ring to give gaseous products – may be the source of methyl radicals:
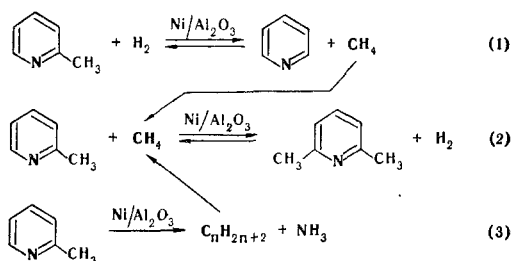
The selective demethylation of primarily the 2-methyl group is evidently a consequence of the greatest polarization of the bond of this methyl group with the pyridine ring; this is apparent from a comparison of the differences in the chemical shifts of the carbon atoms of the pyridine ring and the methyl group, as well as the chemical shifts of the protons of the CH_3 groups, in isomeric methylpyridines (Table 1).

In addition, coordinate reagent–catalyst interaction with the participation of the unshared electron pairs of the nitrogen atom of the methylpyridines and the vacant orbitals of the nickel atoms of the catalyst also possibly

TABLE 1. ^{1}H and ^{13}C NMR Spectroscopic Data for Substituted Pyridines [1, 2]

Position of the substituent	Substituent	Chemical shifts of the protons, δ, ppm						[13]C chemical shifts, δ, ppm					
		2-H	3-H	4-H	5-H	6-H	CH3*	2-C	3-C	4-C	5-C	6-C	CR
	—	8,29	6,77	7,15	6,77	8,29	—	150,6	124,5	136,4	124,5	150,6	— —
2	CH3	—	7,00	7,43	6,92	8,51	2,45	159,9	123,4	137,2	122,0	149,8	— 21,5
3	CH3	8,54	—	7,45	7,13	8,54	2,19	150,5	133,8	137,2	124,1	147,8	— 18,9
3	CH2—CH3	—	—	—	—	—	—	150,3	143,0	138,5	127,7	151,6	26,8, 15,4
4	CH3	8,55	7,04	—	7,04	8,55	2,27	150,1	126,7	147,7	126,7	150,1	— 21,5

* These data were obtained in the present research.

TABLE 2. Results of the Gas-Phase Transformation of Alkylpyridines on a Nickel–Aluminum Catalyst (330° C, alkylpyridine space velocity 0.3 liter/liter cat.-h, alkylpyridine partial pressure 0.02 MPa, hydrogen partial pressure 0.08 MPa)

Starting alkylpyridines	Yields of pyridine bases per pass, %	Conversion of the alkylpyridine, %
2-Methylpyridine	Pyridine 14.9; 2,3-dimethylpyridine 3.0; 2,5-dimethylpyridine 1.6; 2,6-dimethylpyridine 11.4	43.1
3-Methylpyridine	Pyridine 0.3; 2-methylpyridine 0.5; 2,5-dimethylpyridine 30.9; 2,4-dimethylpyridine 8.0; 2,3-dimethylpyridine 5.3	54.5
4-Methylpyridine	Pyridine 0.6; 2,4-dimethylpyridine 35.2	45.6
2-Methyl-5-ethyl-pyridine	Pyridine 0.2; 2-methylpyridine 0.7; 3-methylpyridine 1.7; 2,5-dimethylpyridine 2.1; 3-ethylpyridine 31.7	38.4

TABLE 3. Calculated Bond Orders in the Pyridine Bases and Data on Their Thermal Stabilities

Starting compounds	Calculated bond orders	Rate constants for gas formation, h⁻¹		
		800°	840°	880°
Pyridine		0,9	1,4	2,1
2-Methylpyridine		1,1	1,9	2,7
3-Methylpyridine		0,8	1,06	1,25
4-Methylpyridine		0,55	0,95	1,3

promotes the demethylation of precisely the 2-methyl group in the investigated catalytic reaction. This may lead to pronounced weakening of the α-carbon bond adjacent to the coordinate bond.

Different transformations are characteristic for 3- and 4-methylpyridines. The principal products of the transformation of these methylpyridines are, respectively, 2,5- and 2,4-dimethylpyridines (Table 2). Consecutive reactions, viz., cleavage of the pyridine ring to give gaseous products (similar to reaction 3) and only subsequent alkylation of the starting compounds by the resulting alkanes in the 2 position of the pyridine ring (similar to reaction 2), predominate in this case.

TABLE 4. Quantitative Indexes of Reactions Involving the Alkylation of Pyridine Bases by Methane on a Nickel-Aluminum Catalyst (330° C, pyridine base space velocity 0.3 liter/liter cat.-h, alkylpyridine partial pressure 0.02 MPa, methane partial pressure 0.01 MPa, hydrogen partial pressure 0.03 MPa, helium partial pressure 0.04 MPa)

Starting pyridine bases	Yields of α-methyl-substituted alkylpyridines based on the starting pyridine bases, %	
	passed	converted
Pyridine	40,0	65,0
2-Methylpyridine	15,0	35,0
3-Methylpyridine	20,0	70,0
4-Methylpyridine	30,0	65,0

The possibility of the occurrence and some principles of reactions 2 and 3, the existence of which also evidently explains the series of observed transformations of isomeric alkylpyridines on a nickel-aluminum catalyst, were subjected to special study. Thus a quantitative estimate of the thermal stability of the pyridine ring of the simplest pyridine bases (reaction 3) in the absence of a catalyst from the rate constants for the formation of gaseous products (Table 3) calculated from the integral curves of the yields of these products from the arbitrary contact time is given.

The thermal stabilities of the pyridine ring in the simplest pyridine bases differ and decrease in the order 4-methylpyridine $\approx$ 3-methylpyridine > pyridine > 2-methylpyridine.

The same transformations evidently take place at lower temperatures (250-370° C) on the nickel–aluminum catalyst, since coordinate interaction of the catalyst and ligands (the pyridine bases) weakens the carbon–carbon bonds and the bonds of the pyridine ring, particularly those adjacent to the coordinate bond.

The experimental data obtained are in agreement with the C–N bond orders in the investigated compounds (Table 3) calculated by means of a standard program within the framework of the simple MO LCAO method [3].

The possibility of the gas-phase catalytic alkylation of pyridine and its homologs by alkanes on the nickel–aluminum catalyst with the predominant formation of individual α-substituted methylpyridines (reaction 2, Table 4) was also demonstrated by special experiments [4].

Thus the experimental data on the catalytic contact of pyridine bases on an industrial nickel–aluminum catalyst presented in this research demonstrate the possibility of various pathways for their conversion to the corresponding mono- or dialkylpyridines as a function of the structure of the starting pyridine bases; this is substantiated by the peculiarities of their electronic structures.

EXPERIMENTAL

The dealkylation and alkylation of the alkylpyridines were investigated in the gas phase at atmospheric pressure in a flow reactor of the integral type on a heterogeneous nickel-aluminum catalyst (containing 25.82% nickel) (TU-6-03-237-69).

Hydrogen with a partial pressure of no less than 0.03 MPa was fed into the reaction zone to ensure constant activity of the catalyst (on the order of 17 h with subsequent regeneration and reduction of the catalyst). We also established that the investigated process on the industrial granulation catalyst is not complicated by diffusion phenomena.

The thermal transformation of the pyridine bases was carried out in a quartz reactor, the reaction zone of which was filled with an inert material.

The description of the equipment, the conditions for activation, regeneration, and reduction of the catalyst, and the methods used for the analysis of the reaction mixtures are presented in [5].

The NMR spectra of solutions of the alkylpyridines in carbon tetrachloride were recorded with a Tesla BS 487-C NMR spectrometer with hexamethyldisiloxane as the internal standard.

1. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, High-Resolution NMR Spectroscopy, Pergamon, Oxford (1965).
2. G. C. Levy and G. L. Nelson, Carbon-13 Nuclear Magnetic Resonance for Organic Chemists, New York (1972).
3. N. I. Zatsepina, I. F. Tupitsyn, and L. S. Éfros, Zh. Obshch. Khim., 34, 4065 (1964).
4. V. V. Antonova, K. P. Bespalov, V. K. Promonenkov, and B. F. Ustavshchikov, USSR Inventor's Certificate No. 696018; Byull. Izobret., No. 41, 97 (1979).
5. K. P. Bespalov, V. V. Antonova, B. F. Ustavshchikov, N. A. Bednyakova, and V. V. Voronenkov, Zh. Prikl. Khim., 47, 2309 (1974).

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

N. S. Prostakov, A. V. Varlamov,
M. Torres, B. N. Anisimov,
and M. A. Ryashentseva

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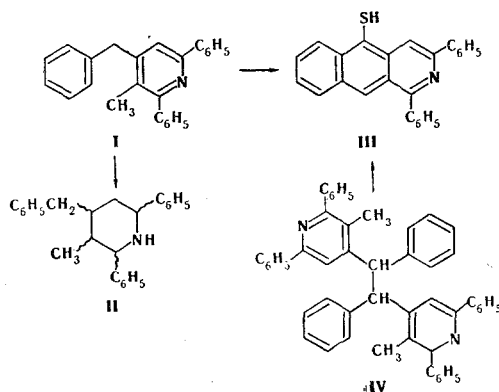
In a study of the catalytic dehydrocyclization of pyridine base I it was established that it is converted to condensed heterocycles, viz., 1,3-diphenyl-2-azaanthracene and 2-phenyl-1-azabenzo[f]fluoranthene [2]. We used a K-16 industrial dehydrogenating catalyst as the catalyst. We attempted to bring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