- 2. E. Colomer and R. Corriu, J. Organomet. Chem., <u>82</u>, 367 (1984).
- 3. A. Kim and K. N. Ahn, J. Org. Chem., <u>49</u>, 1717 (1984).
- 4. A. J. Gordon and R. A. Ford, The Chemist's Companion, Wiley, New York (1973).
- 5. M. Makosza and M. Wawrzyniewicz, Tetrahedron Lett., 4659 (1969).
- A. N. Nesmeyanov and K. A. Kochetkov, Methods of Heteroorganic Chemistry [in Russian], Nauka, Moscow (1974), p. 181.
- 7. A. Gomez-Carrera, M. Mena, P. Royo, and R. Serrano, J. Organomet. Chem., 315, 329 (1986).
- 8. R. S. Shank and H. Schechter, J. Org. Chem., <u>24</u>, 1825 (1959).
- 9. D. Seiferth, H. Yamazaki, and D. L. Alston, J. Org. Chem., 28, 703 (1963).
- 0. M. Nefedov, N. N. Novitskaya, and A. D. Petrov, Dokl. Akad. Nauk SSSR, <u>152</u>, 629 (1963).

SYNTHESIS OF ARYL-SUBSTITUTED PYRIDINES BY LIQUID-PHASE CONDENSATION OF ALDEHYDES WITH UREA, CATALYZED BY TRANSITION METAL COMPLEXES

U.	Μ.	Dzhemilev,	F. A. Selimov,	UDC 542.97:542.953:547.281:
Α.	Zh.	Akhmetov,	and A. A. Fatykhov	547.57:547.495.2:547.882.4

According to [1-3], the gas-phase condensation of benzaldehyde (BzH) with acetaldehyde (AcH) or butyraldehyde (PrCHO) and  $NH_3$  in the presence of heterogeneous catalysts based on  $Al_2O_3$  impregnated with transition metal complexes, at 300-500°C, results in a mixture of 2- and 4-phenylpyridines in an overall yield of not more than 30%. Attempts to react other substituted aromatic and aliphatic aldehydes, including those containing functional substituents in this manner were unsuccessful.

We have recently developed a highly selective method for the synthesis of pyridine bases by liquid-phase condensation of aliphatic aldehydes with urea at a temperature of 150-200°C by the action of cobalt-containing metallocomplex catalysts [4, 5].

To develop effective methods of synthesis of aryl- and heteroaryl-substituted pyridines and to broaden the scope of their application, we studied the reaction of BzH and substituted benzaldehydes, furfural and 4-pyridinecarboxaldehyde with aliphatic  $C_4-C_8$  aldehydes and urea, catalyzed by low-valency Fe, Co, Ni, V, Cu, Pd, Ti, Zr, Hf, W, Rh complexes.

The complex catalysts were obtained by reducing soluble compounds of these metals by means of AlEt<sub>3</sub>, Al(OEt)<sub>2</sub>, ClAlEt<sub>2</sub>, Cl<sub>2</sub>AlEt, MgEt<sub>2</sub>, BBu<sub>3</sub>, and BPr<sub>3</sub> in a toluene or THF solution, at a temperature of  $0-10^{\circ}$ C.

To select the optimal conditions for carrying out the reaction, using the example of the reaction of BzH with PrCHO and urea, we studied the influence of the nature of the catalyst on the yield and composition of the condensation products. It was found that the Co- $(2-\text{ethylhexanoate})_{2-AlR_3}$  system has the highest catalytic activity (Table 1). In its presence, a maximum yield of pyridines (80%) is attained in the course of 4 h at 200°C, and in the mixture obtained, the yield of 2-phenyl-3,5-diethylpyridine (I) and 2-propyl-3,5-diethylpyridine (V) reaches ~95%. In a homocondensation of BzH with urea under the selected conditions, the formation of arylpyridines is not observed. A general scheme of reaction is given below



Institute of Chemistry, Bashkir Scientific Center, Urals Branch, Academy of Sciences of the USSR, Ufa. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2335-2340, October, 1988. Original article submitted May 12, 1987.

No. of	Catalytic system	Overall yield of reaction products,	Composition of reac- tion products, %		
ment			<b>(1</b> )	( <b>V</b> )	
1 2 3 4 5 6 7 8 9 10 11 12 13 14	$\begin{array}{l} Co \left(2-EH\right)_{2} : Al(C_{2}H_{5})_{3} \\ Co (acac)_{2} : A_{5} above \\ Ni (acac)_{2} : * \\ Al (acac)_{3} : \\ Cr (acac)_{3} : \\ Cr (acac)_{3} : \\ Co (2-EH)_{2} : Al(C_{4}H_{5})_{3} \\ The same HAI (C_{4}H_{6})_{2} \\ * : Mg (C_{2}H_{5})_{2} \\ * : ClAl (C_{2}H_{5})_{2} \\ * : Cl_{2}AlC_{2}H_{5} \\ * : B (C_{4}H_{9})_{3} \\ * : B (C_{4}H_{9})_{3} \\ * : B (C_{4}H_{9})_{3} \\ \end{array}$	80 65 60 58 60 58 60 58 72 70 59 59 59 59 59 38 25 18	95 94 96 73 91 78 94 93 94 93 90 88 65 55 70	4 5 3 25 6 20 4 5 2 6 7 30 32 20	

TABLE 1. Influence of Nature of Catalyst on the Yield and Composition of Products of Condensation of BzH with PrCHO and Urea\*

\*Experimental conditions: T 200°C,  $\tau$  4 h, solvent - toluene, ratio of starting reagents: BzH:PrCHO:urea = 1:1.5:1. Conversion of BzH in experiments 1-11 - 90-100%, in exps 12-14 - 50-70%.

	Starting a	Idenydes	Reaction products,	yield. %
Ni	R'CHO	RCH2CHQ	R R R'	
1	он	PrCHØ	(IX), 59	(I), 39
2	-CHO	As above	(X), 44	(I), 54
3	осн,	>	(X1), 63	(1), 27
4	о-ССНо	»	(XII), 45	(I), 35
5	0,N-CHO	»	(XVI), 60	(I), 20
6	NCHO	*	(XVII), 56	(1), 37
7 8	As above	BuCHO p-C6H11CHO	(XVIII), 55 (XIX), 54	(II), 38 (III), 39
9	CHO	PrCHO	(XX), 56	(I), 42
10 11	As above »	BuCHO p-C7H13CHO	(XXI), 12	(II), 86 (IV), 98

TABLE 2. Synthesis of 2-Aryl(Heteroaryl)-3,5-dialkylpyridines\*

\*Temperature 200°C, duration of reaction 6 h.

On transition from PrCHO to aliphatic  $C_5-C_8$  aldehydes, the direction of the reaction does not change, and the yields of the corresponding 2-aryl-3,5-dialkylpyridines (II)-(IV) decreases to ~70%, while the fraction of the 2,3,5-trialkylpyridines (VI)-(VIII) increases to ~30%.

The nature and position of the substituents in the aromatic aldehydes practically do not influence the direction of the reaction, and the content of the 2-arylpyridines (IX)-(XV) in the reaction mixture is 70%. Similar results were obtained with paramitrobenzaldehyde and 4-formylpyridine, which give with aliphatic  $C_4$ - $C_7$  aldehydes the corresponding pyridines



Fig. 1. Structure of pyridines (XVII) and (XX).

(XVI)-(XIX) in fairly high yields. In experiments with furfural, a considerable decrease in the yield of 2-furylpyridines (XX)-(XXI) is observed on transition from PrCHO to higher aliphatic aldehydes, while in the case of the  $C_7$  and  $C_8$  aldehydes, in general, no formation of 2-furylpyridines takes place (in this case, 2,3,5-trialkylpyridines are the main reaction products) (Table 2).

We also introduced  $\alpha,\beta$ -unsaturated aldehydes into the condensation with other aldehydes in the presence of ammonia sources (urea, ammonium sulfate) and the Co(2-ethylhexanoate)<sub>2</sub>-Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> catalytic system. From 2-ethyl-2-hexen-1-al (XXII), a product of a crotonic condensation of PrCHO, and BzH or ortho-fluorobenzaldehyde and urea, 2-phenyl- or 2-fluorophenyl-3,5-diethylpyridines are formed in a yield of not less than 80%. If the benzaldehydes are replaced in this reaction by PrCOH, trialkylpyridine (V) is obtained in an 85-90% yield.

The structure of the pyridine bases obtained was verified by <sup>13</sup>C NMR and PMR spectroscopy, as well as by mass spectrometry. The structure of pyridines (XVII) and (XX) obtained was established by <sup>13</sup>C NMR spectroscopy (Fig. 1).

Considering that the gas-phase reaction of paraldehyde with BzH and  $NH_3$  leads to the formation of 2- or 4-phenylpyridines [6, 7], we carried out the reaction under milder conditions, using cobalt-containing catalysts (paraldehyde:BzH:urea = 1:1:1, 200°C, 10 h). As a result, a mixture of 2-benzyl-4-phenyl-pyridine (XXIII), and 2-methyl-5-ethylpyridine (1:1) was obtained unexpectedly in an overall yield of ~90%, ortho-fluorobenzaldehyde reacts with paraldehyde and urea in a similar way to give a 2,4-disubstituted pyridine (XXIV) and 2-methyl-5-ethylpyridine



## R = H (XXIII); o-F (XXIV).

Thus, the reaction of liquid-phase cocondensation of aromatic and aliphatic aldehydes, including  $\alpha,\beta$ -unsaturated aldehydes, with urea under the action of low-valency cobalt complexes is a convenient preparative method for the synthesis of various trisubstituted pyridine bases.

## EXPERIMENTAL

Aldehydes with ~99% purity were used in the investigation. The GLC was carried out on a Chrom-5 chromatograph with a flame ionization detector, a column 1.2 m long and 3 mm in diameter, filled with 15% Apiezone on zeolite-545, using nitrogen as carrier gas. The PMR spectra were run in CDCl<sub>3</sub> on a Tesla BS-467 spectrometer and the <sup>13</sup>C NMR in CCl<sub>4</sub> spectra on a Jeol-900 spectrometer. The IR spectra were run in mineral oil on a UR-20 spectrophotometer in mineral oil. The mass spectra were obtained on a MX-1306 spectrometer with energy of ionizing electrons of 70 eV (temperature in the ionization chamber 200°C).

<u>Condensation of Aliphatic Aldehydes with Benzaldehyde and Urea Under the Action of Co-(2-ethylhexanoate)<sub>2</sub>-Al( $C_2H_5$ )<sub>3</sub> Catalytic System. A 9 mmole portion of Al( $C_2H_5$ )<sub>3</sub> was added at 0°C in an argon current, to a solution of 3 mmoles of Co(2-ethylhexanoate)<sub>2</sub> in 1 ml of benzone and stirred for 10 min. The solution of the catalyst obtained was transferred into a steel autoclave (V = 17 cm<sup>3</sup>), where in 12 mmoles of the aliphatic aldehyde, 3 ml of benzene and 4 ml of a 50% solution of urea had preliminarily been introduced. The autoclave was</u>

TABLE 3. Physical Constants of Pyridines Obtained

Com-	Bp, ⁺C		Found, %			Empirical	Calculated, %		
pound	(pmmHg)		С	н	N	Iormula	с	н	N
(1) (11) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (111) (11	$\begin{array}{c} 150-153 \ (1.5) \\ 160-164 \ (1-1,5) \\ 181-184 \ (1-1,5) \\ 198-200 \ (1-1,5) \\ 150 \ (3) \\ 140 \ (2) \\ 159-162 \ (1,5-2) \\ 189-194 \ (1-1,5) \\ 160-162 \ (1,5-2) \\ 170 \ (3) \\ 188 \ (1,5-2) \\ 170 \ (2) \\ 130 \ (2) \\ 132-134 \ (1,5-2) \\ 140-144 \ (1-1,5) \\ 130 \ (2) \\ 138-140 \ (1,5-2) \\ 205-210 \ (2,5-3) \\ 190-198 \ (2,5-3) \end{array}$	$\begin{array}{c} 1.5680\\ 1.5620\\ 1.5620\\ 1.5530\\ -\\ 1.5530\\ 1.5580\\ 1.5510\\ 1.5570\\ -\\ -\\ 1.5610\\ 1.5620\\ 1.5600\\ 1.5600\\ 1.5600\\ 1.5500\\ 1.6130\\ 1.6130\\ 1.6110\\ \end{array}$	$\begin{array}{c} 85.5\\ 83.1\\ 85.3\\ 85.3\\ 79.1\\ 78.4\\ 79.3\\ 81.4\\ 80.4\\ 59.0\\ 66.0\\ 70.1\\ 79.8\\ 80.9\\ 77.4\\ 88.0\\ 76.6\end{array}$	7,855,137,79,31,413,44,333,10,3	$\begin{array}{c} \textbf{6.37} \\ \textbf{5.761} \\ \textbf{4.09} \\ \textbf{5.562} \\ \textbf{5.542} \\ \textbf{5.542} \\ \textbf{3.271} \\ \textbf{4.442} \\ \textbf{5.761} \\ \textbf{4.447} \\ \textbf{6.7655} \\ \textbf{4.771} \\ \textbf{6.771} \\ \textbf{4.771} \\ \textbf{6.771} \\ 6.7$	$\begin{array}{c} C_{15}H_{17}N\\ C_{17}H_{21}N\\ C_{21}H_{22}N\\ C_{23}H_{23}N\\ C_{15}H_{17}NO\\ C_{15}H_{16}NF\\ C_{16}H_{19}NO\\ C_{22}H_{31}NO\\ C_{17}H_{19}NO\\ C_{17}H_{19}NO\\ C_{15}H_{17}BrNO\\ C_{23}H_{33}BrNO\\ C_{15}H_{16}N_{2}O_{2}\\ C_{14}H_{20}N_{2}\\ C_{20}H_{28}N_{2}\\ C_{20}H_{28}N_{2}\\ C_{20}H_{28}N_{2}\\ C_{3}H_{15}NO\\ C_{15}H_{19}NO\\ C_{15}H_{19}NO\\ C_{16}H_{15}N\\ C_{16}H_{15}F_{2}N\end{array}$	85.3 83.36 85.42 85.45 85.45 79.30 78.60 79.67 81.23 80.63 70.31 79.25 8.00 81.08 77.61 78.60 88.16 76.87	$\begin{array}{c} 8,1\\ 8,79\\ 9,83\\ 10,21\\ 7,49\\ 6,99\\ 7,88\\ 9,54\\ 7,55\\ 6,67\\ 7,55\\ 6,67\\ 9,46\\ 7,46\\ 8,30\\ 6,12\\ 4,63\end{array}$	$\begin{array}{c} 6.6\\ 5.86\\ 4.75\\ 4.33\\ 6.11\\ 5.81\\ 4.31\\ 5.53\\ 4.58\\ 3.35\\ 10.94\\ 13.21\\ 11.67\\ 9.46\\ 6.97\\ 6.11\\ 5.71\\ 4.98\end{array}$

TABLE 4. Spectral Characteristics of Compounds Obtained

Com- pound	M <sup>+</sup> (mas spec- trum)	$\frac{\text{IR spectrum}}{\nu, \text{ cm}^{-1}}$	PMR spectrum δ, ppm
(I)	211	830, 1480, 2950, 1580	1,08 (CH <sub>3</sub> ), 1,22 (CH <sub>3</sub> ), 2,58 (2CH <sub>2</sub> ), 7,22–7,35 (C <sub>6</sub> H <sub>5</sub> ), 7,87–7,8 (C <sub>5</sub> H <sub>5</sub> N)
(11)	239	835, 1482, 1580, 2950	0,9 (2CH <sub>3</sub> ), 1,53 (2CH <sub>2</sub> ), 2,53 (2CH <sub>2</sub> ), 7,20 $-7,30$ (C <sub>6</sub> H <sub>5</sub> ), 7,8 $-8,3$ (C <sub>5</sub> H <sub>2</sub> N)
(III)	295	840, 1485, 1580, 2955	$0.9 (2CH_3), 1.3 (6CH_2), 2.5 (2CH_2), 7.2-7.3 (C_6H_5), 7.8-8.2 (C_5H_2N)$
(IV)	323	835, 1480, 1580, 2950	0.9 (2CH <sub>3</sub> ), 1,3 (8CH <sub>2</sub> ), 2,5 (2CH <sub>2</sub> ), 7,2-7,3 (C <sub>6</sub> H <sub>5</sub> ), 7,8-8,3 (C <sub>5</sub> H <sub>2</sub> N)
(IX)	272	770, 1390, 1610 1470, 2950, 3100	$1.25 (2CH_3), 2.75 (2CH_2), 7.08-7.5 (C_6H_4), 7.8-8.2 (C_5H_2N), 10.9 (OH)$
(X)	229	780, 850, 1185 1460, 2950	1,25 (2CH <sub>3</sub> ), 2,5 (2CH <sub>2</sub> ), 7,08-7,55 (C <sub>6</sub> H <sub>4</sub> F), 7,85-8,34 (C <sub>5</sub> H <sub>2</sub> N)
(XI)	241	760, 890, 1185, 1460, 2950	1,09 (CH <sub>3</sub> ), 1,22 (CH <sub>3</sub> ), 2,58 (2CH <sub>2</sub> ), 3,8 (CH <sub>3</sub> O), 7,22 $-$ 7,35 (C <sub>6</sub> H <sub>4</sub> ), 7,8 $-$ 8,3 (C <sub>5</sub> H <sub>9</sub> N)
(XII)	325	760, 890, 1180, 1465, 2955	0.9 (2CH <sub>3</sub> ), 1,3 (6CH <sub>2</sub> ), 2.5 (2CH <sub>2</sub> ), 3,8 (CH <sub>3</sub> O), 7.2–7.3 (CeH <sub>4</sub> ), 7.8–8.3 (CeH <sub>2</sub> N)
(XIII)	253	760, 890, 1180, 1460, 1690, 2950	1,0 (CH <sub>3</sub> ), 1,2 (CH <sub>3</sub> ), 2,33 (CH <sub>3</sub> ), 2,5 (2CH <sub>2</sub> ), 7,2 $-7.4$ (C <sub>6</sub> H <sub>4</sub> ), 7,5 $-8.3$ (CH <sub>9</sub> N)
(XIV)	306	770. 830. 1390, 1590, 3100	1.25 $(2CH_3)$ , 2.75 $(2CH_2)$ , 6,75-7,6 $(C_6H_3)$ , 7,6-8.3 $(C_5H_2N)$ , 10.9 $(OH)$
(XV)	418	770, 835, 1400 1595, 3100	$0.9 (2CH_3), 1.3 (8CH_2), 2.5 (2CH_2), 6.8-7.5 (C_6H_3), 7.6-8.3 (C_8H_2N), 10.8 (OH)$
(XVI)	256	780, 850, 1185, 1460, 2950	1.28 (2CH <sub>3</sub> ). 2.5 (CH <sub>2</sub> ). 6.6-7.3 (C <sub>6</sub> H <sub>4</sub> ) 7.5-8.3 (C <sub>5</sub> H <sub>2</sub> N)
(XVII)	212	920, 1320, 1360, 1590, 2930, 3030	1.08 (CH <sub>2</sub> ), 1.3 (CH <sub>3</sub> ). 2.58 (2CH <sub>2</sub> ), 7,07 $-7.7$ (C <sub>3</sub> H <sub>2</sub> N), 8.42 $-8.68$ (C <sub>5</sub> H <sub>2</sub> N)
(XVIII)	240	930, 1325, 1360 1605, 2950, 3030	0.9 (2CH <sub>3</sub> ), 1.53 (2CH <sub>2</sub> ), 2.58 (2CH <sub>2</sub> ) 7.07 $-7.7$ (C <sub>5</sub> H <sub>3</sub> N), 8.4 $-8.6$ (C <sub>5</sub> H <sub>2</sub> N)
(XIX)	296	920, 1320, 1360 1600, 2950, 3030	0.9 (2CH <sub>3</sub> ), 1.3 (6CH <sub>2</sub> ), 2.5 (2CH <sub>2</sub> ) 7.07 $-7.7$ (C <sub>5</sub> H <sub>3</sub> N), 8.4 $-8.6$ (C <sub>5</sub> H <sub>3</sub> N)
(XX)	201	770, 920, 1020 1410, 1490, 2980	1.2 $(2CH_3)$ , 2,73 $(2CH_2)$ , 6,47–7,3 (C,H <sub>3</sub> O), 7.5–8.3 $(C_3H_2N)$
XXI)	229	755, 920, 1015. 1415, 1490, 1590	0.9 $(2CH_3)$ , 1.53 $(2CH_2)$ . 2.73 $(2CH_2)$ , 6.4-7.3 $(C_4H_3O)$ , 7.5-8.3 $(C_5H_5N)$
XXIII)	245	710. 760, 1310, 1570, 2960	$3.97 (CH_2), 7,25-7.42 (2C_6H_5), 7,93-8,45 (C_5H_3N)$
XXIV)	281	710, 745, 1170, 1235, 1610, 2930	3.8 (CH <sub>2</sub> ), 6.98-7.37 (C <sub>6</sub> H <sub>4</sub> F), 7.85-8,43 (C <sub>5</sub> H <sub>3</sub> N)

heated for 4 h at 200°C with continuous stirring, and then was cooled. The reaction mixture treated with a 40% KOH solution, and then extracted with benzene ( $3 \times 50$  ml), and the combined extracts were dried over anhydrous MgSO<sub>4</sub>. The solvent was distilled off, and the residue was fractionated in vacuo. The physical constants of the 3,5-dialkyl-2-phenylpyridines are given in Table 3.

<u>Condensation of Functionally Substituted Aldehydes with PrCHO and Urea</u>. A solution of the catalyst, prepared as described above, was placed in a steel autoclave ( $V = 17 \text{ cm}^3$ ), wherein 4 ml of a 50% solution of urea, 3 ml of benzene, 20 mmoles of PrCHO, and 15 mmoles of a substituted benzaldehyde had preliminarily been introduced. The autoclave was heated for 4 h at 200°C. After the treatment with KOH and removal of the solvent, the reaction mixture was distilled in vacuo. The physical constants of the compounds are given in Table 3.

<u>Condensation of 4-Pyridinecarboxaldehyde or Furfural with Aliphatic Aldehydes and Urea</u>. A solution of the catalyst, prepared as described above was placed in an autoclave, into which 4 ml of a 50% carbamide solution, 15 mmoles of the heterocyclic aldehyde, 20 mmoles of the aliphatic aldehyde and 3 ml of benzene had been preliminarily introduced. The autoclave was heated for 6 h at 210°C, and then was cooled, and after the usual treatment and removal of the solvent, the reaction mixture was distilled in vacuo. The spectral and physical characteristics of the compounds obtained are given in Table 4.

<u>Reaction of Paraldehyde with BzH and Urea Under the Action of a  $Co(2-ethylhexanoate)_2-Al(C_2H_5)_3$  Catalytic System</u>. A solution of the catalyst obtained by reduction of 3 mmoles of  $Co(2-ethylhexanoate)_2$  with 9 mmoles of  $Al(C_2H_5)_3$ , in 1 ml of benzene was introduced at 0°C, in an argon current, into a steel autoclave, wherein, 4 ml of a 50% solution of urea, 12 mmoles of BzH, 20 mmoles of paraldehyde and 3 ml of benzene had preliminarily been charged. The autoclave was heated with stirring for 4 h at 200°C, was then cooled, and after treatment with a KOH solution, the reaction mixture was distilled in vacuo.

## CONCLUSIONS

The synthesis of a series of 2,3,5-substituted pyridine bases was carried out by reaction of aldehydes with urea in the presence of a  $Co(2-ethylhexanoate)_2-Al(C_2H_5)_3$  system.

## LITERATURE CITED

- 1. A. E. Chichibabin and D. I. Orochko, Zh. Russk. Fiz.-Khim. Ova, 62, 1201 (1930).
- 2. A. E. Chichibabin, Usp. Khim., <u>5</u>, 481 (1936).
- 3. N. S. Prostakov, A. T. Soldatenkov, V. O. Fedorov, and V. M. Polosin, Inventors Certificate No. 761,463 (USSR); Byull. Izobret., No. 33 (1980).
- 4. U. M. Dzhemilev, F. A. Selimov, V. R. Khafizov, et al., IUPAC on Organic Synthesis, 1st Intern. Conf., Summaries of Lectures [in Russian], Moscow (1986), p. 053.
- 5. F. A. Selimov, A. Zh. Akhmetov, and U. M. Dzhemilev, Izv. Akad. Nauk SSSR, Ser. Khim., 2042 (1987).
- 6. I. Ya. Lazdin'sh and A. A. Avots, Catalytic Synthesis and Reactions of Heterocyclic Compounds [in Russian], Zinatne, Riga (1976), p. 99.
- 7. I. Ya. Lazdin'sh and A. A. Avots, Khim. Geterotsikl. Soedin., 1011 (1979).