CATALYTIC METHODS OF OBTAINING PYRIDINE BASES (Survey)

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UDC 542.97:547.821 + 547.828/(047)

At the present time the need of the chemical and pharmaceutical industries for pyridine and the smaller alkylpyridines is not satisfied by the quantity of bases isolated from coal tar. Consequently the industrial manufacture of synthetic pyridine bases is adjusted [1-3]. The cost of the latter is significantly less than the cost of substances isolated from the products of the coal-tar chemical industry.

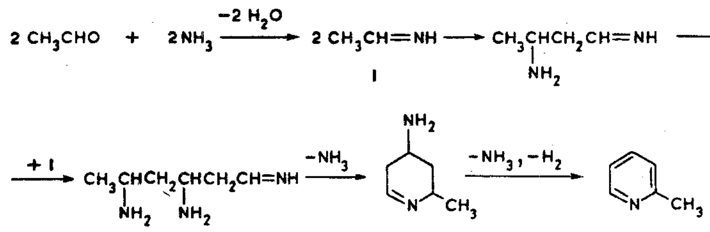
In addition to detailed reviews on the catalytic synthesis of alkylpyridines [4-6] generalizing literature data generally up to 1967, it is possible to name several papers [7-15] in which the separate problems of manufacture and use of pyridine bases are considered. In the monographs [16, 17] possibilities for using pyridine bases and also problems of the manufacture of pyridine bases from coal tar are considered in detail. However, in these studies little attention was paid to the catalytic method of obtaining pyridine bases. Literature information on the synthesis of pyridine bases from acetylenes and ammonia have been obtained since these reactions have recently been discussed [18].

Since it was not possible to obtain such bases as vinylpyridine and monoethylpyridine with the aid of the Chichibabin—Bayer reaction and furthermore the low selectivity of this reaction aggravates on the whole the problem of using high-boiling pyridine bases [19], certain conversions of pyridine bases were also considered briefly by us – particularly reactions of alkylation, dehydrogenation, and dealkylation.

SYNTHESIS OF PYRIDINE BASES VIA THE CHICHIBABIN REACTION. REACTION STAGES

The mechanism of the catalytic formation of pyridine bases from aliphatic aldehydes and ammonia has been discussed by many investigators [4-6, 15, 20-32]. Some of them [20-25] propose that initially aldimines are formed which undergo further addition (of the aldol type) or condensation with subsequent intramolecular cyclization. Other authors [26-32] consider that ammonia enters into the reaction only on formation of the pyridine ring which is preceded by a crotonic condensation of aldehydes or a Michael reaction. However, there is no direct proof in favor of one or the other opinion with the exception of some data [21, 22] confirming to some extent the initial formation of aldimine.

The mechanism proposed by Strain [20] of forming pyridine bases from aliphatic aldehydes and ammonia through aldimines (1) was later investigated by Farberov and coworkers [15, 21, 24, 25]. The conversion of aldehyde into aldimine they explained [15, 24] by sequential stages including the formation of the corresponding carbocation (2) and the detection of 2-methyl-5-(1-aminoethyl)pyridine in the reaction products confirmed, in their opinion [21], the addition of aldimines (by an aldol-type reaction). Participation of a carbocation in the formation of aldimine and also the further conversions of the latter were in accordance with the increase in activity of the catalyst on raising its acidity [25, 33].



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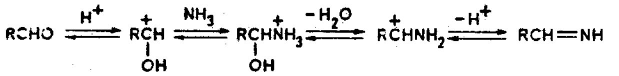
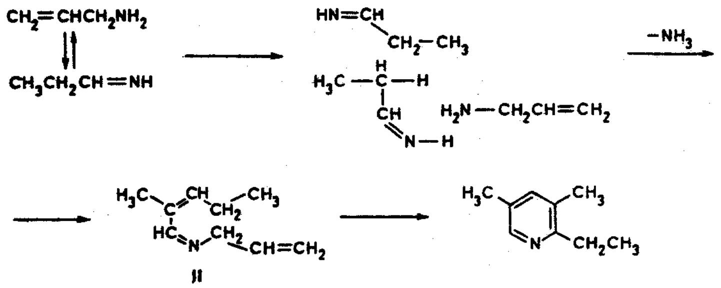
Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1011-1026, August, 1979. Original article submitted April 19, 1978; revision submitted January 6, 1979.



$$\mathrm{RCHO} \xrightleftharpoons{H^+} \mathrm{R}\underset{\mathrm{OH}}{\overset{+}{\mathrm{C}}}\mathrm{H} \xrightleftharpoons{NH_3} \mathrm{R}\underset{\mathrm{OH}}{\mathrm{C}}\mathrm{H}\overset{+}{\mathrm{N}}\mathrm{H_3} \xrightleftharpoons{-H_2O} \mathrm{R}\overset{+}{\mathrm{C}}\mathrm{HNH_2} \xrightleftharpoons{-H^+} \mathrm{RCH{=}NH} \qquad (2)$$

The intermediate N-alkenylidenallylamine (II) was isolated from the products of the liquid phase condensation of allylamine and was quantitatively converted into a pyridine base [22].

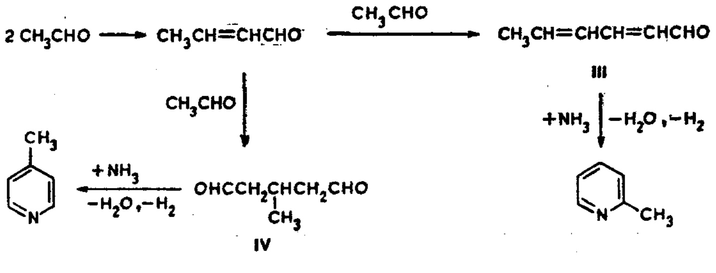


The mechanism of formation of pyridine bases by condensation of aldimines into N-alkenylidenallylamines with subsequent intramolecular cyclization and dehydrogenation [22, 23] deserves, in our view [34, 35], some preference since in the presence of dehydrogenating catalysts [36], the condensation products, aldimines may probably be converted there and then into N-alkenylidenimines with the separation of ammonia.

The scheme for the formation of pyridine bases from acetylene and ammonia includes the initial formation of acetaldimine which is then converted into N-alkenylidenallylamine either by direct reaction with acetylene [37] or through a dehydrogenation step into acetonitrile with subsequent addition of two molecules of acetylene [38]. Since mixtures of pyridine bases of approximately the same composition are formed from acetylene and ammonia, then an analogous reaction mechanism as from acetaldehyde and ammonia is possible. While clarifying this, Chichibabin proposed [39] that acetylene in the presence of traces of water vapor is converted on the catalyst into acetaldehyde which then condensed further with ammonia into pyridine bases.

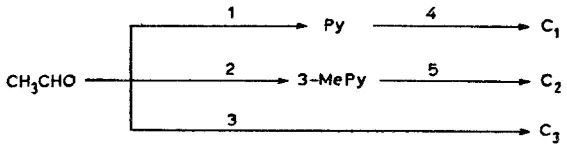
Investigations of isomerization, dehydrogenation, and heteroaromatization of unsaturated alkylamines and alkylimines over K_2O–Al_2O_3 into pyridine confirmed opinions on N-alkenylidenallylamine as a possible intermediate product in the synthesis of pyridine bases [40-42].

Suggestions have also been made [26-32] that crotonaldehyde is formed initially from acetaldehyde and then interacts with a second molecule of acetaldehyde by a type of crotonic or Michael reaction. The resulting hexadiene (III) or 3-methylglutaric (IV) aldehyde is cyclized with ammonia into pyridine bases:



However since heteroaromatization of the intermediate aldehydes (III, IV) probably takes place through an aldimine (or aldehyde ammonia), it is also possible to achieve formation of aldimines in the initial stages of the reaction. In the opinion of the authors of [28] the intermediate products of the reaction were derivatives of pyran or dihydropyran. But it is known [43] that replacement of the heteroatom in pyran proceeds with breaking of the pyran ring.

To make the mechanism of forming pyridine bases more precise kinetic investigations are necessary which are very difficult on account of the nonstationary nature of the process, the multistage nature of the overall reaction, etc. Only in study [44] have distinct kinetic parameters been given for the synthesis of pyridine bases from acetaldehyde, formaldehyde, and ammonia in the presence of an aluminosilicate catalyst. With a threefold excess of formaldehyde and ammonia the rate of conversion of acetaldehyde may be described by a first-order equation. The kinetics correspond to the parallel—sequential reaction scheme:



where C_i are secondary products (other alkylpyridines, resins). Values of the rate constants at 400°C were as follows: $k_1 = 0.16$, $k_2 = 0.17$, $k_3 = 0.06$, $k_4 = 0.0046$, and $k_5 = 0.40$. Values of the energy of activation were determined from the sizes of the rate constants found in the range 370-450°C: $E_1 = 11.8$, $E_2 = 6.1$, $E_3 = 11.9$, $E_4 = 9.5$, $E_5 = 6.1$ kcal/mole. However in the study under consideration the nonstationary nature of the process was not considered and in addition analysis of the presented values of E_i made it possible to propose the influence of diffusion phenomena. On investigating the kinetics of the reaction to form pyridine bases from benzaldehyde, acetaldehyde, and ammonia in the presence of Al_2O_3 and other catalysts we established the evident nonstationary nature of the process [35]. Experimental data corresponded to a model of sequential deactivation [45].

The studies [46, 47] should also be referred to in which it was shown that a change in structure of the catalyst pores may show a stronger influence on the process of forming pyridine bases than a change in other physicochemical properties of the catalyst.

CONDITIONS OF CARRYING OUT THE REACTION

The Chichibabin—Bayer reaction, with rare exception, proceeds with a low selectivity and gives a mixture of pyridine bases the detailed analysis of which for the actual process has been given in studies [48-50]. The composition of the initial mixture has far more influence than a change in other conditions or catalyst on the selectivity of the process. With the same catalyst, aluminosilicate for example, the preparation of a mixture of 2- and 4-methylpyridines from acetaldehyde [48], 2,6-dimethylpyridine from a mixture of acetone and formaldehyde [51], a mixture of pyridine and 3-methylpyridine from acrolein [52], or from formaldehyde and acetaldehyde [53] went equally well. The pyridine—3-methylpyridine ratio may vary from 1:2 to 15:1 (at a comparable overall yield of 60-70%) depending on the composition of the initial mixture [54-57]. At the same time the same substances are formed from an initial mixture of the same composition on different catalysts. For example, the formation of a mixture of 2- and 4-methylpyridines from acetaldehyde proceeds in approximately the same way on aluminosilicate [58], aluminum oxide [59], and metal phosphates [60]. Multifold investigations made it possible to show certain overall procedures for directing the selectivity of this complex reaction.

Vapor Phase Processes

Pyridine bases are obtained in the vapor phase both on a stationary catalyst and in a fluidized layer. The latter variant has certain advantages in view of the nonstationary nature of the process. The conditions for carrying out the process in the majority of cases are as follows: volume rate of aldehydes 0.25-0.5 h^{-1}, duration of contact 2-6 sec, the molar ratio of RCHO to NH_3 is maintained at 1:2, and the temperature in the synthesis of pyridine and low alkylpyridines is 400-430°C. Drastic conditions lead to a drop in the number of alkyl substituents and their amounts. Consequently to obtain complex alkylpyridines, phenylpyridines, and dipyridines lower temperatures are used (310-320°C). Frequently the process is improved by introducing into the reaction mixture nonstoichiometric components: inert gases (N_2, CO_2), hydrocarbons (CH_4, C_6H_6), oxygen, water, or other substances.

The catalysts used may be provisionally divided into four groups.

Aluminosilicates. Recently aluminosilicate catalysts have more frequently been used having the composition 8-30% (usually 11-15%) aluminum oxide and 70-92% silicon dioxide and containing no free aluminum oxide phase. Seemingly this explains the somewhat higher selectivity of these catalysts in comparison with aluminum oxide. Their specific surface area reaches 350-500 m^2/g [61-63]. The active phase of aluminosilicates is considered to be the structure $(HAlSiO_4)_x$ [64]. Modification of aluminosilicates by halides, phosphates, or oxides of metals, inorganic acids, and other compounds leads to a significant increase in the yield of pyridine bases [65, 66]. The best catalyst promoters were fluorides of zinc, cadmium, lead, bismuth, cobalt, and magnesium and also hydrofluoric acid. Somewhat less active were the chlorides and oxides of these metals. Modifiers in amounts of several percent of the weight of catalyst (individual cases up to 20%) were usually applied by impregnating the catalyst with aqueous solutions of the modifier with subsequent evaporation of water and calcination of the catalyst at 400-500°C. A certain time after beginning operation (usually 6-20 h) the catalyst became deactivated due to the deposition of resinous products on its surface. However subsequent regeneration (purging with air at 450-550°C) completely restored the initial activity.

Aluminum Oxide Catalysts. About 20% of studies have been devoted to the study of the synthesis of pyridine bases over γ-aluminum oxide, the most active of all the aluminum oxide modifications. Its specific surface area was 160-200 m^2/g [67]. The influence of water on the formation, change, and distribution according to potency of the aluminum oxide active centers was more marked than for aluminosilicates [64] consequently it was possible to improve the selectivity of the reaction under consideration by changing the degree of dehydration of $\gamma\text{-}Al_2O_3$ [35]. The same modifiers in the same quantitative ratios as for aluminosilicates are used for aluminum oxide catalysts. Aluminum oxide catalysts have been used in the condensation of ammonia with 1,4-dioxan [68], tetrahydrofuran derivatives [69], acetaldehyde diethylacetal [70], propionaldehyde [71], propylene oxide [72-74], alkylidenalkylamines [75-77], diethanolamine [78], acetaldehyde [60], benzaldehyde [47], etc.

Phosphate Catalysts. The phosphates of calcium, aluminum, cobalt, zinc, nickel, cadmium, and lead which may also be modified by chlorides of zinc, nickel, cobalt, etc., have been used for obtaining 2- and 4-methylpyridines from acetaldehyde or ethylene oxide [60, 79-84], although 2-methylpyridine is formed more selectively on these catalysts (30-35% yield). On mixed cobalt—aluminum phosphates at 340-370°C 2-ethyl-3,5-dimethylpyridine was obtained from propionaldehyde and 2-propyl-3,5-diethylpyridine was obtained from butyraldehyde [85]. 2,3,6-Trimethylpyridine was formed from methylethylketone on calcium—nickel phosphate at 500°C. Phosphate catalysts have also been used when obtaining dipyridyl and phenylpyridines [67] and also for the ammonolysis of dihydropyrans into pyridine [87-89]. The specific surface area of phosphate catalysts (5-30 m^2/g) was significantly less than the surface area of aluminosilicates and of γ-aluminum oxide but they were distinguished by larger pores [67].

Metallic Catalysts (Platinum and Palladium). These catalysts, supported on aluminum oxide or aluminosilicate, have mainly been used for obtaining pyridine from oxygen-containing heterocyclic compounds such as tetrahydrofurfuryl alcohol [90, 91], derivatives of dihydropyran [87-89, 92, 93], δ-valerolactam [94], and also glutaraldehyde [95]. The reaction was carried out at 300°C, the yield of pyridine was from 20 to 80%. For the vapor phase synthesis of pyridine bases calcium oxide [96] and zinc halides [97, 98] have also been used as catalysts.

Liquid Phase Processes

The synthesis of pyridine bases in the liquid phase has been carried out at 180-250°C under a pressure of 50-190 atm. Acetates of ammonia, copper, manganese, iron, cobalt, ammines of copper and palladium, and also platinum and palladium supported on aluminum oxide have been used as catalysts. In industry this process has been used for obtaining 2-methyl-5-ethylpyridine [4-6, 17].

SYNTHESIS OF SEPARATE GROUPS OF PYRIDINE BASES

Pyridine and 3-Methylpyridine

Principal initial carbonyl compounds used for obtaining pyridine were a mixture of formaldehyde with crotonaldehyde [57, 66, 99-103], a mixture of acrolein and acetaldehyde [71, 104-108], and acrolein in the presence of oxygen [62, 63, 109-114]. The condensation of aldehydes with ammonia has been carried out over aluminosilicate catalysts. Best yields were obtained on modification of these with halides of oxides of zinc [57, 63, 103], lead [63, 103], cadmium [57, 63, 103, 107], or magnesium [100, 115]. By passing oxygen into the reaction mixture it was possible to direct the reaction into the selective formation of pyridine not only on condensation of acrolein with ammonia but even on condensation of acetaldehyde with ammonia [116] where pyridine is formed in only insignificant amounts without addition of oxygen. For the synthesis of pyridine there have been used ethylene oxide [80-84], a mixture of diethanolamine and formaldehyde [78], and various compounds containing up to five carbon atoms [56, 75-77, 87-95, 96, 117-120]. Industrially the process of obtaining pyridine is by direct ammonolysis of the contact gases from the catalytic oxidation of propylene into acrolein [62, 109, 111].

A good yield of pyridine (54-59%) was obtained on using a mixture of formaldehyde with crotonaldehyde and diluting the reaction mixture with water vapor [99, 100, 103, 115], methyl alcohol [57, 103], or benzene [101], and also on dilution with oxygen [107]. Selective formation of pyridine was also observed on using a mixture of 3-methoxybutyraldehyde with formaldehyde (62% yield) [56], tetrahydrofurfuryl alcohol (48-80%) [90, 91], pentane-1,5-diol (56%) [120], and dihydropyran derivatives (38%) [87-89, 92, 93]. However these starting materials are fairly expensive in comparison with acetaldehyde or even with crotonaldehyde. In the liquid phase reaction of ammonia with glutaraldehyde in the presence of large quantities of quinonoid oxidizing agents [121, 122] or with 2-alkoxy-3,4-dihydro-2H-pyran in the presence of aqueous solutions of ammonium salts under pressure in an oxygen atmosphere [123-126] up to 90% pyridine was formed. These starting materials are also impractical at the present time for the industrial manufacture of pyridine.

A mixture of pyridine and 3-methylpyridine was obtained by the condensation of a mixture of formaldehyde and acetaldehyde with ammonia [53, 55, 65, 115, 127-139] or acrolein with ammonia [52, 54, 140-142] over aluminosilicate modified with salts of lead [65, 131, 132, 134], zinc [65, 132, 133], cadmium [65, 115, 131-133], bismuth [54, 65], etc. The yield of 3-methylpyridine in the first case was 25-31%, and of pyridine 35-42%; in the second case it was 37-52 and 24-25% respectively. 3-Methylpyridine and pyridine were also obtained from a mixture of acrolein and propylene oxide [72, 73]. In this case the yield of 3-methylpyridine was significantly greater than that of pyridine (49 and 13% respectively). Furthermore a mixture of acrolein, propionaldehyde, and acetaldehyde [71], and acetaldehyde diethylacetal [70] may be used as starting material but the yield of pyridine bases in these cases was not high.

Condensation of acrolein with ammonia in the liquid phase gave 3-methylpyridine in low yield [143] while the yield of 3-methylpyridine reached 35-40% from 1,1,3-triisopropoxypropane [144] or 3-methyl-2-morpholino-3,4-dihydro-2H-pyran [145] and ammonia under analogous conditions.

2-Methyl- and 4-Methylpyridines. In industry 2- and 4-methylpyridines have been obtained by the condensation of acetaldehyde with ammonia [48, 58-61, 79, 97, 98, 146-154]. Over aluminosilicate catalyst at 400°C these methylpyridines were formed in various ratios (about 25-27% of each). Modification of the catalyst with fluorides of zinc [148], lead [151], or cadmium [151, 152] with an overall increase of yield of pyridine bases increased the selectivity of formation of 2-methylpyridine, and modification of the catalyst with cobalt oxide [59] increased the yield of 4-methylpyridine. If fused zinc chloride was used as catalyst [97, 98] through which the reaction mixture was passed at 325°C then the yield of 2-methylpyridine was 44%. Zinc salts and also calcium phosphate selectivity promoted the formation of 2-methylpyridine and the synthesis of pyridine bases from ethylene oxide and ammonia [80, 81] but modification of this catalyst with nickel or cobalt chloride increased the selectivity of the reaction towards 4-methylpyridine or pyridine. Hydrofluoric acid was also a good modifier of aluminosilicate [149, 150]. The conditions of synthesis of 4-methylpyridine from acetaldehyde and ammonia over aluminosilicate were optimized using methods of planning experiments [48].

The gas phase condensation of acetaldehyde with ammonia led to the formation, in addition to the main reaction products, of small quantities of 2-methyl-5-ethylpyridine, pyridine, and other pyridine bases [48, 49, 60]. If the condensation was conducted at a temperature less than 250°C then the main reaction product was 2-methyl-5-ethylpyridine [61, 146].

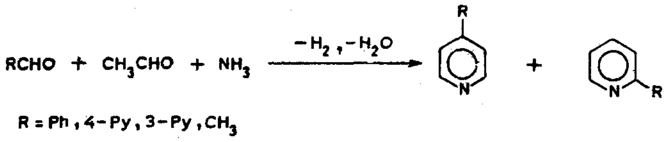
2-Methyl- and 4-methylpyridines were also formed on ammonolysis of 1,4-dioxan in the gas phase [68] and ethylene in the liquid phase under pressure [155, 156]. For the selective preparation of 4-methylpyridine amination of 4-methyl-5,6-dihydropyran over modified aluminosilicate may be used [157] and for the preparation of 2-methylpyridine the reaction of hexadienal with ammonia [158] is suitable. The preparation of 4-methylpyridine from propylene oxide and ammonia has been reported [74].

Other Alkylpyridines. On an industrial scale 2-methyl-5-ethylpyridine (70-73% yield) has been obtained by the liquid phase condensation of paraldehyde with ammonia in the presence of copper acetate at a temperature of 180-280°C and a pressure of 100-190 atm [4-6, 17, 159-164]. Other alkylpyridines were formed in insignificant amounts [50]. 2-Methyl-5-ethylpyridine was also the main product of condensation of paraformaldehyde with hydroxylamine or its salts in aqueous solution at 230°C and increased pressure. However in this case the yield only reached 45% [165]. With the aim of obtaining 2-methyl-5-ethylpyridine the reaction of vinyl esters with ammonia was investigated [166].

The other use of aliphatic aldehydes and ketones, pyran derivatives, and certain other oxygen-containing compounds in the Chichibabin—Bayer reaction has made it possible to obtain various alkylpyridines. For example 2,6-dimethylpyridine was obtained in 38-40% yield with a reaction mixture of acetone and formaldehyde with ammonia in the vapor phase over aluminosilicate catalyst [51, 167]. By the condensation of methylethylketone with ammonia over a phosphate catalyst at 500°C 2,3,6-trimethylpyridine was obtained in 28% yield [86]. The reaction of propionaldehyde or butyraldehyde with ammonia over phosphates led to the formation of 2-ethyl-3,5-dimethyl- or 2-propyl-3,5-diethylpyridine respectively in 65-75% yield [85]. This synthesis went in 45% yield in the liquid phase in the presence of manganese or cobalt acetates [168]. The reaction of 2,6-dialkoxy-3-(1-alkoxyalkyl)tetrahydropyrans with ammonia at 350°C over aluminum oxide led to 3-alkylpyridine in 47-54% yield [169]. Under the same conditions 3,5-diethylpyridine was obtained from 1,1,1-trimethoxypropane in a yield of about 45% [169, 170].

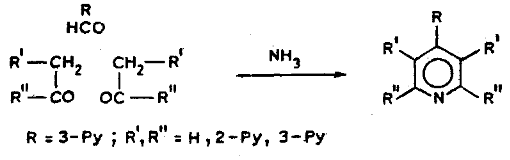
Phenylpyridines and Dipyridyls. The preparation of phenylpyridines by the condensation of benzaldehyde, acetaldehyde, and ammonia over aluminum oxide in the vapor phase was described for the first time in studies [171-173]. At an optimal temperature of 305-310°C a mixture of 4-phenyl- and 2-phenylpyridine (4:1) was obtained in 20-25% yield. The formation of the 4-isomer took place more selectively if cinnamaldehyde was taken in place of benzaldehyde. 2,6-Dimethyl-4-phenylpyridine was obtained by the condensation of benzaldehyde, acetone, and ammonia under the same conditions [173].

Recently it was shown by us [34, 47, 67, 174] that the condensation of acetaldehyde and ammonia with pyridinaldehydes under analogous conditions led to the preparation of dipyridyls:



In somewhat more detail we studied the conditions of condensing benzaldehyde and also cinnamaldehyde and acetaldehyde with ammonia [34, 35, 175, 176]. The greatest selectivity with respect to the formation of 4,4'-dipyridyl was displayed by $Al_2Co_3(PO_4)_4$ and calcium phosphate modified with copper chloride. For the formation of 4-phenylpyridine the best proved to be catalysts based on active aluminum oxide modified with cobalt chloride, copper chloride, or acids [47]. For the synthesis of 4,4'-dipyridyl (40-45% yield) and 4-phenylpyridine (45-54% yield) optimal conditions were a temperature of 310-320°C, molar ratios of starting materials PyCHO (or PhCHO)—MeCHO—NH_3—N_2 = 1:5-10:50:25, and volume flow rate 1500-1800 h^{-1} [47, 67]. The use of 3-pyridinaldehyde led to the formation of 3,4'-dipyridyl (46% yield in the presence of cobalt phosphate) [67].

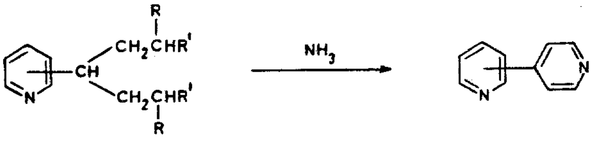
The reaction of pyridinaldehyde and pyridylketones with ammonia in the liquid phase under pressure at 250°C in the presence of ammonium acetate led to polypyridyl in a yield of 5-30% [177].



3,4'-Dipyridyl was synthesized by the same method from 3-pyridinaldehyde, acetaldehyde, and ammonia in 32% yield [178, 179] and 2,4,6-triphenyl- and pentaphenylpyridines were made from phenylacetaldehyde or desoxybenzoin respectively, benzaldehyde, and ammonia [26, 27, 180, 181].

The 2,2'-, 3,2'- or 4,2'-dipyridyls may be obtained from 2-, 3-, or 4-aminomethylpyridines and acetaldehyde in the vapor phase at 450°C over modified aluminosilicate or zinc phosphate [182]. Reaction of the cyclic dimer of acrolein with ammonia over boron phosphate at 300-370°C with a low conversion (3-5%) led to a mixture of 4,4', 4,2'-, and 2,2'-dipyridyls together with pyridine and alkylpyridines [183].

According to studies [184-191] substituted pyridines were used as starting materials in the catalytic synthesis of dipyridyls and were cyclized in the vapor phase at 350-380°C over oxides of aluminum, silicon, chromium, or copper, aluminosilicate, or platinum or palladium supported on aluminosilicate. The yield was 8-86% depending on the initial pyridine. Dipyridyls with the highest yield were obtained from glutaraldehyde derivatives. It was possible to carry out this same synthesis in the liquid phase at 80-130°C and 50 atm in the presence of oxygen and the acetate of ammonia, copper, or iron; however the yield of dipyridyls was low (25%) [192]. Almost all the isomers of dipyridyl were obtained by this method by varying the starting pyridine derivative. However the complex and multistage synthesis of substituted pyridines used subsequently for the catalytic synthesis of dipyridyls reduced the practical value of this method in general.

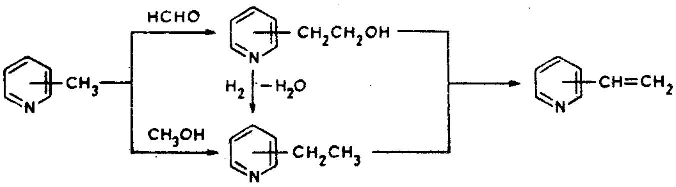


R, R' = H, OH, SH, N(Alk)₂, OAlk, NH₂

By catalyzing 4,4'-di-4H-pyran with ammonia at 350°C over nickel oxide supported on Al_2O_3 in the presence of oxygen of the air it was possible to obtain 4,4'-dipyridyl in 56% yield [193]. However the preparation of the initial dipyran from 4-iodo-4H-pyran was no less complicated than the direct dimerization of pyridine with metallic sodium into 4,4'-dipyridyl [194].

ALKYLATION AND DEHYDROGENATION OF THE SIDE CHAINS OF PYRIDINE BASES

On condensing 2- and 4-methylpyridines with formaldehyde in the ratio 1:1-3 over silica gel or aluminum oxide modified with zinc chloride, or phosphoric or boric acids in the vapor phase at 400-500°C a mixture of vinyl- and ethylpyridine was formed [195]. The conversion of methylpyridine was 12-32% in this case. A mixture of vinyl- and ethylpyridines were also formed on interaction of 2- and 4-methylpyridines, methyl alcochol, and oxygen of the air in the vapor phase at 400-450°C over oxide catalysts of molybdenum, vanadium, and bismuth supported on silicon dioxide which was impregnated with boric acid or other substances of an acidic character [196]. These conversions probably proceed according to the following scheme:



On alkylation of 2-methylpyridine with methanol in the vapor phase over silica gel impregnated with hydrogen chloride at 450°C, apart from the formation of 2-ethylpyridine, there also occurred a demethylation and isomerization reaction. However alkylation occurred more selectively if the reaction was conducted under a pressure of 200 atm at 350°C for several hours [197]. Under analogous conditions over an aluminosilicate catalyst containing a fluorine compound 2-ethylpyridine was obtained in a yield of about 30% [198]. Methylation of pyridine with methyl alcohol or other alkylating agents over nickel on Ni_2O_3 [199] or

Al_2O_3 [200] in the vapor phase led selectively to 2-methylpyridine in a yield of 50-60%. If acetic [201] or chloroacetic [202] acid was used as catalyst then a mixture of 2-methyl, 3-methyl-, and 3-ethylpyridines was formed. Methylation of pyridine with methyl alcohol in the presence of aluminosilicate or boron phosphate in the liquid phase at 300°C and a pressure of 200-250 atm gave mainly 3-methylpyridine [203].

Reaction of pyridine with acetic anhydride in the presence of iron filings at 75°C gave 2-ethylpyridine in 50% yield [204]. On interacting pyridine with 1,2-dichloroethane in phenol N-(β-chloroethyl)-pyridinium chloride was obtained which was converted by treatment with sodium hydroxide into 2-vinylpyridine in 80% yield [205].

Dehydrogenation of ethylpyridines into vinylpyridines is usually carried out in the presence of steam or other diluents (H_2, CO_2, N_2, etc.) over chromium—potassium—iron oxide [206] or zinc—oxide [17] catalysts at 500-700°C. Dehydrogenation of 2-methyl-5-ethylpyridine under these conditions led to 2-methyl-5-vinylpyridine (78% yield).

A two-stage method of obtaining vinylpyridines has been developed [207-209]. Reaction of alkylpyridines (2- and 4-methylpyridines, 2,6-dimethylpyridine, 2-methyl-5-ethylpyridine) with formaldehyde at a ratio of reagents alkylpyridine—formaldehyde = 4:1 was carried out at 140-240°C in the liquid phase under pressure. As a result of this reaction the corresponding pyridylethanols were formed with a selectivity of 66-72% on formaldehyde and 75-85% on alkylpyridine. These were dehydrated in the following stage into vinylpyridines with sodium hydroxide at 90-100°C or in a flow-through system over calcium phosphate at 250°C. The selectivity of vinylpyridine formation on vapor-phase dehydration of pyridylethanols was 90-92% and the conversion of the latter was 91-94%.

Pyridine bases may also be obtained on dehydrogenation of saturated heterocycles. For example, on dehydrogenation of piperidines, alkylpiperidines, and partially hydrogenated pyridines carried out in the vapor phase at 450°C in the presence of hydrogen over platinum [210] or in the presence of stoichiometric amounts of oxygen over aluminosilicate [211] the yield of pyridine bases was 64-80%. In the case of liquid phase oxidative dehydrogenation of piperidine in the presence of copper acetate the yield of pyridine was 50% overall [212].

DEALKYLATION OF PYRIDINE BASES

Dealkylation of alkylaromatic hydrocarbons has been widely applied in industry. Regretfully the analogous processes of dealkylation in the pyridine series have still not been mastered although the method is extremely promising for the treatment of a large number of the higher pyridine bases not directly used in industry. At the present time the dealkylation of only methylpyridines has been investigated in detail [19]. Under conditions of thermal cracking over aluminosilicate at 700-850°C demethylation proceeded with a low selectivity with fission of the pyridine ring. The yield of pyridine did not exceed 25% and furthermore the catalyst was rapidly deactivated [213, 214].

On hydrodealkylation of 2-methylpyridine over aluminosilicate at 600°C the yield of pyridine also did not exceed 25% while quinoline was formed from methylquinolines on the same catalyst with a yield of 40-48% [215]. However in the presence of catalytic amounts (less than 1% of the initial pyridine base) of carbon disulfide or hydrogen sulfide at 625-900°C and a hydrogen pressure of 15-45 atm pyridine was obtained in 55% yield from 2-methyl-5-ethylpyridine at a degree of conversion of the latter of 98% [216]. Over nickel—aluminum catalyst 3-methyl- and 3-ethylpyridine were formed on hydrodealkylation of 2-methyl-5-ethylpyridine with a selectivity of 90-95% [217]. A silver catalyst was also investigated over which 46% pyridine was obtained from 2-methylpyridine although the yield of pyridine did not exceed 33% from other methylpyridines and dimethylpyridines [218].

Thermal hydrodealkylation proved to be less selective. Pyridine was obtained in 20-30% yield from methylpyridines at 800-850°C and on complete conversion of 2-methyl-5-ethylpyridine a mixture consisting of 34% 2-methylpyridine, 21% 2,5-dimethylpyridine, 16% 2-methyl-5-vinylpyridine, 8% 3-methylpyridine, and only 13% pyridine was obtained [219]. The comparatively low yield of pyridine, the need to carry out the reaction at high temperatures, the significant consumption of hydrogen, the formation of undesirable byproducts (HCN for example), and the rapid deactivation of the catalyst are probably the reasons why catalytic cracking and hydrodealkylation of alkylpyridines have not been used in industry up to the present.

Dealkylation in the presence of steam enables the reaction to proceed at a lower temperature at which destructive conversion of the pyridine ring is reduced and reaction selectivity is increased. The reaction was carried out over a nickel catalyst supported on Al_2O_3 at a ratio of alkylpyridine—water = 1:25-70 and a temperature of 400-450°C [220-222]. The selectivity of formation of pyridine from 2-methylpyridine was 83% and the yield 43%. On dealkylation of 2-methyl-5-ethylpyridine 3-ethylpyridine was obtained with a selectivity of 95% [222, 223]. Dealkylation of 2,6-dimethylpyridine [224] and 2,2'-dimethyl-4,4'-dipyridyl has been investigated over a nickel catalyst [225] as has the demethylation of 3-methylpyridine on a platinum catalyst supported on γ-Al_2O_3 [226].

In recent years the oxidative dealkylation of methylpyridines has been investigated [227-231]. This attracted attention because the vanadium—molybdenum oxide catalysts used retained activity for a long time. Moreover the process did not require the use of high temperatures and pressures. Vanadium—molybdenum catalysts, supported on a nickel—aluminum alloy, containing an oxide ratio V_2O_5—MoO_3 = 3:1 were usually modified with up to 3% oxides of manganese, zinc, sodium, or chromium. The reaction was carried out in the presence of oxygen of the air and steam at 430-440°C. 2-Methyl-, 2,6-dimethyl-, and 2,4,6-trimethylpyridines were converted into pyridine with yields of 75, 36, and 10% respectively. Cerium—zirconium phosphate has also been used as a catalyst in oxidative dealkylation [232].

Pyridine may be obtained from 2-methylpyridine in an overall yield of up to 90% in a process combining oxidative ammonolysis of methylpyridine and hydrolysis of the 2-cyanopyridine formed in the first stage with subsequent decarboxylation of pyridine carboxylic acid [233]. The oxidative ammonolysis was carried out over a vanadium—titanium oxide catalyst in the presence of steam at 330-380°C in a circulating system.

The authors of [234] have proposed a method of obtaining pyridine according to which isomeric methylpyridines (or mixtures of them) were subjected to vapor phase oxidation over vanadium—molybdenum catalyst promoted with titanium in the presence of steam at 430-440°C with subsequent decarbonylation of the condensed reaction products containing pyridinaldehydes over a chromium—zinc—manganese catalyst at 410°C. By this method pyridine was obtained from 2-, 3-, and 4-methylpyridines with selectivities of 78, 54, and 63% respectively.

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It is evident from the presented literature material that various preparative methods for obtaining pyridine, alkylpyridines, phenylpyridines, and dipyridyls have been developed at the present time. Some of these are applicable in industry. The methods include both the direct condensation of aldehydes with ammonia and comparatively simple transformations such as alkylation, dealkylation, and dehydrogenation. The shortcomings of the investigations on the kinetics and mechanisms of these reactions should be recognized.

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