

## Metal complex catalysis in a synthesis of pyridine bases

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**Dedicated to Professor Mikhail G. Voronkov on the occasion of his 80<sup>th</sup> birthday**

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### Abstract

The review systematizes for the first time literature data of the last 15 years on a synthesis of pyridine bases including those of natural structure with the use of metal complex catalysts. The catalyzed by complexes of transition metals (Co, Ni, Pd, Zr) and rare-earth elements reactions of heterocyclization of acetylenes with nitriles, liquid phase condensation of aldehydes with amines, linear and cyclic oligomerization of vinylpyridines with 1,3-dienes and condensation of carbonic acid chloroanhydrides with olefins, acetylenes, tertiary alcohols to give substituted pyridines, quinolines and phenanthrolines of a set structure are considered. The mechanisms of molecule generation of pyridine bases in the presence of metal complex catalysts are discussed, and data on an effect of transition metal nature, initial monomer structure and reaction conditions on a reaction direction of a formation of six-membered nitrogen heterocycles are listed.

**Keywords:** Catalysis, metal complex, synthesis, pyridine bases

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## 1. Introduction

More than 150 years passed from the moment of a discovery of simple pyridine, but a limited assortment of pyridine bases is produced in a commercial scale so far due to the absence of universal and commercially efficient methods of a synthesis of the latters. A development of prospective synthetic methods to produce pyridines including those of complex structure will allow to make the latters more available and, hence, pyridine bases will be widely used in industry.

At present the commercial methods to gain pyridines, such as, 2-methyl-5-ethyl- and 2-methylvinylpyridines initiating from acetaldehyde and ammonia with the use of heterogeneous Co-containing catalysts are known together with the classic laboratory methods of pyridine synthesis based on the use of Skraup, Doebner–Miller and Friedlaender reactions.

A sufficient hitch in a field of a synthesis of pyridine bases was observed in 1973, when Japanese researchers showed a possibility to give substituted pyridines in one step via a heterocyclization of two molecules of acetylenes with acetonitriles in the presence of catalytic amount of cobalt complexes. Later this reaction was studied in detail by German authors, particularly, Boennemann and colleagues, and prospects of the use of the reaction in a synthesis of pyridine bases of various structure, including vitamins of pyridine series were shown.

It should be noted the application of metal complex catalysts in pyridine chemistry allowed to develop a series of perspective for commercial realization methods of their synthesis, including di- and tricyclic nitrogen heterocycles including pyridine rings – quinolines, naphthyrididines and phenanthrolines by heterocyclization of carbonyl compounds with amines.

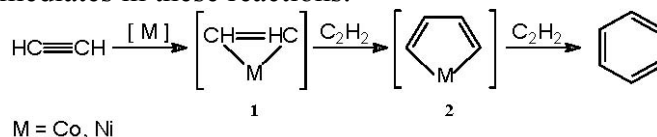
As a result for the last years a sufficient data material concerning the application of metal complex catalysts in a synthesis of pyridine bases was accumulated in the world literature and scattered about the numerical papers, patents and theses.

Hence, the necessity appeared to systematize the literature data on a synthesis of pyridine bases with the use of homogeneous metal complex catalysts. The authors paid a special attention to the discussion and critical analysis of publications by the foreign and native researchers for the last 10–15 years concerning the application of metal complex catalysts in a synthesis of pyridine bases by heterocyclization of acetylenes with nitriles, carbonyl compounds with amines, and chloroanhydrides of carboxylic acids with amines under the effect of Lewis acids.

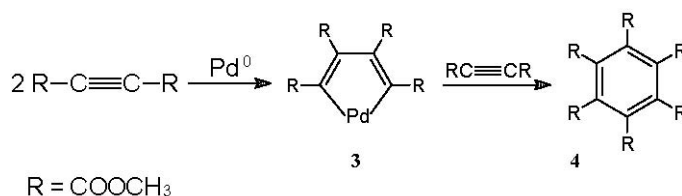
The numerical publications concerning functionalization of pyridines and their derivatives in the presence of metal complex catalysts were not discussed in the review due to the limited volume.

## 2. Heterocyclization of acetylenes with nitriles catalyzed by cobalt complexes

The first papers on a possibility to carry out catalytic trimerization in benzene or cyclooctatetraene in the presence of low valence cobalt or nickel complexes appeared at the beginning of 60's.<sup>1-3</sup> Metallacycloprenes **1** or metallacyclopentadienes **2** were supposed by the authors to be key intermediates in these reactions.<sup>4-6</sup>



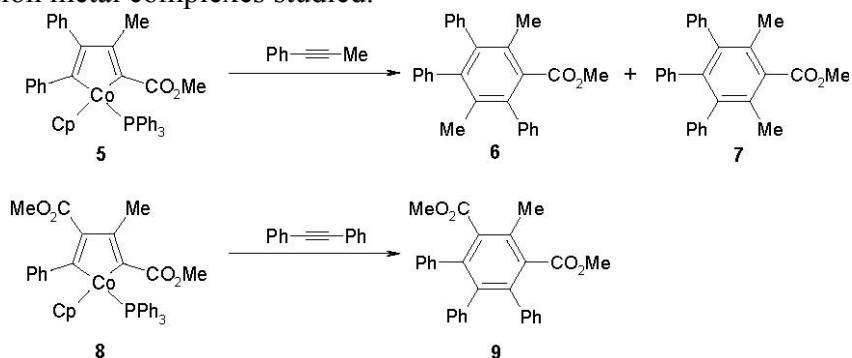
The paper<sup>7</sup> confirmed acetylene trimerization proceeded via a step of a formation of metalocyclic intermediates, the interaction of bis(dibenzylidene)palladium with dimethyl ester of acetylenedicarbonic acid was shown to give palladacyclopentadiene **3**, the further reaction of the latter with dimethyl ester of acetylenedicarbonic acid led to the formation of hexamethyl ester of mellitic acid **4**. As a result, metallacyclopentadiene formed from acetylene and transition metal complex was stated by the authors<sup>7</sup> to be catalytically active intermediate in cyclization reactions.



According to the methodology,<sup>7</sup> platinacyclopentadiene complexes were isolated and characterized together with palladacyclopentadienes.<sup>7,8</sup>

Later a series of cobalt metal cycles **5** and **8** was studied, the reaction of the latters with acetylenes was shown to give substituted benzene derivatives **6**, **7** and **9**.<sup>9,10</sup>

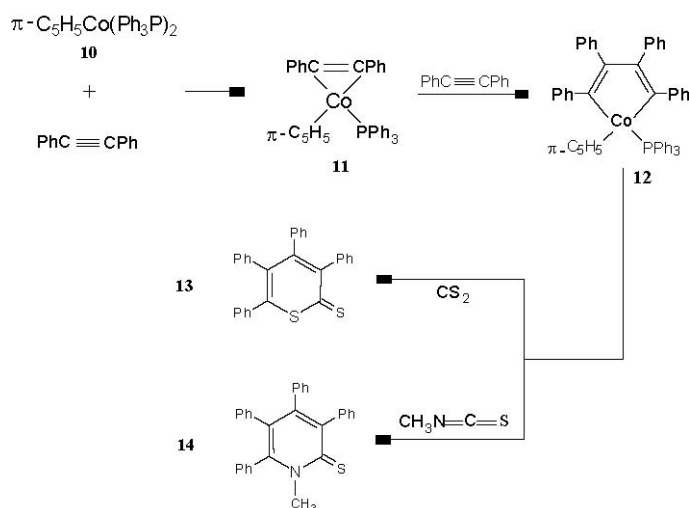
Then cobalt compounds were found to have the highest activity in cyclization reaction in a series of transition metal complexes studied.<sup>11,12</sup>



For example, the reaction of ( $\eta^5$ -cyclopentadienyl)bis(triphenylphosphine)cobalt **10** with diphenylacetylene gives cobaltacyclopentadiene **12**, under reaction conditions the latter includes heterocumulene on M-C bond to give heterocyclic compound. An interaction of **12** with carbon disulfide leads to a formation of 3,4,5,6-tetraphenyldithiopyron-2 **13** in 10% yield.<sup>12</sup>

Thus, at the beginning of 70's cobalt-containing complexes were stated to be the most active

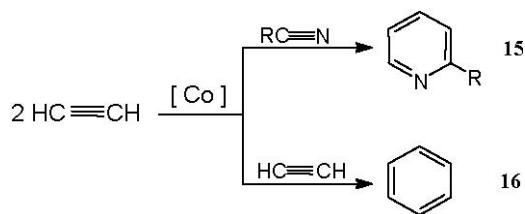
and selective catalysts of acetylene cyclotrimerization leading to the formation of substituted benzenes of the set structure.<sup>3,13</sup>



Thus, to the beginning of 1973 the researchers from Japan and Germany have realized the reactions of acetylene cyclocotrimerization with nitriles catalyzed by highly active Co complexes to give substituted pyridines under mild conditions.

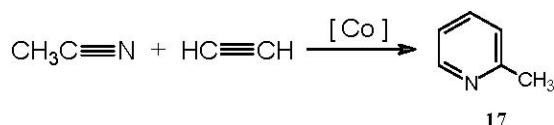
The first experiments on the common acetylene heterocyclization with nitriles in the presence of cobalt-containing catalysts showed the prospect of the application of the reaction to give substituted pyridines **15**.<sup>12, 14-17</sup>

To some extent the results obtained were predicted, as in the reactions of one of the  $\text{-C}=\text{C}$  groups in acetylenes was changed for nitrile group  $\text{-C}=\text{N}$ . A formation of benzene **16** was observed in the reactions in the absence of nitrile (RCN).

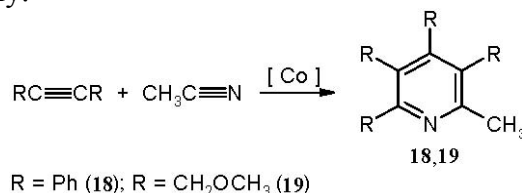


A formation of pyridine derivatives was stated experimentally<sup>18,20</sup> to be preferable under the conditions favorable for the competitive proceeding of the both reactions. The data are in a good agreement with quantum-mechanical calculations,<sup>21</sup> the latter confirm acetylene heterocyclization with nitriles is energetically more favorable than acetylene homocyclotrimerization.

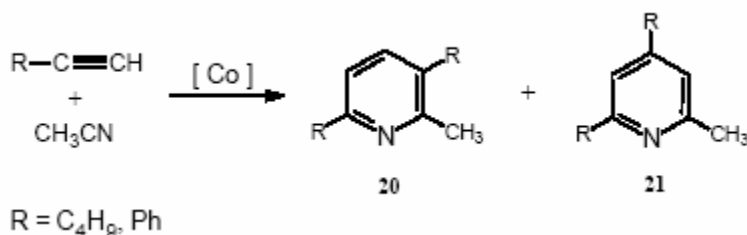
The first paper on a synthesis of substituted pyridines by acetylene heterocyclization with nitriles  $\text{RC}=\text{N}$  ( $\text{R}=\text{CH}_3$ , Ph,  $\text{PhCH}_2$ ) in the presence of Co-containing complex catalysts was published by Japanese researchers.<sup>12</sup>  $\alpha$ -Picoline **17** was shown for the first time to be formed in 23% yield during heating ( $\sim 70^\circ\text{C}$ , benzene) of acetonitrile and acetylene for 7 hours in the presence of ( $\eta^5$ -tetraphenylcyclopentadienyl)(triphenylphosphine)cobalt.



Under similar conditions diphenylacetylene and 1,4-dimethoxy-2-butyne with acetonitrile give 2-methyl-3,4,5,6-tetraphenylpyridine **18** and 2-methyl-3,4,5,6-tetramethoxymethylpyridine **19** in 38 and 8% yield, respectively.



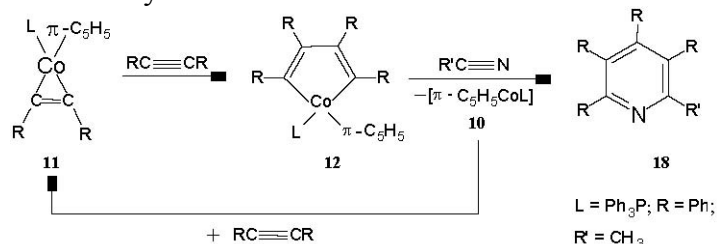
Under the conditions mentioned mono-substituted acetylenes react with acetonitrile to give the mixture of regioisomeric 2-methyl-3,6-dialkyl- and 2-methyl-4,6-dialkylpyridines **20** and **21** respectively.<sup>12</sup>



The low yield of pyridine bases and multistep synthesis of the initial catalysts are the considerable shortcomings of the method developed.<sup>12</sup> Really, complex (η<sup>5</sup>-tetraphenylcyclopentadienyl)(triphenylphosphine)cobalt used by the authors is synthesized from difficult initial reagents in several steps in 10% yield.<sup>22</sup>

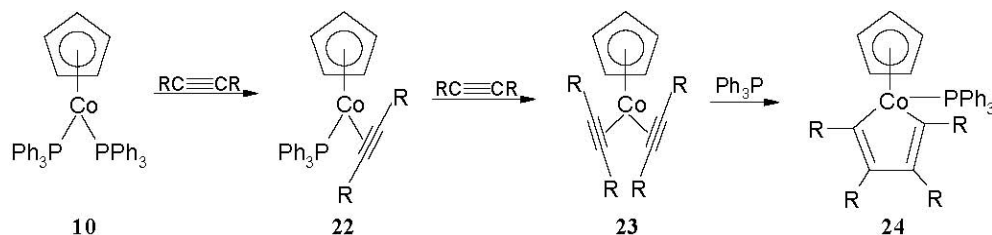
In the same 1973 Japanese authors have supposed the formation of pyridine molecules **18** proceeded via a step of a formation of cyclic metal complex intermediates **11** and **12** when they discussed a mechanism of nitrile cyclotrimerization.<sup>14</sup>

In the authors' opinion, cobaltacyclopentadienes **12** formed from cobaltacycloprenes **11** and initial acetylenes are the key intermediates in the above reactions.<sup>14, 22</sup>



The subsequent reaction of **12** with initial nitriles led to the formation of the corresponding substituted pyridines **18**.

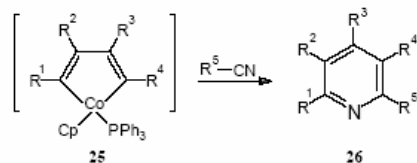
The reaction of acetylene cyclotrimerization with nitriles in the presence of catalyst CpCo(PPh<sub>3</sub>)<sub>2</sub> **10** was studied in detail, and a series of five-membered metal cycles **24** and cobalt acetylene complexes **22** and **23** responsible for the formation of pyridine molecules were isolated from the reaction mixture and characterized.<sup>9, 23-27</sup>



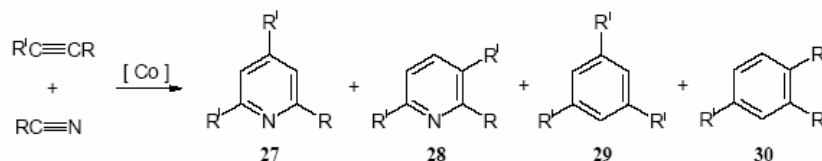
The intensive investigations in this field allowed to produce and identified a series of cobaltacyclopentadiens **25** having various substituents in a five-membered cycle. A stoichiometric reaction of **25** with nitriles leads to the formation of asymmetrically substituted pyridines **26**, this is confirmed by the mechanism of the pyridine formation proposed by the authors.<sup>28</sup>

The mentioned above papers on formation, isolation and identification of cobalt metal cycles, and inclusion of the latters to the subsequent reactions of cyclization with nitriles<sup>12,14,28</sup> played a significant role in understanding of a mechanism of the reaction and in a successful development of the direction in the pyridine chemistry.

It should be noted, that presently cobaltacyclopentadiene metal cycles are indisputable key intermediates in the above reactions of cyclocotrimerization.

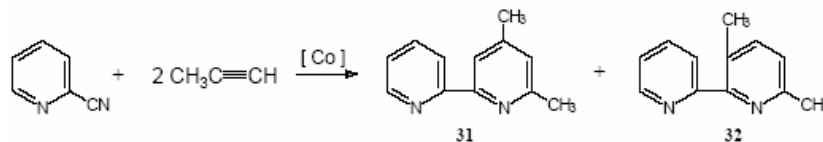


Approximately at the same time H Boennemann and colleagues have found that the reaction of acetylene cyclotrimerization with nitriles might be catalyzed by low valence Co complexes formed in situ by the reduction of compounds of two- or trivalent cobalt with the use of NaBH<sub>4</sub>, BuLi, EtMgX, Hg, Li, LiH, LiAlH<sub>4</sub>, etc. In that case isomeric pyridines **27** and **28** are afforded in high yields<sup>16</sup> from nitriles RC≡N (R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, CH=CH<sub>2</sub>, Ph, PhCH<sub>2</sub>) and acetylenes R'C≡CH (R' = CH<sub>3</sub>, C<sub>5</sub>H<sub>11</sub>, Ph, PhCH<sub>2</sub>) in contrast to the experiments, where complexes prepared beforehand are used as catalysts.

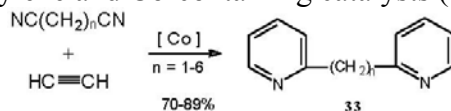


Thus for example, cyclocotrimerization of propionitrile with methylacetylene under the effect of Co-containing catalyst (CoCl<sub>2</sub>/BuLi) proceeds to give isomeric trialkylpyridines **27** and **28** in 71% yield.

2,2'-Dipyridyl was produced in 95% yield in a heating of 2-cyanopyridine with acetylene (toluene, 120 °C, 10 h) in the presence of a catalyst (η<sup>5</sup>-cyclopentadienyl)(η<sup>4</sup>-1,5-cyclooctadiene)cobalt(II).<sup>29</sup> Under similar conditions a mixture of 2,4-dimethyl-6-(pyridyl-2)pyridine **31** and 2,5-dimethyl-6-(pyridyl-2)pyridine **32** was produced in 72:28 ratio in 91% yield.

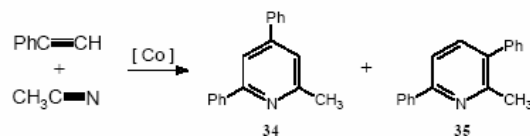


According to the above reaction,  $\alpha,\omega$ -dipyridylalkanes **33** may be easily produced initiating from  $\alpha,\omega$ -dicyanoalkanes, acetylene and Co-containing catalysts (toluene, 140–150 °C).<sup>29</sup>

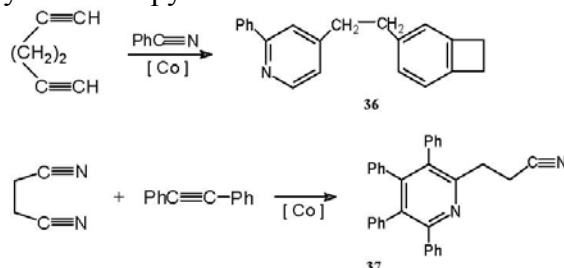


Later informations (preferably patents) on cyclocotrimerization of acetylenes with nitriles in the presence of salts of two- and trivalent cobalt, and prepared beforehand low-valence cobalt complexes, such as,  $(\eta^1\text{-cyclooctenyl})(\eta^4\text{-1,5-cyclooctadiene})\text{Co(I)}$ ,  $(\text{methylheptadienyl})(\text{butadiene})\text{Co(I)}$  or  $(\eta^5\text{-cyclopentadienyl})(\eta^4\text{-1,5-cyclooctadiene})\text{Co(I)}$  appeared in the world literature.<sup>30-32</sup> The reaction of methylacetylene with acetonitrile in the presence of  $(\text{methylheptadienyl})(\text{butadiene})\text{Co(I)}$  leads to the formation of 2,4,6- and 2,3,6-colidines in 43% and 19% yields, respectively. It should be noted that the prepared beforehand low-valence cobalt complexes are low stable and hardly prepared, that limits their wide use.

The patent<sup>17</sup> describes a synthesis of substituted pyridines by reaction of cyclocotrimerization of nitriles  $\text{RCN}$  ( $\text{R} = \text{alkyl, aryl, alkenyl}$ ) with acetylene or dialkylacetylene in the presence of heterogeneous catalysts (metallic cobalt or  $\text{Co}_2\text{O}_3$ ). Alkyl- and arylphosphines, substituted  $\beta$ -diketones or poly(pyrazoline)borates are used as ligands in these reactions. In spite of strict conditions of the reaction (200–350 °C, 105 atm.), yields of substituted pyridines are rather low in these experiments. When  $\text{Co}^{+2}$ -dihydrobis(1-pyrazoline)borate was used as a catalyst, yield of 2-methylpyridine consisted of 44%. The higher yields of substituted pyridines are managed to be produced with the use of cobalt compounds put on zeolites.<sup>33</sup> The catalysts showed a high selectivity with respect to the target pyridines. A cyclocotrimerization of phenylacetylene with acetonitrile gives a mixture (80:20) of 2-methyl-4,6-diphenyl- and 2-methyl-3,6-diphenylpyridines **34** and **35** in total 60–70% yield.

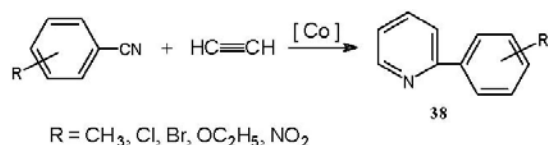


A cyclocotrimerization of benzonitrile with  $\alpha,\omega$ -diacetylene hydrocarbons, and  $\alpha,\omega$ -dinitrile with diphenylacetylene leading to the formation of complex substituted pyridines **36** and **37** is a significant invention in a synthesis of pyridine bases.<sup>15</sup>

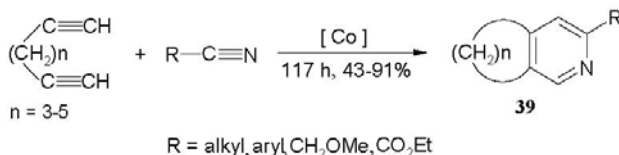


During the comparison of catalytic activity and selectivity of catalysts used in the reaction of heterocyclization the authors in most cases gave preference to the prepared beforehand cobalt complexes.<sup>34-38</sup> However later the most research centres refused from the application of specially prepared complexes as catalysts due to the hard preparation and passed to more available cobaltocene  $\text{Cp}_2\text{Co}$ ,<sup>39</sup> and a series of other Co-containing catalysts, the base of which is "CpCo".<sup>40,41</sup>

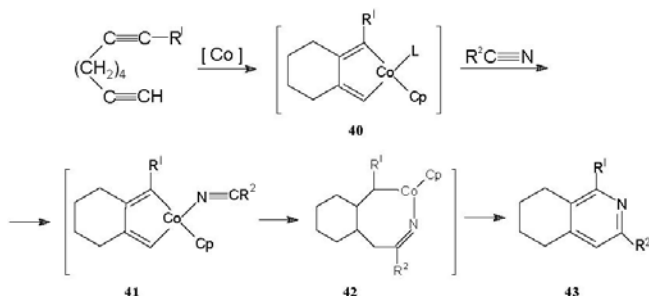
A cyclotrimerization of acetylene with benzonitrile in the presence of the mentioned catalysts gave 2-phenylpyridines **38**. The authors systematically studied an effect of functional groups in initial nitriles on the direction and total yield of the reaction products.<sup>42,43</sup>



Developing the previous research work,<sup>15</sup> American researchers synthesized a series of bicyclic pyridines **39** by the interaction of  $\alpha,\omega$ -diacetylenes with nitriles in the presence of catalytic amount of  $(\eta^5\text{-cyclopentadienyl})\text{cobalt dicarbonyl}$ .<sup>44</sup>



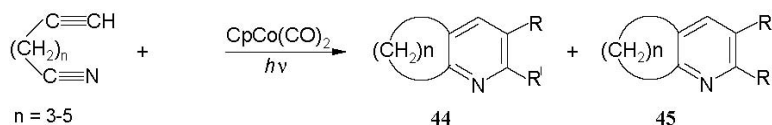
Nitriles containing electron-attracting substituents form pyridines in very low yields. This fact may be explained by the reaction of cyclocotrimerization begins from the formation of cobaltacyclopentadiene **40**, then nitrile molecule is coordinated due to the unshared pair of electrons on the central atom of the catalyst and then pyridine molecule is formed. Nitriles with electron-attracting substituents cannot compete with acetylene for the ligand place on the catalyst central atom, that leads to the formation of substituted benzenes. When nitrile is introduced to the sterically less hindered Co-C bond,  $\text{R}^2\text{C}\equiv\text{N}$  nitrogen passes to  $\alpha$ -position to Co **41**, and substituted pyridines **43** are formed from the complex **42**.



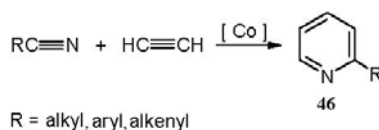
5,6,7,8-Tetrahydroquinolines are formed by "one-pot" method under the above reaction conditions.<sup>45</sup>

The reaction of heterocyclization of disubstituted acetylenes with  $\alpha,\omega$ -acetylenenitriles leading to bicyclic pyridines **44** and **45** is of special interest.<sup>46</sup>

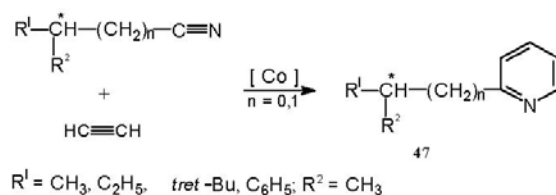




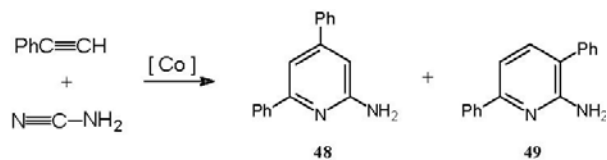
In the middle of 70's and beginning of 80's a number of licence material on a synthesis of 2-substituted pyridine bases **46** in the presence of cobaltocene as highly active and selective catalyst was published.<sup>47-49</sup> Yield of the target products is rather high (~90%), but benzene in 9–10% is formed as a side product in each experiment.



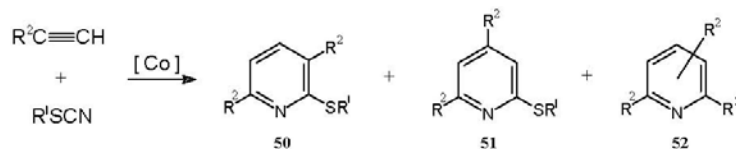
A reaction of cyclocotrimerization of acetylenes with chiral nitriles was used by Italian researchers for the synthesis of optically active pyridines **47**.<sup>50,51</sup>



The research works concerning a synthesis of practically useful aminopyridines initiating from aminonitrile and acetylenes attract an attention.<sup>34,48,49</sup> The interaction of phenylacetylene with cyanamide gives a mixture of 2-amino-4,6- **48** and 2-amino-3,6-diphenylpyridines **49** in one step in 87% yield.



A realization of the catalyzed by Co complexes reaction of alkylthiocyanates with acetylene allowed to develop a method for a synthesis of alkylthiopyridines,<sup>34,52</sup> the latter are hardly available so far.<sup>53</sup> Yield of the reaction products **50–52** depends mainly on a ratio of initial monomers and reaction conditions.



From the beginning of 70's the researchers carry out a search of the other transition metals able to proceed the reaction of cyclotrimerization of acetylenes with nitriles. On the basis of the studies it was stated that there are no catalysts equal in activity and selectivity to those of Co-containing. The rhodium catalysts are inferior to cobalt complexes in a reaction of cyclocotrimerization.<sup>54,55</sup> The development of more effective and selective Co-containing catalysts for these reactions attracts a special attention.

For example, the paper<sup>56</sup> proposes the suitable method to obtain cyclopentadienyl cobalt complexes active in the reaction of cyclocotrimerization of acetylenes with nitriles. Cobalt salts are introduced to the reaction with activated magnesium and anthracene or magnesium adducts with anthracene in the presence of complex-forming ligands – halogen-hydrocarbons – in THF or diglyme. The authors<sup>56</sup> produced cobaltocene in 63% yield and phenylcyclopentadienyl-Co-cyclooctadiene-1,5 in 40% yield.

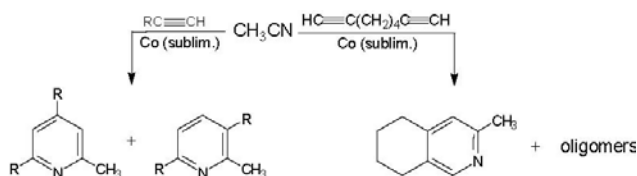
The other approach to the synthesis of the above catalytic complexes is based on the direct reduction of cobalt salts in the presence of complex-forming ligands with the use of AlEt<sub>3</sub> or NaBH<sub>4</sub>.<sup>57</sup> Yield of cobalt complexes consists of 70%.

P Hardt<sup>58</sup> proposed the improved method to give cobaltocene based on the reaction of cyclopentadienylsodium with anhydrous CoCl<sub>2</sub> in acetonitrile. Yield of cobaltocene consists of no less than 80% under the described conditions.

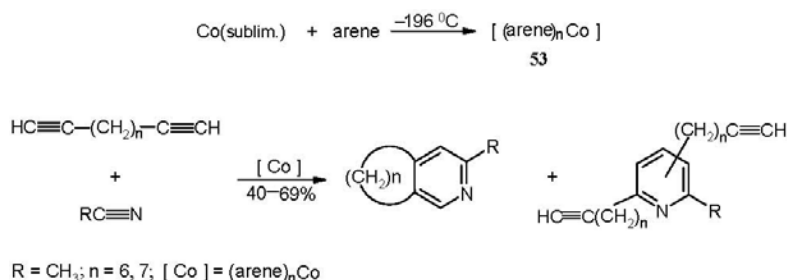
The synthesis of pyridines by cyclocotrimerization of acetylenes with nitriles in the presence of Co-containing catalysts modified by bioorganic compounds gave interesting results.<sup>59,60</sup> The choice of boron-containing ligands was not accidental, as the latter promote a proceeding of cyclocotrimerization under milder conditions and in high yields of target pyridines.

The research works to rise the catalytic activity of organocobalt catalysts were carried out by Japanese researchers.<sup>61</sup> The object was attained by the application of (η<sup>5</sup>-methoxycarbonylcyclopentadienyl)(η<sup>4</sup>-cyclooctadiene)Co and (η<sup>5</sup>-methoxycarbonylcyclopentadienyl)(η<sup>4</sup>-cyclooctatetraene)Co as catalysts.<sup>62</sup>

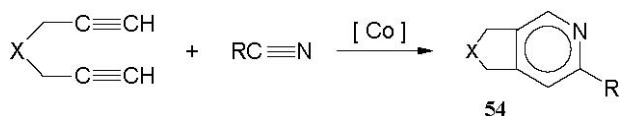
Italian researchers proposed to use freshly sublimated metal cobalt, that is condensed directly to the reaction mixture, as catalysts for cyclocotrimerization.<sup>63</sup> Yields of substituted pyridines according to this method consist of more than 80%.



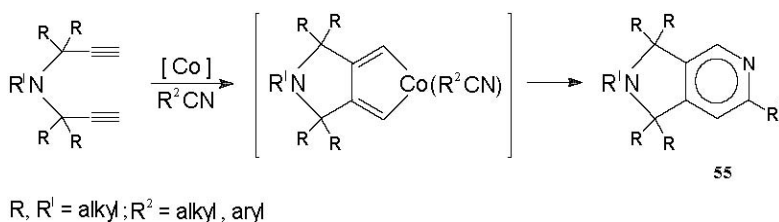
For higher activity and selectivity of the catalyst developed Italian researchers proposed to use metallic cobalt **53** solvated with arenes.<sup>64,65</sup>



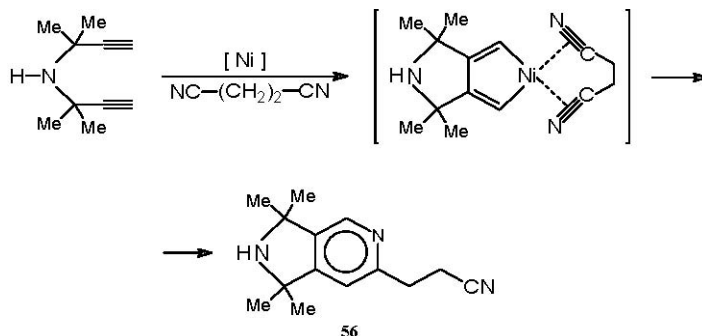
According to the licence literature<sup>66,67</sup> American researchers carried out a synthesis of bicyclic pyridines by the interaction of  $\alpha,\omega$ -diacetylenes with nitriles in the presence of a catalyst  $\text{CpCo}(\text{CO})_2$ . The reactions said above were carried out in a liquid-phase in equimolar ratio of acetylene and nitriles in toluene, xylene or n-octane in 47–81% yield of the target products. The chosen catalytic system allows to include functionally substituted  $\alpha,\omega$ -diacetylenes to the reaction.



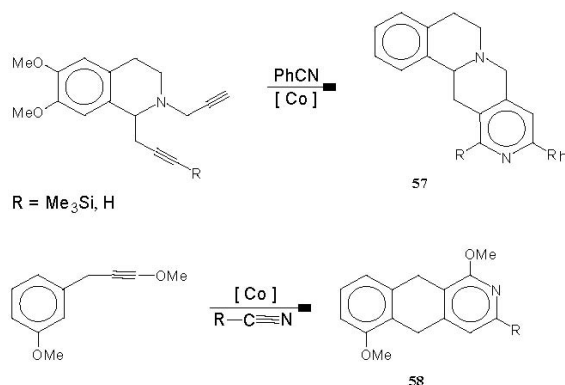
Dipropargyl amines<sup>68,69</sup> containing gem-dialkyl groups easily enter to the analogous transformations in the presence of catalytic system  $\text{CoCl}_2/\text{Mn}$ . The presence of gem-dialkyl groups in a molecule of initial diacetylene allowed to rise yield of dihydropyrrolopyridines **55** up to 90-98% and to decrease reaction temperature to 80 °C.



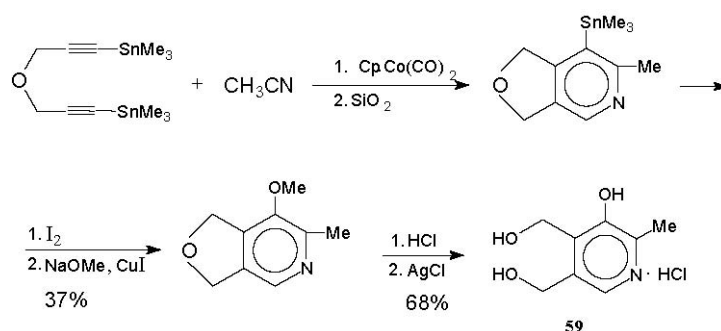
It should be noted that the above dipropargyl amine reacts with  $\alpha,\omega$ -dinitriles not only in the presence of Co-containing catalysts, but in the presence of phosphine nickel complex  $\text{Ni}[\text{P}(\text{OPr}^i)_3]_4$  to give dihydropyrrolopyridine **56**.<sup>68</sup>



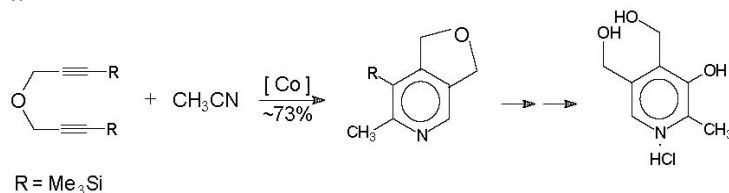
The research works concerning the studies on cyclocotrimerization of acetylene with nitriles for a synthesis of complex pyridine bases, including natural compounds are of great theoretical and practical interests. For example, a cyclocotrimerization of the corresponding diacetylenes with nitriles catalyzed by cyclopentadienyl cobalt complexes ( $\text{CpCo}(\text{CO})_2$ ) allowing to obtain compounds with i-naphthyridine **57**<sup>70</sup> or 2-azaanthracene **58** skeleton in one step.<sup>36</sup>



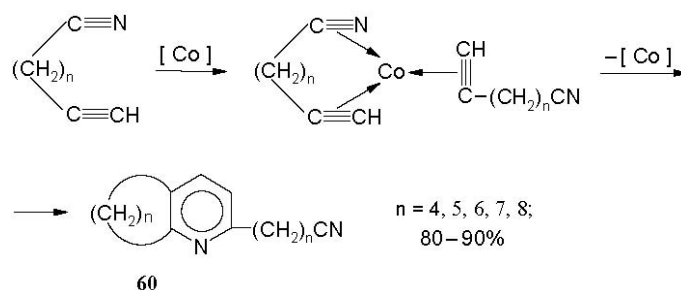
The application of dipropargyl ether as initial diacetylene makes regioselective synthesis of vitamin B<sub>6</sub> **59** to be possible practically in three technologic steps.<sup>36,71</sup>



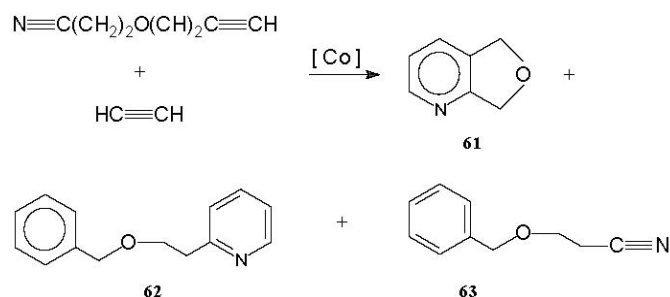
The analogous approach to a synthesis of vitamin B<sub>6</sub> from silylated dipropargyl ether was proposed by the authors.<sup>72</sup> Cobaltocene was used as a catalyst, and acetonitrile was used as initial reagent and a solvent.



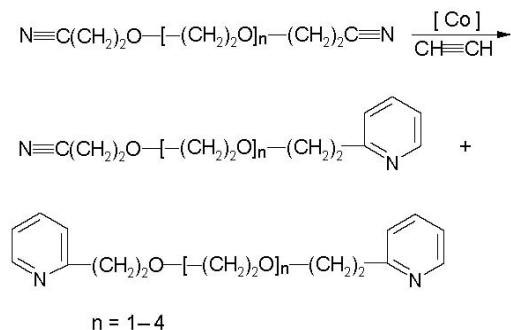
According to the above examples, substituted pyridines may be generated by the reaction of nitriles with mono- or disubstituted acetylenes in the presence of metal complex catalysts. In 1983 the first paper<sup>73</sup> on cyclocodimerization of  $\alpha,\omega$ -cyanoacetylenes to bicyclic pyridines **60** under the effect of two-component system consisting of Co(2-ethylhexanoate)<sub>2</sub> and AlEt<sub>3</sub> in a molar ratio 1:3 was published. The total absence of benzene derivatives resulted from acetylene homocyclotrimerization is a peculiarity of the reaction. The authors<sup>73</sup> suppose that nitrile and acetylene groups of the initial  $\alpha,\omega$ -cyanoacetylenes under reaction conditions enter a coordination sphere of a metal and hinder an approach to a central atom of a catalyst simultaneously of three acetylene molecules and their activation, and hence, a formation of benzene derivatives. A formation of pyridines from  $\alpha,\omega$ -cyanoacetylenes is appeared to be energetically more advantageous process than a formation of benzene molecules.



All attempts to carry out homodimerization of oxygen-containing cyanoacetylenes were unsuccessful.<sup>74</sup> In all experiments independently of changes in reaction conditions and of a nature and a concentration of a catalyst homocyclotrimerizations products of initial cyanoacetylenes to the corresponding trisubstituted benzenes were generated in insufficient amount. It may be, oxygen atom in molecule of  $\alpha,\omega$ -cyanoacetylenes due to the unshared pair of electrons takes in a formation of coordination sphere of catalyst central atom binding to the approach and coordination of acetylene and nitrile groups simultaneously in initial monomers. At the same time, cyclocodimerization of oxygen-containing  $\alpha,\omega$ -cyanoacetylenes with acetylene on a catalytic system consisting of  $\text{Co}(\text{2-ethylhexanoate})_2$  and  $\text{AlEt}_3$  proceeds easily in toluene at 150 °C and acetylene pressure of 10–15 atm. to result in a mixture of pyridine **61** and **62** and cyanoethylated derivative of benzyl alcohol **63**.<sup>74</sup>



The papers on a catalytic synthesis of the novel type of polyfunctional  $\alpha,\omega$ -mono- and dipyridines attract an attention.<sup>75,76</sup> Polyfunctional dinitriles in contrast to simple nitriles were found to react with acetylene only with the use of significant amount of the catalyst ( $\text{Co}:\text{Al}:\text{nitrile} = 1:3:10-20$ ) to give the corresponding mono- and dipyridines in high yields (90%).

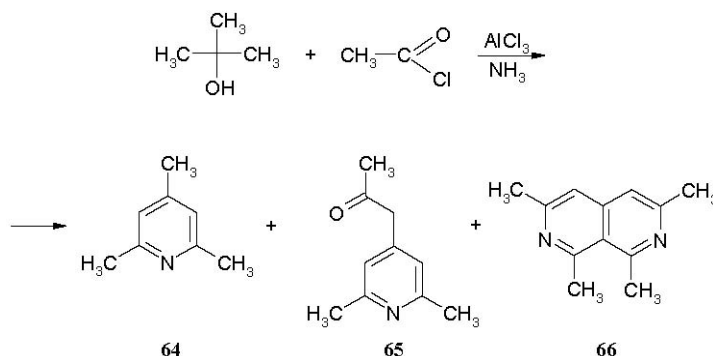


The reaction of acetylene derivatives with nitriles under the effect of metal complex preliminarily Co-containing catalysts was shown in the examples to be the most prospective

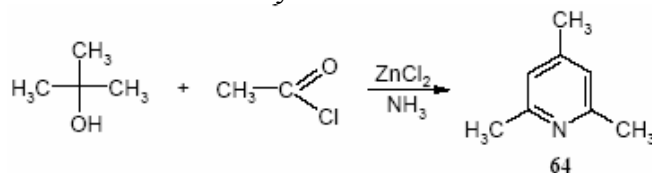
method of one-step synthesis of substituted pyridines at present.

### 3. Liquid-phase condensation of carboxylic chloroanhydrides with amines in the presence of Lewis acids

At the end of 70's the first paper<sup>77</sup> on a synthesis of alkyl-substituted pyridines by a reaction of *t*-butanol with acetylchloride and gaseous ammonia in the presence of  $\text{AlCl}_3$  as condensing agent was published. The reaction proceeds unselectively to give a mixture of 2,4,6-trimethylpyridine **64**, 4-acetyl-2,6-dimethylpyridine **65** and 1,3,6,8-tetramethyl-2,7-naphthyridine **66** in common 85% yield.

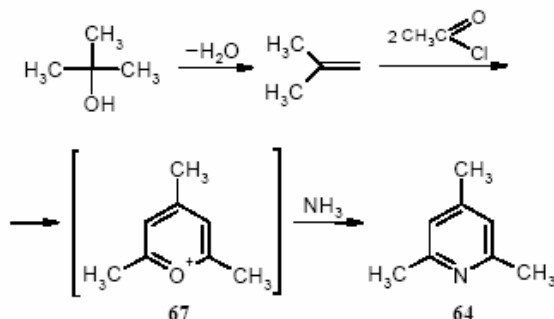


The reaction was studied to state a change of  $\text{AlCl}_3$  for  $\text{ZnCl}_2$  allowed to obtain a target product **64** in 95% and with 100% selectivity.<sup>78,79</sup>

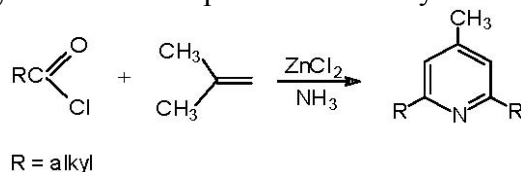


A high selectivity of condensation reaction may be explained by the properties of zinc dichloride, the latter is "milder" Lewis acid and promotes to decrease sufficiently initial monomers directing the reaction to a formation of practically important trimethylpyridine **64**.

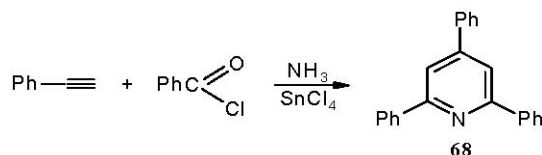
As to a mechanism of the reaction developed, the authors suppose alcohol dehydration to isobutylene proceeds firstly, then the latter interacts with acetylchloride to give pyrylium salt **67**, a treatment of the latter by ammonia gives trimethylpyridine **64** according to Scheme below:



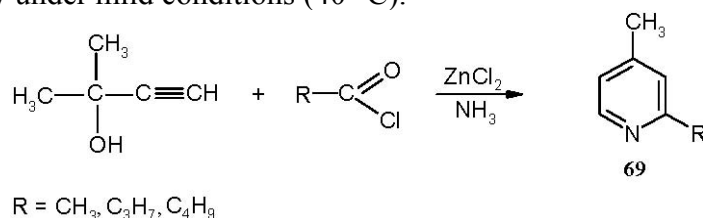
The supposition was confirmed experimentally by changing t-butanol for isobutylene.<sup>80,81</sup> The reaction was supposed to result in 2,4,6-trimethylpyridine **64** in high yield (88%). The studies in this direction was prospective to give alkyl-substituted pyridines from chloroanhydrides of carboxylic acids in the presence of catalyst ZnCl<sub>2</sub> and InCl<sub>3</sub>, SnCl<sub>4</sub>.<sup>82,83</sup>



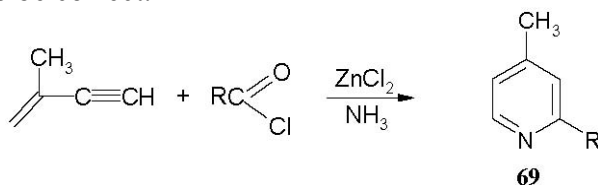
The positive results<sup>83,86</sup> on a synthesis of alkyl-substituted pyridines by the reaction of tertial alcohols and olefins with carboxylic chloroanhydride and NH<sub>3</sub> in the presence of Lewis acids allowed to involve ethynylcarbinols, vinylacetylenes and their derivatives to the above reaction. A paper on a formation of triphenylpyridine **68** from chloroanhydride of benzoic acid, phenylacetylene and NH<sub>3</sub> in the presence of SnCl<sub>4</sub> as a catalyst is appeared to be the precondition for the studies mentioned.<sup>84-86</sup>



The interaction of dimethylethynylcarbinol with carboxylic chloroanhydrides and NH<sub>3</sub> in the presence of ZnCl<sub>2</sub> was experimentally shown to give 2-alkyl-4-methylpyridines **69** in high yields (90%) and selectivity under mild conditions (40 °C).<sup>87,88</sup>

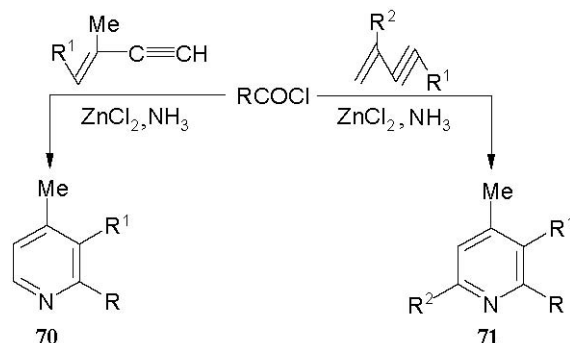


Under reaction conditions the dehydration of dimethylvinylcarbinol to vinylacetylene, which then interacts with carboxylic chloroanhydride and ammonia in the presence of catalytic amount of ZnCl<sub>2</sub> to give 2-alkyl-4-methylpyridine **69** was supposed by the authors<sup>87,88</sup> to proceed initially. The condensation of 2-methylvinylacetylene with acetylchloride with a subsequent treatment of the reaction products by NH<sub>3</sub> was carried out to confirm the above supposition.<sup>89</sup> The selective formation of 2,4-dimethylpyridine in 90% yield confirmed the supposed mechanism of a formation of substituted pyridines via a step of a dehydration of initial dimethylvinylcarbinols to be correct.



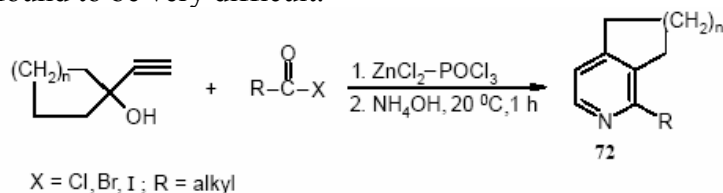
The experiments carried out and conclusions drawn<sup>87,89</sup> open the prospects for the directed

synthesis of di-, tri- and tetraalkylpyridines. Really, under the conditions obtained the reaction of 1,2-dialkyl-1,3-enines with carboxylic chloroanhydrides leads to only 2,3,4-trialkylpyridines **70**, while an application of 2,4-dialkyl-1,3-enines in high selectivity gives 2,3,4,6-tetraalkylsubstituted pyridines **71**.<sup>87</sup>

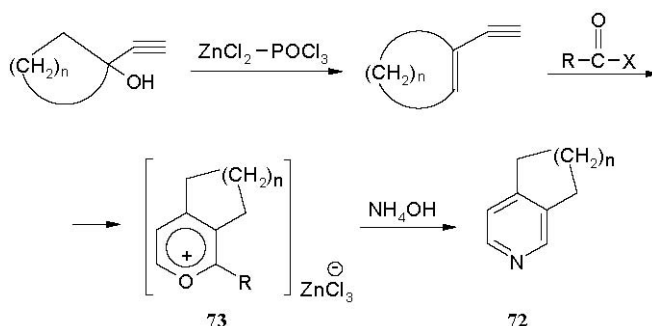


The reaction of ethynylcarbinols, substituted vinyl- and methyleneacetylenes with carboxylic chloroanhydrides and NH<sub>3</sub> was found experimentally by the isolation of intermediates to proceed via a step of a formation of pyrylium salts and to open a perspective way to the directed synthesis of substituted pyridines in high yields and selectivity.<sup>90</sup>

The studies in a field of the directed synthesis of bicyclic pyridine bases from 1-ethynylcycloalkanes and carboxylic chloroanhydrides were the logical continuation of the reaction developed. The interaction of cyclic ethynylcarbinols with chloro-, bromo- and iodoanhydrides of carboxylic acids in the presence of two-component catalysts ZnCl<sub>2</sub>-POCl<sub>3</sub> (1:1) under mild conditions (20 °C, 1 h) and a subsequent treatment of the mixture by NH<sub>4</sub>OH at 0 °C was found<sup>91</sup> to give 2-alkyl-3,4-cycloalkenopyridines **72**. The synthesis of the latter by the other methods was found to be very difficult.



The analysis of literature<sup>92,94</sup> and own results allowed the authors<sup>91</sup> to conclude that the formation of bicyclic pyridine molecules **72** from ethynylcarbinols and halogenated anhydrides of carboxylic acids proceeded via a step of a formation of pyrylium salts **73**, then the latter were transformed to the target products in the treatment by NH<sub>4</sub>OH according to the following Scheme.



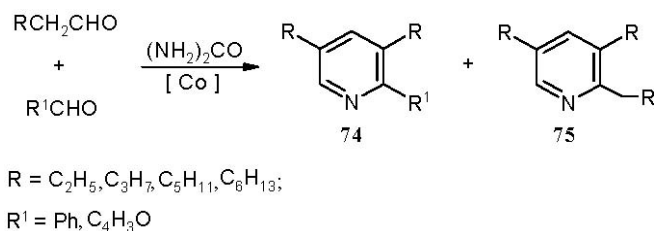


The method developed for a synthesis of bicyclic pyridines by a condensation of cyclic ethynylcarbinols with halogenated anhydrides of carboxylic acids in the presence of  $\text{ZnCl}_2$ – $\text{POCl}_3$  opens the new, simple and efficient way to a synthesis of hardly accessed pyridine bases.<sup>91–95</sup>

#### 4. Pyridine synthesis by liquid-phase condensation of aldehydes with $\text{NH}_3$ under the effect of metal complex catalysts

According to the reports<sup>95–97</sup> a gas-phase condensation of benzaldehyde with acetic or butyric aldehydes and  $\text{NH}_3$  in the presence of heterogeneous catalysts on the basis of  $\text{Al}_2\text{O}_3$  modified by transition metal complexes at 300–500 °C led to the formation of a mixture of 2- and 4-phenylpyridines in total yield of no more than 30%. The other substituted aromatic or aliphatic aldehydes including those containing functional substituents were not managed to be involved to the above reaction. On the other hand, alkylpyridines may be generated by a condensation of aliphatic aldehydes with  $\text{NH}_3$  in gas or liquid phase on heterogeneous catalysts. For example, 2-methyl-5-ethylpyridine is produced from paraldehyde and  $\text{NH}_3$ , and  $\text{MeCO}_2^-\text{NH}_4^+$ ,  $\text{CoCl}_2$ ,  $\text{NH}_4\text{F}$  or a mixture of  $\text{NH}_4\text{F}$  and  $\text{KF}$  are used as a catalyst.<sup>98,99</sup> The method may be realized under strict conditions (250–500 °C, 80–100 atm.) with low selectivity and in 60% yield. The reaction became complicated in the transition from formaldehyde and acetaldehyde to the highest aliphatic aldehydes.<sup>98</sup>

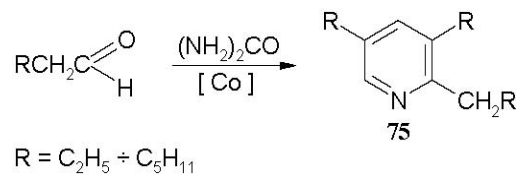
The synthesis of arylalkyl-substituted pyridines from alkyl(aryl)aldehydes under mild conditions was carried out in the presence of homogeneous Co-containing catalysts. Thus, a liquid-phase condensation of benzaldehyde with alkylaldehydes and urea in the presence of two-component catalyst  $\text{Co}(\text{2-ethylhexanoate})_2\text{-AlR}_3$  at 200 °C for 4 h leads to a mixture of 2,3,5-trisubstituted pyridines in total 80–95% yield.<sup>100</sup> The authors accentuate the target products **74** and **75** may be produced in a joint condensation of benzaldehyde with alkylaldehydes. A formation of arylpyridines in condensation of benzaldehyde with urea under the set conditions is not observed.



The catalytic system developed by authors<sup>100</sup> allowed to fulfil the known gas-phase reaction of paraldehyde with benzaldehyde and ammonia under milder conditions in higher yields.<sup>101–103,104</sup>

In the reactions described above a role of urea concluded in a generation of  $\text{NH}_3$  under elevated temperature.  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_2\text{OH}\cdot\text{HCl}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{CH}_3\text{NH}_2$ ,  $\text{NH}_4\text{OH}$  may be used as sources of  $\text{NH}_3$ .<sup>105,106</sup> Maximum yield of **75** was found to be achieved with the use of  $(\text{NH}_4)_2\text{SO}_4$

or  $(\text{NH}_2)_2\text{CO}$  and a catalyst  $\text{Co}(\text{2-ethylhexanoate})_2\text{-AlEt}_3$  in MeCN,  $\text{C}_2\text{H}_5\text{N}$ ,  $\text{C}_6\text{H}_6$  for 2 hours at 180–200 °C on the example of the reaction of paraldehyde with amines mentioned. Yield of **75** consists of 88-90%, and a selectivity of a target product 98%.



Under similar conditions a mixed condensation of benzaldehyde with butyric aldehyde and urea allows to give phenyl-3,5-diethylpyridine in 85% yield and with high selectivity.

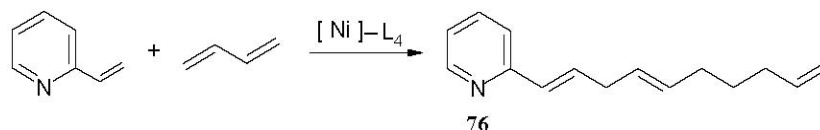
The analogous approach was used in a generation of pyridines from acetaldehydes and  $(\text{NH}_2)_2\text{HPO}_4$  (donor  $\text{NH}_3$ ) under the effect of catalytic amount of copper salts.<sup>107</sup>

The application of metal complex catalysts in the reactions described allowed to give alkyl(aryl)substituted pyridines under comparatively mild conditions in high yield and selectivity.

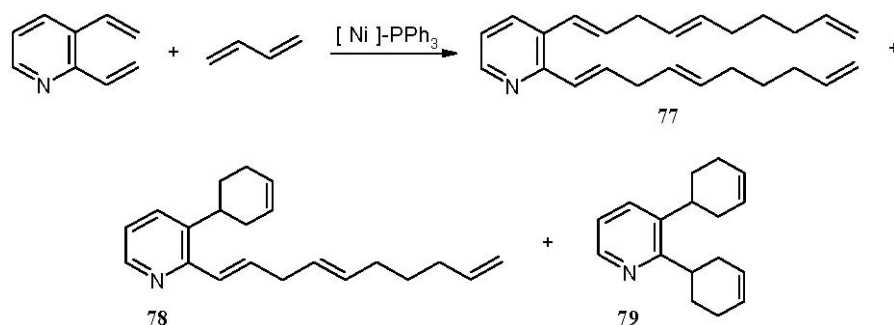
## 5. Synthesis of cycloalkenyl- and alkatrienylpyridines by codimerization of vinylpyridines with 1,3-dienes catalyzed by Zr and Ni complexes

At the beginning of 50-s the first papers on a synthesis of cycloalkenylpyridines by thermal cyclocodimerization of vinylpyridines with 1,3-dienes were published.<sup>108–111</sup> As a rule, the reactions mentioned proceed under strict conditions (170 °C) and in low yields (25–30%). At the end of 80-s the highly effective methods for a synthesis of practically importance cycloalkenyl- and alkatrienylpyridines in high selectivity and yields were developed with the use of metal complex catalysts.

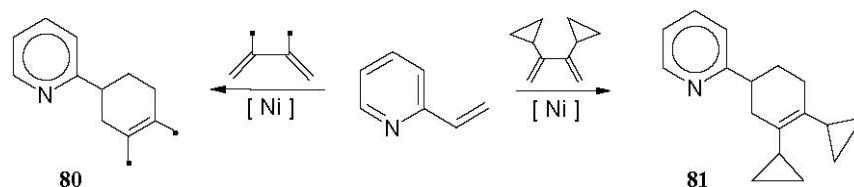
Thus, for example, the interaction of 2-vinylpyridine with butadiene in molar ratio of 2,5:6 respectively, in the presence of three-component catalytic system  $\text{Ni}(\text{acac})_2\text{-PPh}_3\text{-AlEt}_3$  in benzene at no less than 110 °C for 6 hours gives 2-(deca-1E,4E,9-trienyl)pyridine **76** in no less than 55% yield.<sup>112,113</sup>



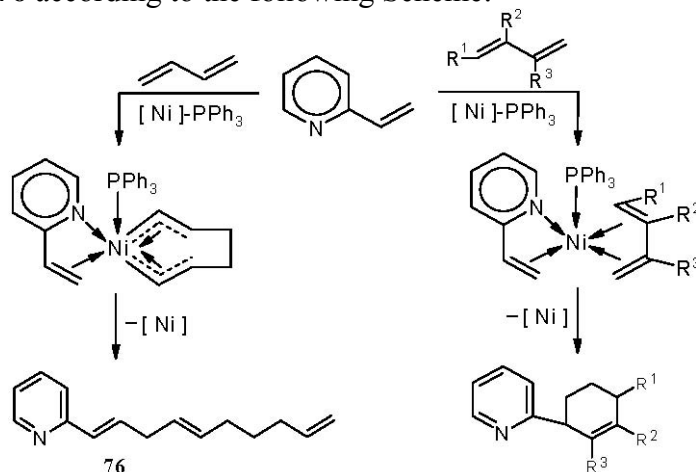
Under the optimum conditions 2-methyl-5-vinylpyridine, 4-vinylpyridine, and divinylpyridine react with butadiene to give decatrienylpyridines. In a case of divinylpyridines, for example, 2,3-divinylpyridine in the reaction with 1,3-butadiene, the authors<sup>114</sup> observed together with linear cooligomers **77** a formation of mixed **78** and cycloooligomers **79** in a ratio of (~20):35:45 in total yield of 65%.



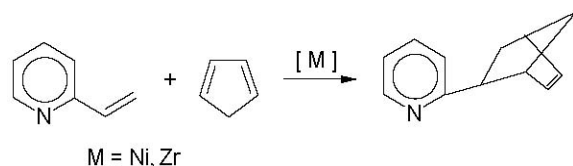
In contrast to butadiene, the other 1,3-dienes, for example, isoprene, 2-cyclopropyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene, piperilene, 2,3-dicyclopropylbutadiene react with vinylpyridines under the effect of phosphine complexes of nickel to give cycloalkenylpyridines **80** and **81**.<sup>115</sup>



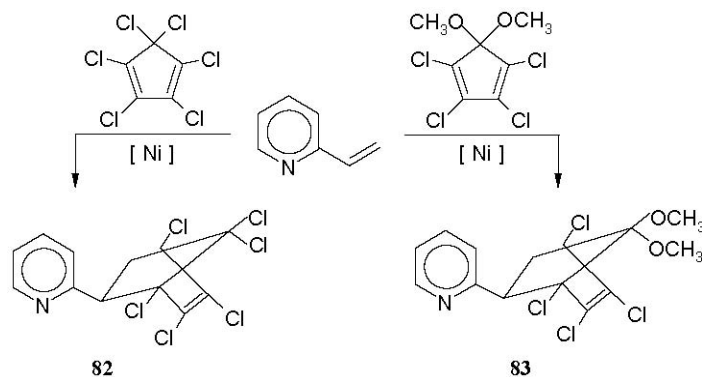
The authors<sup>115</sup> propose the most probable mechanism for the interaction of 1,3-dienes with 2-vinylpyridine in the presence of low-valence nickel complexes. In experiments with rather volume molecules of 1-, 2- or 2,3-disubstituted dienes (piperilene, isoprene, 2-cyclopropylbutadiene, 2,3-dimethylbutadiene, 2,3-dicyclopropylbutadiene) catalytic active Ni complexes are generated. The latters include by one molecule of 2-vinylpyridine and 1,3-diene to the coordination sphere of a central atom, that leads to [1:1]-cycloadducts. Complexes including two molecules of 1,3-diene and one molecule of 2-vinylpyridine are generated in a case of spatially less volume butadiene. A subsequent reduced elimination of a catalyst central atom from a catalytic matrix leads to a formation of the new C–C bonds and to a generation of linear<sup>116</sup> cooligomer **76** according to the following Scheme:



A cyclocodimerization of 2-vinylpyridine with cyclopentadiene was shown to be able to give selectively norbornenylpyridines in the presence of metal complex catalysts.<sup>117</sup> From a number of catalysts tested on the basis of compounds Ni, Pd, Fe, Co, Cu, Rh, and Zr modified by phosphine ligands, reduced by organoaluminium and -magnesium reagents the three-component system of Ni(acac)<sub>2</sub>-PPh<sub>3</sub>-AlEt<sub>3</sub> (1:3:4) or a catalyst Cp<sub>2</sub>ZrCl<sub>2</sub> were found to have the highest activity on a reaction in benzene or toluene at 100–110 °C for 4–6 hours.<sup>118</sup>



Substituted cyclopentadienes, such as, hexachlorocyclopentadiene and 1,1-dimethoxy-2,3,4,5-tetrachlorocyclopenta-2,4-diene<sup>119,120</sup> were involved to the reaction of cyclocodimerization with 2-vinylpyridine (2-methyl-5-vinylpyridine, 4-vinylpyridine) in the presence of highly active and selective catalysts on the basis of Ni and Zr complexes to give halogen-containing norbornenylpyridines **82** and **83** prospective for the subsequent functionalization and application in a synthesis of physiologically active preparations.<sup>121</sup>

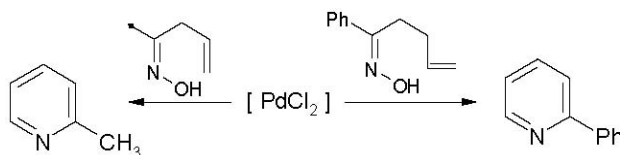


The examples described evidence that homogeneous metal complex catalysts significantly expand the frames of an application of the reaction of codimerization of vinylpyridines with 1,3-dienes and allow to give the new unknown previously unsaturated derivatives of pyridine bases in high yields and selectivity.

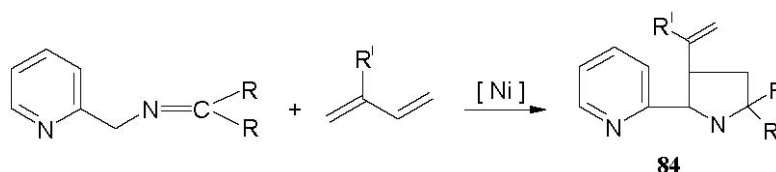
## 6. The other methods for a synthesis of pyridines in the presence of metal complex catalysts

The methods for a generation of alkyl(aryl)substituted pyridines by cyclization of oximes of  $\beta,\gamma$ - and  $\gamma,\delta$ -unsaturated ketones in the presence of catalytic amount of palladium halogenides are

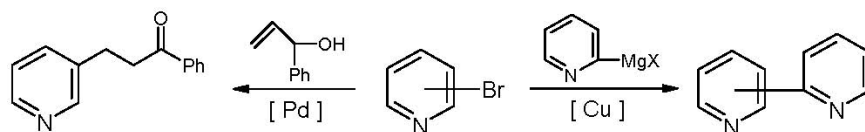
little known and, hence, narrowly used in organic synthesis.<sup>122</sup>



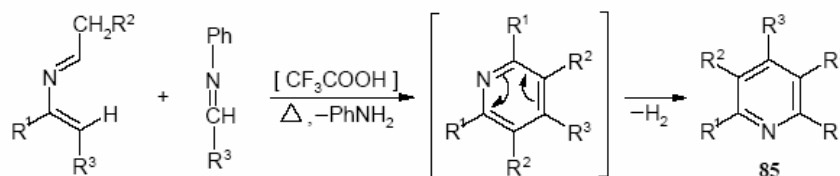
The interaction of 1,3-dienes with imines of pyridine series in the presence of nickel–phosphine catalyst the a reaction of [3+2]–cycloaddition proceeds to give practically important norm nicotine derivatives **84**.<sup>123</sup> The authors pay attention to the generation of complexes with 2-aza- $\pi$ -allyl ligands under reaction conditions.



There are information on a possibility to obtain pyridine bases by the interaction of halogenated pyridines with allyl alcohols in the presence of 1 mole%  $Pd(OAc)_2$ <sup>124</sup> or with pyridylmagnesium halogenides under the effect of catalytic amount of copper salts.<sup>126</sup> Yield of substituted pyridines consists of no more than 60% in both cases.



The paper<sup>126</sup> discusses a regiospecific synthesis of substituted pyridines from 2-azadienes and azomethines. The reactions were carried out in THF in the presence of catalytic amount of trifluoroacetic acid. The Diels–Alder products (pyrimidines or pyrazines) were predicted, however, substituted pyridines **85** were produced in 75-90% yields.



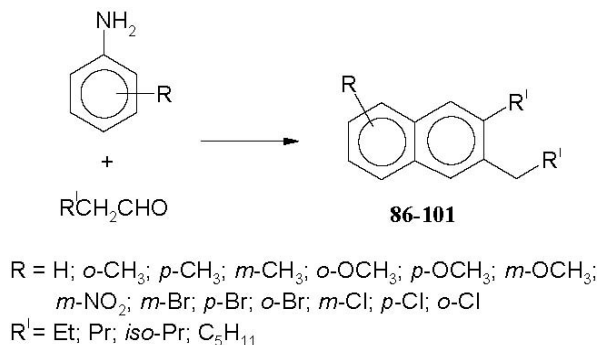
The examples listed in the review evidence the higher importance of metal complex catalysis in a synthesis of pyridine bases. At the same time, substituted pyridines are known to be the important semiproducts in thin organic synthesis and in the most cases to have biological activity, the latters are used as valuable initial compounds in a synthesis of drug preparations.

For example, to the beginning of 90's from 1500 of the more effective and active drug preparations 73 were pyridine derivatives. Substituted pyridines are included to the vitamin composition (B<sub>3</sub>, PP, B<sub>6</sub>), tranquilizers, antidepressants, analeptic, sedative, analgesic, anti-inflammatory, spasmolytic, vaso-dilating remedies and a series of other practically important preparations.<sup>126</sup> Cyclocodimer of 4-vinylpyridine with butadiene is used as intermediate compound for a production of a series of cardiopreparations.<sup>127,128</sup> Vinylpyridine cyclocodimers with 1,3-dienes are a part of compositions of odourants for cosmetic powders, liquid and solid detergents, perfumes, eau-de-Cologne,<sup>129</sup> they are used to increase odour and smell of foods.<sup>130</sup> There are information on the application of alkylpyridines for the extraction of noble metals,<sup>131</sup> plant pest control,<sup>132</sup> and as inhibitors of acidic steel corrosion.<sup>133</sup>

## 7. Rare-earth element complexes in a synthesis of quinolines, phenanthridines and phenanthrolines

To develop studies on a synthesis of pyridine bases initiating from aldehydes and simple amines the change of Co complexes for catalysts containing rare-earth element compounds (PrCl<sub>3</sub>-PPh<sub>3</sub>-DMF) was shown by the authors of the review to carry out a liquid-phase condensation of aromatic amines with aldehydes to give the corresponding substituted quinolines, naphthyridines or phenanthrolines.

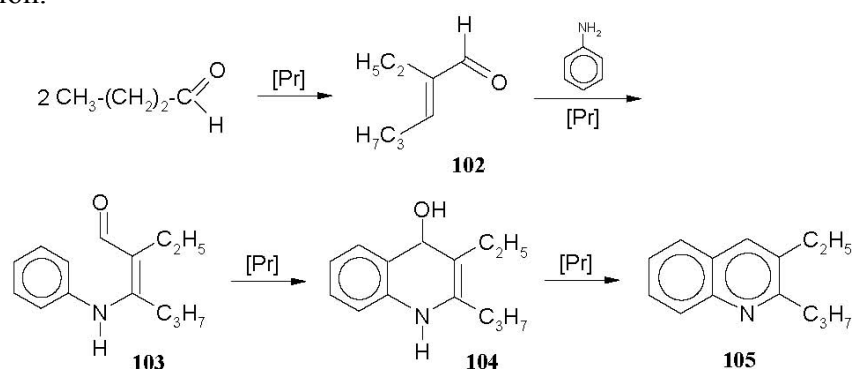
The condensation of substituted anilines with aliphatic aldehydes proceeds to give 2,3-dialkylquinolines **86-101** in high yields (37-91%) under optimum conditions (aniline:aldehyde = 1:2, 100 °C, 6 h). The generation of N-alkylanilines was observed together with that of target quinolines. The increase in alkyl radical sizes in initial aliphatic aldehydes does not effect on the yield of **86-101**.<sup>134</sup>



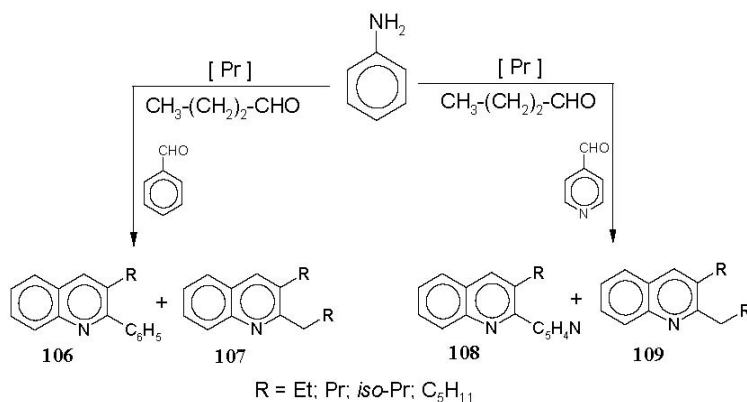
The nature and positions of substituents in a molecule of initial anilines were found to effect sufficiently on a reaction direction and quinoline yields **86-101**.

Thus, *o*- and *p*-substituted anilines form 6- and 8-substituted quinolines, respectively. *m*-Substituted anilines give hardly-separated mixture of 5- and 7-substituted quinolines in low yields. The generation of 7-substituted quinolines in high yields was observed in application of (Pr<sup>+3</sup>-PPh<sub>3</sub>-DMF) as a catalyst in the reaction.<sup>135</sup>

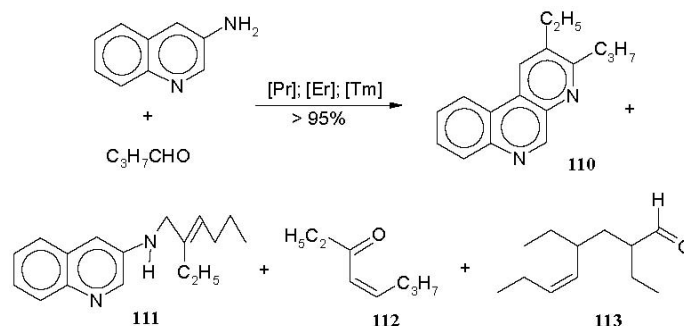
The study on a mechanism of quinoline molecules formation on the example of the reaction of aniline and butyric aldehyde allowed to suppose that during the reaction the Knoevenagel condensation of initial aldehyde to  $\alpha,\beta$ -unsaturated aldehyde **102** proceeded initially, and then the latter reacted (according to Michael) with aniline to give aminoaldehyde **108**. The latter is transformed to 4-oxytetrahydroquinoline **104** in the presence of praseodymium complexes. The dehydration and dehydrogenation lead to a generation of 2,3-disubstituted quinoline under reaction condition.



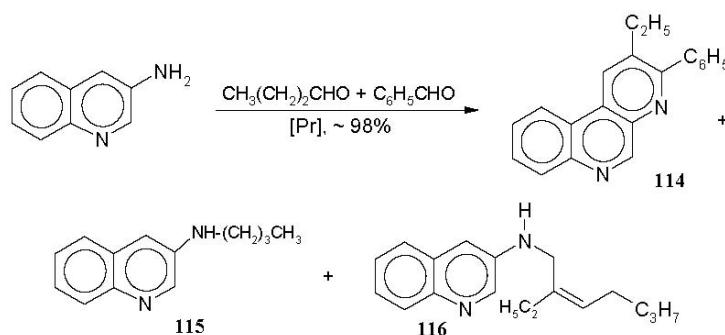
To extend a field of the reaction application and to produce aryl- and heteroaryl-substituted quinolines the authors<sup>135</sup> studied a mixed liquid-phase condensation of aniline with butyric aldehyde, benzaldehyde or 4-pyridinealdehydes to give quinoline **106–109** under the effect of a catalyst  $\text{PrCl}_3\text{-PPh}_3\text{-DMF}$ .<sup>135,136</sup>



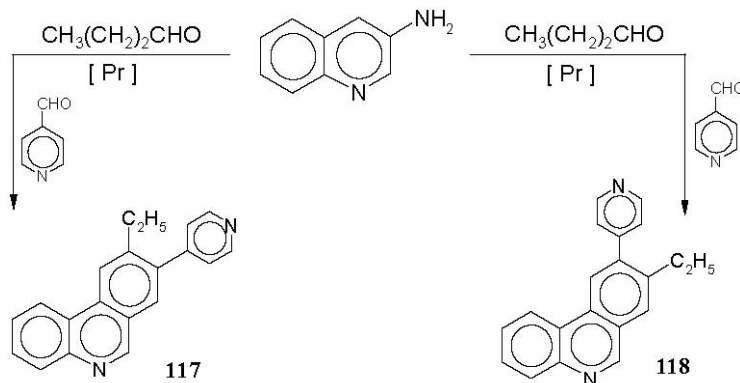
Under optimum conditions 3-aminoquinoline reacts with butyric aldehyde to give 2-propyl-3-ethyl-5,6-benzo-1,7-naphthyridine **110**, N-(2-ethylhexenyl-2)-3-aminoquinoline **111** and condensation products **112** and **113**, initial aldehyde (content of no more than 8%) in total >95% yield.<sup>137</sup>



A mixed liquid-phase condensation of 3-aminoquinoline with butyric aldehyde and benzaldehyde (1:1:1 ratio, 150 °C, 6 h,  $PrCl_3$ - $PPh_3$ -DMF, toluene) was carried out to give 2-phenyl-3-ethyl- and 3-ethyl-4-phenyl-5,6-benzo-1,7-naphthyridine **114** and the corresponding N-arylsubstituted 3-aminoquinolines **115** and **116** in total 98% yield.<sup>138</sup>

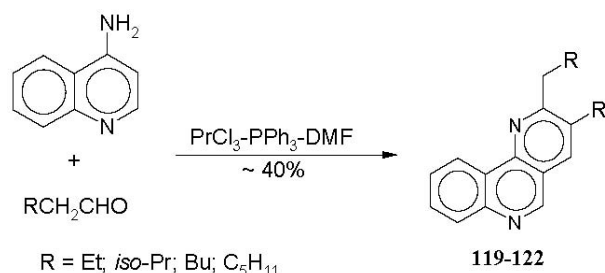


The change of benzaldehyde for 4-pyridinealdehyde allows to synthesize a mixture of 2-ethyl-3-(4-pyridyl)benzo-1,7-naphthyridines **117** and **118** in 26 and 24% yields respectively.<sup>139</sup>

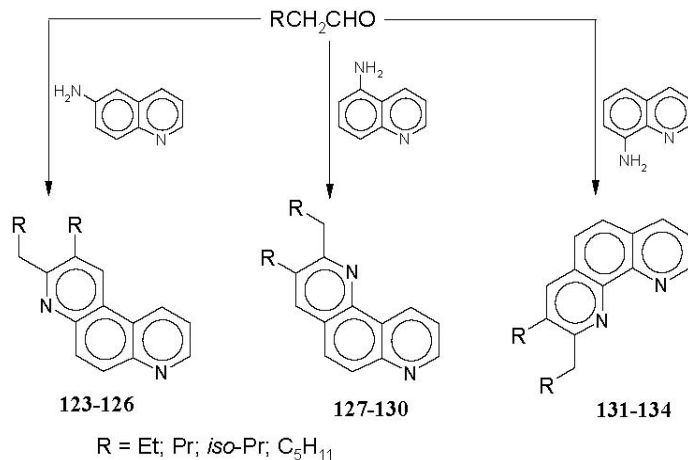


The interaction of 4-aminoquinoline with  $C_4$ - $C_7$  by aliphatic aldehydes gives substituted naphthyridines **119**-**122** under above conditions in 40% yield, and in conversion of initial quinoline 55%. The common amount of side products (alkylquinolines, dimers and trimers of butyric aldehyde) is no more than 10%.<sup>139</sup>

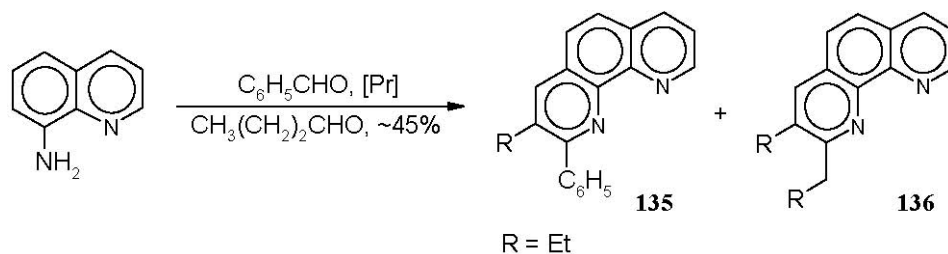




The condensation of 5-, 6- and 8-aminoquinolines with C<sub>4</sub>-C<sub>7</sub> by aliphatic aldehydes, catalyzed by Pr, Tb and Sm complexes (150 °C, 6 h) leads to 1,7-, 4,7- and 1,10-substituted phenanthrolines, a position of amino group in a molecule of initial quinoline effects unsufficiently on the direction and yield of reaction products. In all experiments the yield of the corresponding 2,3-substituted phenanthrolines consists of 40-60%, and in a conversion of initial monomers 95%.<sup>140</sup>

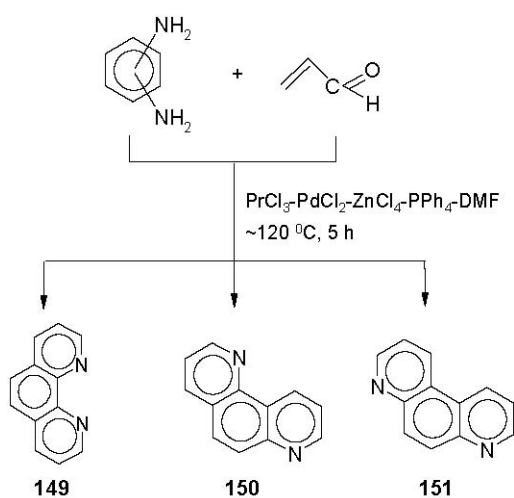
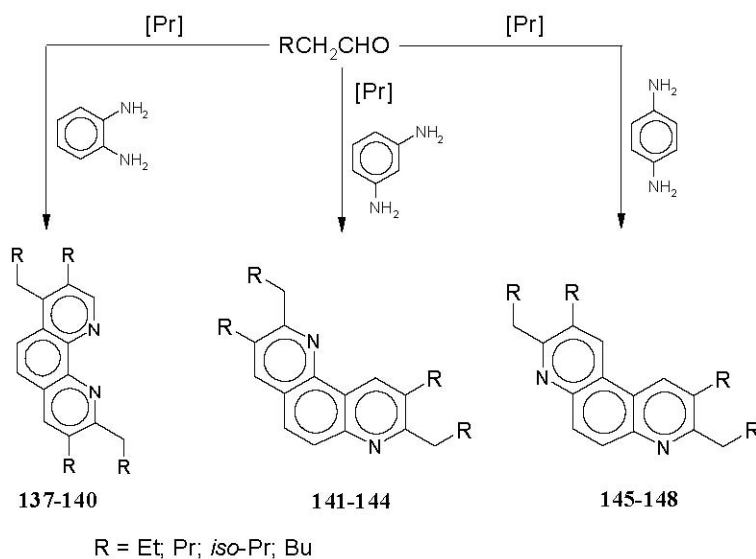


In a condensation of 5- and 8-aminoquinolines a position of amino group predetermines the only possible direction of cyclization to give the corresponding 1,7- and 1,10-phenanthrolines **123-130**. In a case of 6-aminoquinolines, the only 4,7-phenanthrolines **131-134** were produced. A possibility to obtain a mixture of 2-phenyl-3-ethyl- **135** and 2-propyl-3-ethyl-1,10-phenanthrolines **136** in 1:1 ratio in total yield of 45% was shown on the example of a mixed condensation of 8-aminoquinoline with butyric aldehyde and benzaldehyde with the use of PrCl<sub>3</sub>-PPh<sub>3</sub>-DMF catalyst.



According to analogous Scheme below substituted 1,7-, 1,10- and 4,7-phenanthrolines were synthesized by liquid-phase condensation of *o*-, *m*- and *p*-phenylenediamines with butyric aldehyde, that opens a simple and prospective method to synthesize hardly available previously substituted phenanthrolines, initiating from available aromatic diamines.<sup>140,141</sup>

The reaction was studied on the example of a large number of C<sub>4</sub>–C<sub>6</sub> aliphatic aldehydes, and high yields (~60%) of the corresponding phenanthrolines **137–148** were shown to be produced under the reaction conditions (180 °C, 8 h, catalyst PrCl<sub>3</sub>–PPh<sub>3</sub>–DMF, 5 mole%). In contrast to the classic method of a synthesis of unsubstituted phenanthrolines according to the Skraup method based on a condensation of glycerine and acrolein with phenylenediamine in the presence of concentrated H<sub>2</sub>SO<sub>4</sub> or HNO<sub>3</sub>, the authors<sup>142</sup> have found, when the reaction proceeded in the presence of mixed catalyst PrCl<sub>3</sub>–PdCl<sub>2</sub>–ZnCl<sub>2</sub>–PPh<sub>3</sub>–DMF in a ratio of 1:1:2:1:1 at 100–120 °C, the yields of 1,7-, 1,10- and 4,7-phenanthrolines **149–151** rised from 50% to 90%.



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