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CATALYTIC SYNTHESIS AND REACTIONS OF NITROGEN HETEROCYCLES (REVIEW)

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Studies at the Latvian Institute of Organic Synthesis and literature data from 1984-1994 on organic catalysis in the chemistry of N-heterocycles are reviewed. The prospects for further developments in catalytic reactions of N-heterocycles are examined.

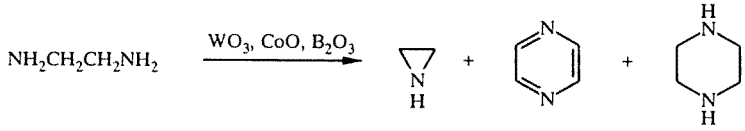
N-Heterocycles are used to synthesize numerous medicinal compounds, agricultural chemicals, polymers, and analytical reagents [1-15].

The principal natural source of N-heterocycles is coal-tar, the production volume of which cannot satisfy the increasing demand for these compounds. Therefore, synthesis methods of N-heterocycles are being developed. In the Latvian Institute of Organic Synthesis, catalytic methods are being devised for synthesizing aziridine, pyrrolidine, pyrroline (dihydropyrrole), pyridine, piperazine, and their derivatives. Vapor- and liquid-phase oxidations of N-heterocycles, hydrogenation, hydrosilylation, alkylation, condensation, and other processes in the presence of various catalysts are being investigated.

1. SYNTHESIS OF N-HETEROCYCLES

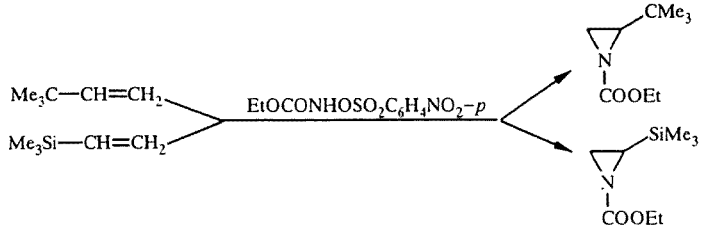
Intramolecular dehydrogeno-, dehydro-, and deaminocyclization in addition to intermolecular condensation of amino-, imino-, and oxygen-containing compounds (aldehydes, ketones, alcohols) are commonly used to form N-heterocycles.

Vapor-phase deaminocyclization of 1,2-ethanediamine in the presence of WO_3 is a promising method for producing aziridine [16, 17]. Aziridine is formed in maximum yield (34%) on a W catalyst treated with B and Co oxides. Competition from intermolecular deaminocyclization forms pyrazine and piperazine. However, their yields are less than 7-11%.



The reaction of 3-amino-1-propanol at 400-440°C produces a small amount of 2-methylaziridine.

Aziridine derivatives are produced in high yields from the reactions of carbenes and azomethines by using phase-transfer catalysis (PTC) [18]. The reaction of 3,3-dimethyl-1-butene and its Si analog with ethyl{[(4-nitrophenyl)-sulfonyl]oxy}carbamate gives 1,2-disubstituted aziridines [19-22]:



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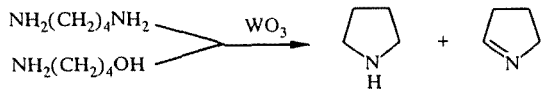
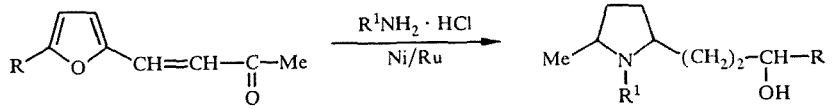
The reaction was performed in the biphasic system $CHCl_2$–alkali-metal carbonates in the presence of catalysts such as triethylbenzylammonium chloride, tetrabutylammonium bisulfate, and tetraoctylammonium bromide.

Pyrrolidine is produced in yields reaching 80% [16, 23] on WO_3 catalysts at 280-500°C from 4-amino-1-butanol.



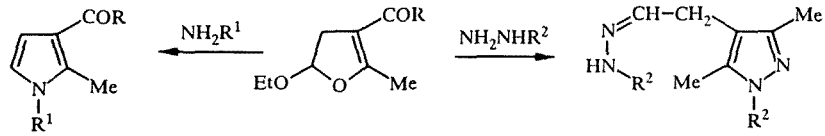
The yield of pyrrolidine is less (45%) from 1,4-butanediamine owing to extensive dehydrogenation and formation of a large amount of 1-pyrroline. This product is favored by increasing the amount of WO_3 on the support and the contact time and by diluting the starting material with inert gas. Under optimal conditions (45% WO_3 on kaolin, 480°C, molar dilution 48:1), the yield of 1-pyrroline reaches 85% of theoretical. For the reaction of 4-amino-1-butanol, the yields of 1-pyrroline are low even in the presence of strong dehydrogenation catalysts (Cu and Group 8 metal oxides). The formation of 1-pyrroline is probably influenced by NH_3, which is present in the reaction mixture after deamination of 1,4-butanediamine.

Pyrrole and pyrrolidine derivatives are catalytically synthesized through intermolecular reaction of NH_3 or amines with the corresponding furan and tetrahydrofuran derivatives [24]. Thus, the reaction of furfurylideneacetone [4-(2-furanyl)-3-buten-2-one] with amine salts in the presence of a Ni catalyst treated with Ru in acidic aqueous alcohol gives hydroxyderivatives of pyrrolidine [25]:



R, R^1 = H, Me

The reaction with amines of 2-methyl-3-acetyl(carbethoxy)-5-ethoxy-4,5-dihydrofuran produces 1-alkyl-2-methyl-3-acetyl(carbethoxy)pyrrole [26].



R = Me, OEt; R^1 = Alk, R^2 = H, Ar

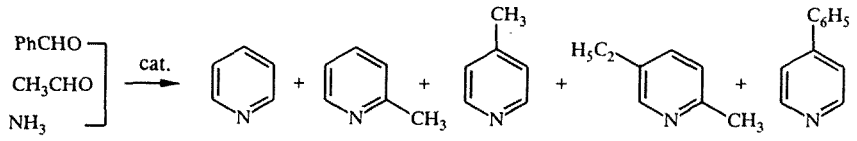
Replacing the amines by hydrazines forms substituted dimethylpyrazoles.

Substituted pyrrolidines and pyrrolenines are obtained in high yields through the reaction of substituted Schiff bases and alkenes or alkynes [18].

The vapor-phase reaction (300-350°C) of succinimide in the presence of Fe, alkali, and alkaline-earth phosphates leads to oxidative dehydrogenation to form maleimide [27].

Definite progress has been made in the development of synthesis methods for pyridines. In several instances the industrial production of synthetic methylpyridines was the principal method for preparing these compounds [28]. An economic analysis indicates that the cost of producing synthetic pyridines for the pharmaceutical industry at a level of 4000 tons per year is 30% lower than if coal-tar is used [29]. Therefore, known methods notable for their insufficient selectivity are being improved and new ones continue to be developed [26].

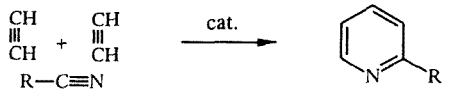
The most widely used vapor-phase method is the condensation of carbonyl-containing aliphatic compounds (formaldehyde, acetaldehyde, acrolein, acetone) and NH_3 on aluminosilicate catalysts. The activities of an aluminosilicate catalyst and γ-Al_2O_3 were compared in the condensation of acetaldehyde and benzaldehyde with NH_3 at 260-420°C [30, 31]:



Primarily 2-methylpyridine and 4-phenylpyridine are formed in the presence of the aluminosilicate catalyst. For synthesizing 4-methylpyridine, γ-Al_2O_3 is preferred. However, this catalyst is more rapidly poisoned. It was found that formaldehyde suppresses the formation of 4-methylpyridine in the presence of the aluminosilicate catalyst [32].

A kinetic model for the accumulation rate of the pyridines that takes into account inhibition by the reaction products was derived [31].

The synthesis of pyridine derivatives through intermolecular condensation of pentenenitrile on W, Mo, Zr oxides and on Co, Ni, and Bi molybdates at 525-575°C in 36-40% yield has been reported [33]. The preparation of methylpyridines through intermolecular condensation of acetylene with nitriles in a homogeneous medium in the presence of complex Co catalysts at 120-220°C was studied in a series of works [34-36]:



R = Alk, AlkO, Ar

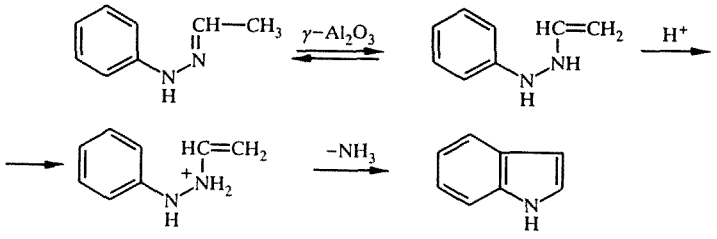
This condensation can be catalyzed by the dinuclear complex Co cyclopentadienide [37]. The reaction involving Co complexes can be photochemically initiated (350-500 nm) at room temperature. The principal product is 2-methylpyridine [38]. Using heterogeneous Co compounds helps significantly to increase the yield and selectivity [39, 40]. A sulfonated styrene–alkylvinyl copolymer is used as a support.

Condensation of acetylene and acetone with NH_3 or acetylene and methanol with NH_3 in the presence of rocks and Zn, Cr, and Al oxides produces 2,4,6-trimethylpyridine [41]. Phosphates and representative fluorides have also been proposed for condensation of alkynes and NH_3 into pyridines [41-44]. The synthesis of chloropyridines through condensation of chloral with acrylonitrile in the presence of metals or their salts, for example, Cu or CuCl, has been reported [45].

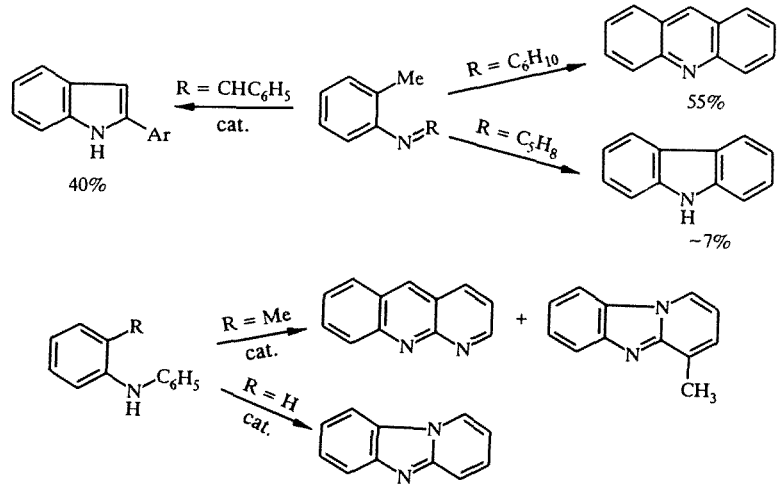
The reaction with NH_3 of tetrahydrofurfuryl alcohol in the presence of an Fe catalyst gives piperidine [46]. Pentanediol and 1-amino-5-pentanol are proposed as intermediates.

Condensed N-heterocycles are prepared mainly by intramolecular cyclization of compounds containing amino or imino groups and by reductive amination of carbonyl derivatives of cycloalkanes and aromatic compounds. The reactions of the first group are often catalyzed by polyphosphoric acid or $ZnCl_2$ [47]. Good results are obtained in hydroamination reactions with Ru or modified Ru–Ni catalysts [48].

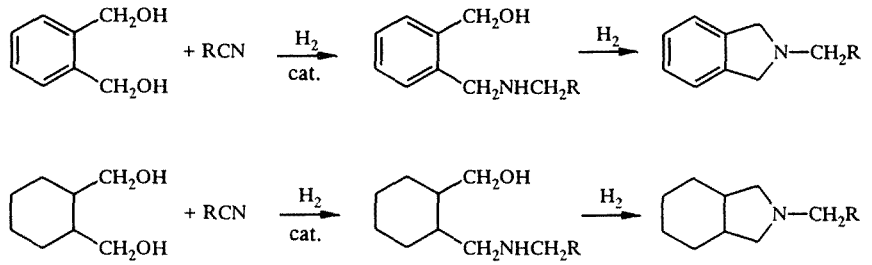
The catalytic activity of Al_2O_3 and various multicomponent systems based on it was studied in the preparation of indole and its derivatives through cyclization of acetaldehyde phenylhydrazone [49]. The catalytic activity of these catalysts is associated with the presence on the surface of Lewis-acid centers. The first step seems to consist of isomerization of the phenylhydrazone on aprotic acid centers and formation of an ene-hydrazine derivative. Then, NH_3 is eliminated and the ring closes:



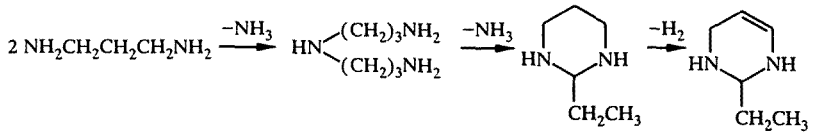
Bi- and tricyclic N-heterocycles are successfully prepared through vapor-phase cyclization of azomethine derivatives of benzene, cyclopentane, or cyclohexane and of pyridines in the presence of a dehydrogenation catalyst [50, 51]:



The reaction of o-bis(hydroxymethyl) derivatives of benzene and cyclohexane with aliphatic nitriles gives N-alkyldi- and N-alkyloctahydroisoindoles [52].

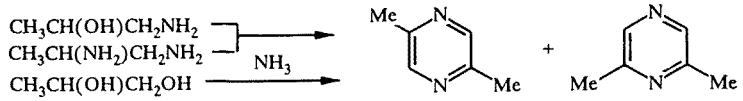


Intermolecular cyclization of bifunctional compounds such as aminoalkylcarbinols and alkanediamines or the reaction of alkanediols with NH_3 or amines is used for catalytic synthesis of heterocycles with two N atoms [53]. In the presence of WO_3 catalysts at 500°C, 1,3-propanediamine cyclizes to hexahydropyrimidines in 26% yield [54]. Bis(3-aminopropyl)amine was found as an intermediate:



Under the studied conditions, less than 10-15% tetrahydropyrimidines is formed.

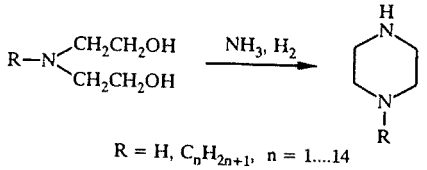
The principal products of intermolecular dehydrogenation of 1-amino-2-propanol and 1,2-propanediamine on Cu chromite catalyst, like condensation of 1,2-propanediol with NH_3 followed by cyclization, are 2,5- and 2,6-dimethylpyrazines [55]:



The 2,5-isomer usually predominates at 230-320°C in a H_2 medium. The yield after dehydrogenation of 1-amino-2-propanol reaches 85%. The ratio of the 2,5- and 2,6-dimethylpyrazines varies from 0.6:1 to 20:1. The reaction of 1,2-propanediamine is less selective. In addition to the dimethylpyrazines, pyrazine, methylpyrazine, and piperazine are formed in comparable amounts.

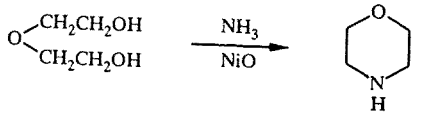
Alkanediols react with NH_3 in the presence of a fused Fe catalyst to form pyrrolidine, N-butylpyrrolidine, 1,4-dipyrrolidylbutane, morpholine, N-ethylmorpholine, piperazine, and N-alkylpiperazines [46].

The catalytic synthesis of piperazine through cyclization of aminoethanol and its derivatives has been reviewed [53, 56]. In addition to the methods examined in these reviews, piperazine and its N-alkyl derivatives can be obtained by dehydrocyclization of bis(2-hydroxyethyl)amine and N-alkylbis(2-hydroxyethyl)amines in aqueous ammonia on a reduced fused treated Fe catalyst [57].



R = H, C_nH_{2n+1}, n = 1....14

Morpholine is obtained from the reaction of diethyleneglycol and NH_3 in the presence of Ni oxide catalysts [58-60].



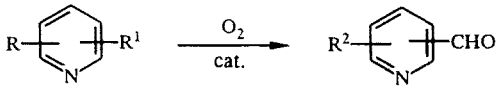
Spillover of the intermediate surface species is observed.

The presented examples of the catalytic synthesis of N-heterocycles do not exclude other possibilities for using catalysis in this area of heterocyclic chemistry. They indicate paths for developing accessible methods to prepare key compounds.

2. OXIDATIVE REACTIONS

The catalytic oxidation of N-heterocycles has been investigated in order to develop industrial methods for producing O-containing derivatives and for destroying molecules, considered the most rational way to eliminate residues in industrial waste streams and off-gases. The pathway of the catalytic reaction and the composition of the products are determined by the catalyst nature and the structural features of the heterocyclic compound. Questions of this type have been discussed in previously published monographs and reviews [53, 61-67].

Vapor-phase heterogeneous catalytic oxidation of methylpyridines by O_2 in air is a convenient method for synthesizing the corresponding pyridinealdehydes.

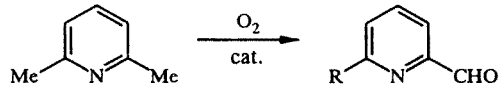


R = H, Me, Et; R^1 = Me; R^2 = H, Me, Et, CHO

The studied catalysts were V−Mo oxides and V phosphates [61-66]. A comparison of the reaction rates of the isomeric mono- and disubstituted pyridines enabled the effect of the structure of the oxidizable molecule on its reactivity to be found [68, 69]. A linear dependence was found between the logarithms of the overall reaction rates of the mono-, di-, and trimethylpyridines and the charge on the heteroatom. The logarithms of the formation rates of the pyridinealdehydes from these compounds correlate with the Hammett constants. Substituents in the 5-position of 2-methylpyridine, regardless of their donor−acceptor properties, decrease the rate of both the overall reaction and 2-pyridinealdehyde formation. The observed phenomenon is explained by the strong donor−acceptor interaction of the oxidizable molecule and the catalyst. The ratio of differently charged V atoms in the V−Mo oxide catalyst in the steady state after the oxidation of a given methylheterocycle changes as a function of the position of the methyl group relative to the heteroatom [69, 70]. Thus, the ratio of V^{5+}, V^{4+}, and V^{3+} is 5:4:1 after oxidation of 2-methylpyridine on a catalyst prepared in NH_3 medium that has a 1:9 ratio of V:Mo. The catalyst on which the 3- and 4-isomers were oxidized contains only V^{5+} and V^{4+} in 7:3 and 2:3 ratios, respectively. This suggests that the reactivity of the heterocycle toward reduction of V oxides, which occurs even in the presence of O_2, varies as the position of the methyl group on the ring varies. The differently charged V ions catalyze different oxidation pathways. If $[V^{5+}]$ in the catalyst increases (by preparing the catalyst in HCl medium), the yield of highly oxidized products increases by almost two times [72-74]. On the other hand, V^{4+} probably favors partial oxidation. The ability of V^{4+} as $(V=O)^{2+}$ to catalyze partial oxidation was demonstrated using vapor-phase oxidation of 2,6-dimethylpyridine. The selectivity for pyridinealdehydes in the presence of vanadyl phthalocyanine was compared with the selectivity for oxidation on a V oxide catalyst [67]. Complexation of the methylpyridines with vanadyl salts caused absorption bands that can be assigned to carbonyl and carboxylate surface species to appear in the IR spectrum [67, 72].

In addition to redox processes, the oxidizable compound interacts with acid−base centers during oxidation of methylheterocyclic compounds. This in turn affects the yield of the reaction products. For example, the oxidation of 3-methylpyridine to 3-pyridinealdehyde is much more selective on V−Mo oxide catalyst treated with alkaline compounds than on untreated catalyst.

The amount of deposited catalytically active compound substantially affects the selectivity of supported catalysts. Thus, the selectivity of 2-methylpyridine oxidation to 2-pyridinealdehyde reaches 93% with a monolayer of V_2O_5 on TiO_2 [74]. A catalyst prepared by depositing 2% of V and Mo oxides (V:Mo = 3.7:1) on carborundum can be used to produce 6-methyl-2-pyridinealdehyde through oxidation of 2,6-dimethylpyridine in 47% yield. A pseudo-first order model was proposed to describe the reaction rate [75]. The best catalysts for preparing 2,6-pyridinealdehyde by oxidation of 2,6-dimethylpyridine are those containing an excess of Mo oxide (V:Mo = 1:1.5) modified with 0.09% silver oxide and supported on Al granules [77].



R = Me, CHO

In the presence of this catalyst, yields of 2,6-pyridinedialdehyde and 6-methyl-2-pyridinealdehyde reach 35%.

Water vapor, which converts surface electron-acceptor centers into proton-donating ones and changes the nature of the interaction of the pyridine with the catalyst, increases the selectivity of the oxidation of N-heterocycles [78].

Zeolite catalysts modified with Pd and Cu compounds (CuNaY and PdNaY) cause mainly extensive oxidation of methylpyridines [79]. These catalysts are interesting in that their structure controls the effect of steric factors on the reactivity of the methylpyridines. At 400°C, 2,6-dimethylpyridine is less reactive than 3-methylpyridine, the least oxidizable pyridine.

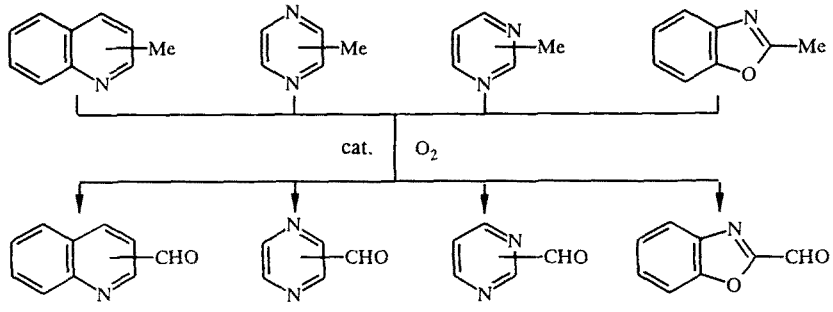
The formation of nitrogen oxides during extensive oxidation of pyridine can be reduced by using a Cu−Cr catalyst compared with a Pt solid, which is most frequently used to treat off-gases [80]. Catalysts of Cu−Mn are recommended for treating waste streams from the production of certain pharmaceuticals, for example, sulfamonomethoxine and madribon (sulfadimethoxine), which contain residual pyridine and methanol groups. Spinel phases are known to decrease their activity [81]. Oxide catalysts of Al−V−Fe are proposed for extensive oxidation of pyridines in off-gases from production of nicotinic acid by oxidative ammonolysis of 2-methyl-5-ethylpyridine. Up to 88% yields are achieved with practically no formation of nitrogen oxides [82].

The high activity and selectivity of a Cu-Al catalyst containing Ti for extensive oxidation of pyridine is due to the presence of isolated or weakly associated Cu^{2+} in a distorted tetrahedral configuration [83]. The catalyst is distinguished by a high adsorptive capacity and a selectivity of at least 99% even at 150°C.

Pyridine and its methyl derivatives are extensively oxidized in the gas phase at 0.0125 g/liter by a highly active V−Sn catalyst prepared by fusing V_2O_5 and Sn oxide (1:0.25) at 1600°C [84, 85]. The pyridines are nearly quantitatively converted to CO_2, N_2, and H_2O on this catalyst. Preparing this fused catalyst at high temperature causes finer crystallites of V oxides to form on the surface and the V ions to be more highly reduced. Methylpyridines are extensively oxidized at lower temperatures than pyridine on both V−Sn oxide and Pt catalysts [86].

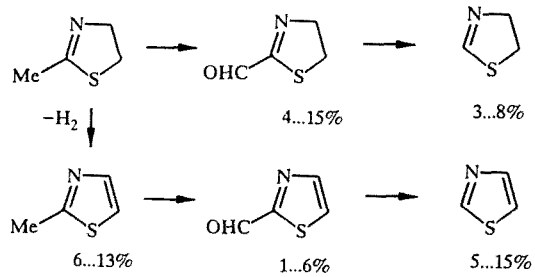
Waste streams from the production of pesticides that contain 3,6-dichloro-2-pyridinecarboxylic acid (lontrel), 3,5,6-trichloro-4-amino-2-pyridinecarboxylic acid (picloram), and 4-pyridineamine (avitrol) are treated by ozonation or photocatalysis in the presence of V, Fe, Co, Cu, Ni [87].

The main reaction products from vapor-phase oxidation of heterocycles such as methylquinoline, methylpyrazine, methylpyrimidine, and methylbenzoxazole on V−Mo and V−phosphate catalysts, like for pyridine derivatives, are the corresponding aromatic heterocyclic aldehydes and C oxides.

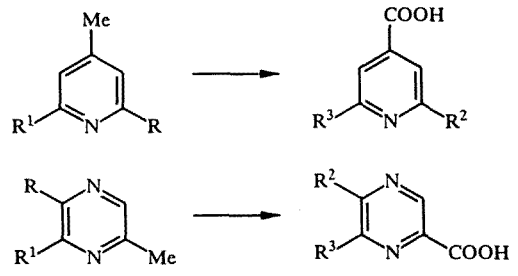


Aldehydes are highly selectively formed (80-100%) in the presence of β-$VO(PO_3)_2$ and $V_2O_5-MoO_3$ modified with Ag oxide [68, 88]. Oxidative demethylation occurs simultaneously for 2-methylpyridine and 2- and 4-methylpyrimidines [62, 89]. In the presence of $V_2O_5-Al_2O_3$ catalyst, 2-methylpyrimidine gives pyrimidine in 42% yield. On a V−Mo catalyst and on zeolite PdCuNaY, 2-methyl-5-arylpyrimidine is extensively oxidized and tar forms [90].

The vapor-phase oxidation of methylthiazoline (methyldihydrothiazole) on V oxide catalysts follows three directions: oxidation of the methyl group to form a formyl derivative and demethylation and dehydrogenation of the ring to form thiazole and its derivatives [91]:



Pyrazine- and pyridinecarboxylic acids are prepared by liquid-phase oxidation with PTC. Mono- and dimethylpyrazines and -pyridines in the presence of t-C_4H_9OK and 18-crown-6 in 1,2-dimethoxyethane are oxidized to the carboxylic acids in 32-89% yield [92-96]:

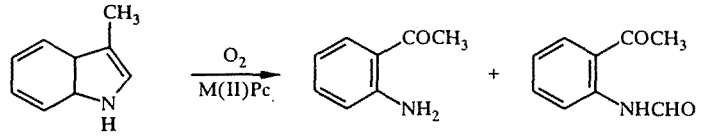


R, R^1 = H, Me; R^2 = H, COOH; R^3 = H, Me, COOH

As a rule, the dimethyl derivatives under the studied conditions are oxidized to the dicarboxylic acids. The exception is 2,6-dimethylpyrazine, which gives 2-methyl-6-pyrazinecarboxylic acid. Electrocatalytic oxidation at a Ni oxide electrode in the presence of Co salts is the only way to prepare 2-methyl-5-pyrazinecarboxylic acid [95]. For 60% conversion, the yield of acid was 42%. Also favorable for the formation of 2-methyl-5-pyrazinecarboxylic acid are Cr compounds. However, they also enhance demethylation.

Oxidation of 2-styryl-5-(4-methoxyphenyl)-2-pyrimidinecarboxylic acid by $KMnO_4$ in the presence of a tributylbenzylammonium chloride catalyst gives 5-(4-methoxyphenyl)-2-pyrimidinecarboxylic acid [90].

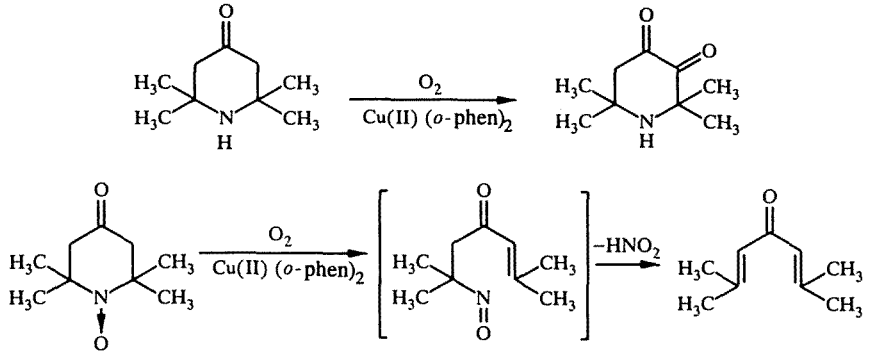
Liquid-phase oxidation of 3-methylindole by O_2 in the presence of Fe, Co, Mn, or Cu phthalocyanines at room temperature opens the five-membered ring and forms o-acetylaniline and its formyl analog [97]:



M = Fe, Co, Cu, Mn

Supposedly a complex formed by the heterocycle and catalyst reacts with O_2.

The oxidation of 2,2,6,6-tetramethyl-4-piperidinone and its N-oxide by O_2 in alkaline medium is catalyzed by Cu complexes of o-phenanthroline [98]. In the first instance, primarily 3,4-piperidinedione is formed. Under the studied conditions, the N-oxide is destroyed, the ring opens, and N is lost as HNO_2.

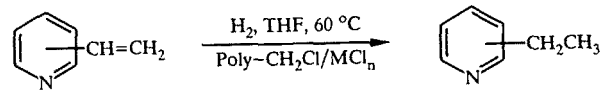


3. REACTIONS IN H_2 ATMOSPHERE

Depending on the catalyst and reaction conditions, N-heterocycles in H_2 atmosphere can undergo saturation in the side functional groups, in the ring, or simultaneously in the substituent and the ring; opening of the ring; and elimination of substituents as a result of hydrogenolysis.

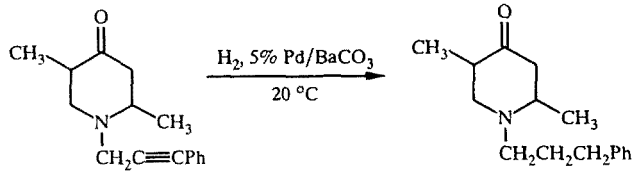
Palladium catalysts on various supports are used most frequently for hydrogenation of functional groups bound to the heterocycle. These reactions include hydrogenation of olefinic or acetylenic bonds to form alkyl derivatives and reduction of aldehydes and ketones to carbinols or alkyl derivatives and of cyano-, nitroso-, or nitro-groups to the corresponding aromatic heterocyclic amines.

Vinylpyridines were hydrogenated on ordinary Ni [99] and heterogenized metal-complex catalysts. The latter were prepared by reacting metal chlorides (Rh, Pd, Co, Ni) with chloromethylated crosslinked styrene–divinylbenzene polymer. It was found that the Pd complexes gave the fastest hydrogenation rates. The rate of conversion of the vinyl group to ethyl decreases in the order: 2- > 3- > 4-isomer [53, 100].



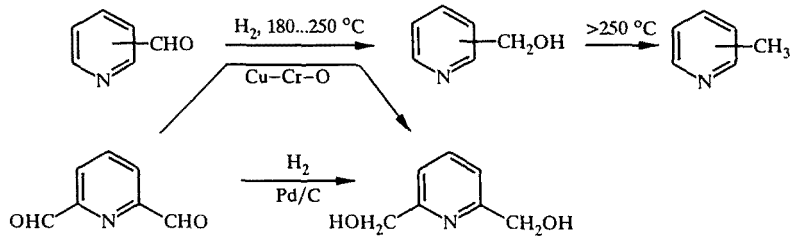
M = Pd, Co, Ni, Rh; n = 2, 3

Saturation of the acetylenic bond in 1-(3-phenyl-2-propynyl)-2,5-dimethyl-4-piperidinone was catalyzed by 2-5% Pd deposited on an inorganic support (Al_2O_3, SiO_2, $BaCO_3$, $CaCO_3$, C). Using the best of the studied catalysts, 5% Pd on $BaCO_3$, the desired product is obtained in 99% yield [101].



Hydrogenation on Raney Ni and its modifications of 8-alkenylthioquinolines such as 8-quinolylallylsulfide, 8-quinolylpropenylsulfide, and 8-quinolylallylsulfone gave 8-quinolylpropylsulfide (first two) or the sulfonic derivative through hydrogenolysis [102].

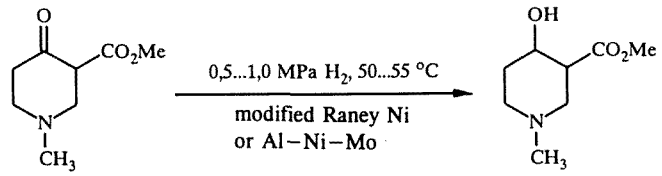
Monoformylpyridines are reduced at 180-250°C in 66-93% yield to the corresponding (hydroxymethyl)pyridines on Cu chromite treated with a Ba salt. At temperatures above 250°C, the carboxylic group is further hydrogenated to form methylpyridines and the pyridine ring is hydrogenolyzed [103]. 2,6-Pyridinedialdehyde was hydrogenated to 2,6-bis(hydroxymethyl)pyridine in ~30% yield. If a more active catalyst, for example 10% Pd on C, is used, 2,6-bis(hydroxymethyl)pyridine is obtained in 89% yield [64].



The reduction of pyridinealdehydes on a heterogenized Pd complex catalyst was also studied. The compounds to be hydrogenated fall in the following order of overall conversion: 2-pyridinealdehyde = 6-methyl-2-pyridinealdehyde > 4-pyridinealdehyde > 2,6-pyridinedialdehyde > 3-pyridinealdehyde [53].

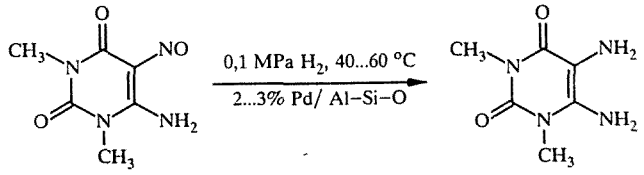
Little data are available for the hydrogenation of aldehydes into other N-heterocycles. Thus, 2-methyl-4-amino-5-pyrimidinecarbaldehyde is converted by 4% Pd on C to 2-methyl-5-(hydroxymethyl)4-pyrimidineamine in 90% yield [104].

The hydrogenation of keto heterocycles was studied on Ni and Al–Ni–Mo catalysts. For example, N-methyl-3-carbomethoxy-4-piperidinone is hydrogenated into N-methyl-3-carbomethoxy-4-hydroxypiperidine in 82.6% yield [105].

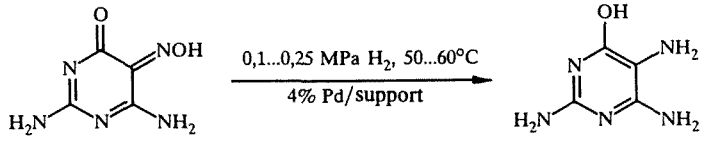


The selective hydrogenation of nitroso groups in heterocycles was studied in order to develop methods for producing the corresponding amino compounds, which are synthons for several medicinal compounds.

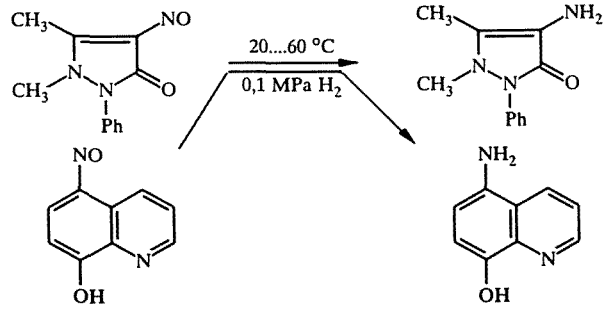
1,3-Dimethyl-5-nitroso-6-uracilamine was hydrogenated on 2-3% Pd catalysts on an aluminosilicate support. 1,3-Dimethyl-5,6-uracildiamine was selectively formed [106].



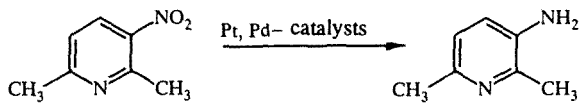
Hydrogenation of 5-isonitroso-6-hydroxy-2,4-pyrimidinediamine in the presence of 4% Pd gave 6-hydroxy-2,4,5-pyrimidinetriamine in 68% yield. The catalyst could be used repeatedly (eight times) without losing activity [107].



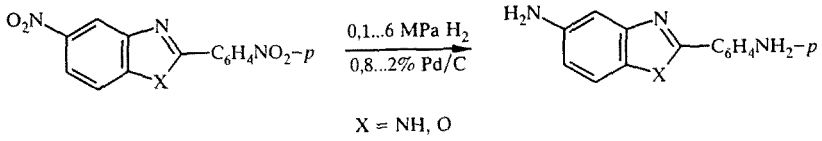
The hydrogenation of nitrosoantipyrine and 5-nitroso-8-quinolinol was studied on Pt group metals. The order of metal activities is Pt > Ru > Rh > Pd. Depositing the metals on a support (C, Al_2O_3, $BaSO_4$, $CaCO_3$) causes the hydrogenation rate to increase by 3-10 times compared with the blacks. The hydrogenation rate of nitrosoantipyrine is two times greater than that of nitrosoquinolinol [108].



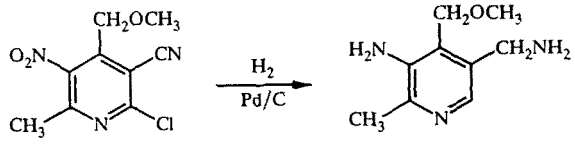
Nitro derivatives of methylpyridines were hydrogenated on Pt and Pd catalysts. The selectivity of the reduction of the nitro group to an amino depended on its position in the molecule: 2,6-dimethyl-3-nitropyridine is readily and smoothly converted to 2,6-dimethyl-3-pyridineamine whereas 2,6-dimethyl-4-nitropyridine under analogous conditions forms side products [109].



The N-heterocycle has no effect on the hydrogenation of functional groups situated at a certain distance from the heterocycle. On Al–Pd catalysts (Pd/Al_2O_3), 4-(2-nitroanilino)pyridine is hydrogenated to 4-(2-aminoanilino)pyridine [110]. A particular functional group can be selectively hydrogenated even if the molecule to be hydrogenated contains several unsaturated rings. Nitro derivatives of 2-phenylbenzimidazole and 2-phenylbenzoxazole are hydrogenated to the corresponding amino derivatives on 0.8-2.0% Pd on C [111].



The rate and sequence of hydrogenation with two nitro groups in the molecule depend on the position of these groups and the nature of the heterocycle [111]. Different reducible groups in a heterocycle can be simultaneously hydrogenated. By using Pd on C, 2-methyl-3-nitro-4-methoxymethyl-5-cyano-6-chloropyridine is hydrogenated to 2-methyl-4-methoxymethyl-5-aminomethyl-3-pyridineamine [112].

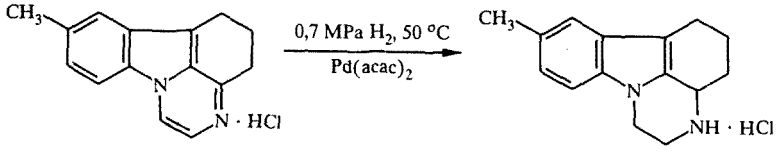


Hydrogenation of 2-methyl-5-cyano-4-pyrimidineamine in aqueous solution at room temperature in the presence of Pd on C gives 2-methyl-5-aminomethyl-4-pyrimidineamine in 90% selectivity. The presence of the side product 2-methyl-5-hydroxymethyl-4-pyrimidineamine is consistent with a reaction with H_2O [113]. Raney Ni treated with Ti was also used to hydrogenate cyano derivatives of pyrimidine to the corresponding amines [114].

Hydrogenation of N-heterocycles can also saturate the ring itself. Thus, homogenized Pd and Rh complexes in addition to Pd and Rh on C or Al_2O_3 catalyze hydrogenation of pyrrole to pyrrolidine. The yield of pyrrolidine on Rh catalysts was 29-100%; on Pd, 8-13% [115].

The pyridine ring of arylpyridines and other compounds containing the pyridine ring have been hydrogenated [116]. 4-Nitropyridine can be hydrogenated to 4-piperidineamine [117]. Thiophene impurities (up to certain concentrations) enhance pyridine hydrogenation in the presence of Rh/SiO_2 catalyst [118]. Various pyridine compounds were fully hydrogenated on industrial catalysts in yields up to 93% [119, 120]. Hydrogenation of the ring of isonicotinic acid has been studied on various catalysts [121, 122].

Derivatives of dihydropyridines are hydrogenated either to tetrahydropyridines or to piperidines depending on the process conditions [123]. Several dihydroquinolines were converted to the corresponding tetrahydroquinolines [124]. 3-Carbethoxy-2-dehydroquinuclidine is hydrogenated to 3-carbethoxyquinuclidine in 60-65% yield on Ni catalyst [125] and 98% on solid NiO [126]. The pyrazine ring of 1,10-trimethylene-8-methylpyrazino-(1,2a)-indole was hydrogenated to the corresponding piperazine derivative in at most 80% yield using Pd bisacetylacetonate [127].



Either the hydrogenolysis products o-phenylenediamine and o-amino-p-cresol or the hydrogenated molecules 4,5,6,7-tetrahydro- and 1,3,4,5,6,7,8,9-octahydro-2-(2-hydroxy-5-methylphenyl)benztriazoles were formed on Raney Ni depending on the solvent during the reaction of 2-(2-hydroxy-5-methylphenyl)benztriazole N-oxide. The change in the rate and extent of hydrogenation on going from alcohol to aqueous-alkaline medium is explained by the solvent effect on the H_2 content of the catalyst and on the ratio of the various H_2 species [128, 129].

The complex chlorotris(triphenylphosphine)rhodium(I) bonded to phosphinated 2-20% crosslinked styrene–divinylbenzene resins was used for regioselective hydrogenation of S- and N-containing polynuclear cyclic compounds [130].

Petroleum products were purified of N-containing impurities by denitrogenation on Cr, Mo, Ti and V nitrides. These were used instead of the usual Ni–Mo or Co–W catalysts on Al_2O_3. The nitrides of Cr and Ti were slightly active; V nitride was moderately active; and Mo nitride had the greatest activity in this reaction [131].

The above examples of reactions and catalysts is not at present comprehensive. However, they do illustrate the synthetic possibilities in this type of compounds and the use of catalytic reactions to protect the environment from contamination by the heterocycles themselves and the N oxides formed during their oxidation.

4. SYNTHESES OF HETEROCYCLE DERIVATIVES

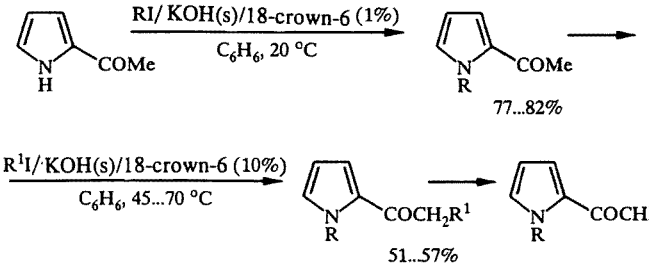
Catalytic methods are used to synthesize many varied derivatives of N-heterocycles. Depending on the heterocycle structure, either N-substituted derivatives or those with modified substituents are synthesized. The first group includes N-alkylation and N-carboxylation; the second, numerous conversions involving functional substituents such as vinyl-, ethynyl-, carbonyl-, carbinolyl-, and carboxyl-groups situated directly on the heterocycle or at a certain distance from it.

4.1. N-alkylation. Phase-transfer catalysts, which are based on an alkaline reagent (solid or liquid) and a PTC catalyst (quaternary salt or crown ether), are successfully used in N-alkylation reactions of many heterocycles. Mono-, di-, tri-, and tetrazoles are alkylated with heptyldimethyl(3-halopropyl)silanes in benzene–KOH (60%) in the presence of tetrabutylammonium bisulfate. Under these conditions pyrrole is alkylated not only on the ring N atom but also on C_2 and C_3. Carbazole, pyrazole, imidazole, benzimidazole, and 1,2,4-triazole are regiospecifically converted to the N_1-derivatives; benzotriazole, to the N_1- and N_2-derivatives; tetrazole, regiospecifically to the 2-alkylated compound [132, 133].

$$\text{Het–H} + \text{Me}_2(n\text{–C}_7\text{H}_{15})\text{Si(CH}_2)_3\text{I} \xrightarrow[80\ ^\circ\text{C, Bu}_4\text{NHSO}_4\text{, 10...12 h}]{\text{C}_6\text{H}_6\text{/60\% KOH}} \underset{80...96\%}{\text{Het(CH}_2)_3\text{Si}(n\text{–C}_7\text{H}_{15})\text{Me}_2}$$

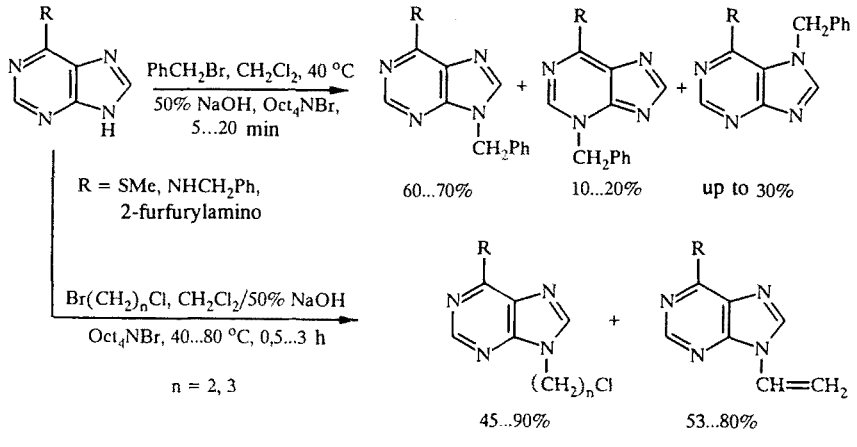
Het–H = mono-, di-, tri-, tetrazoles

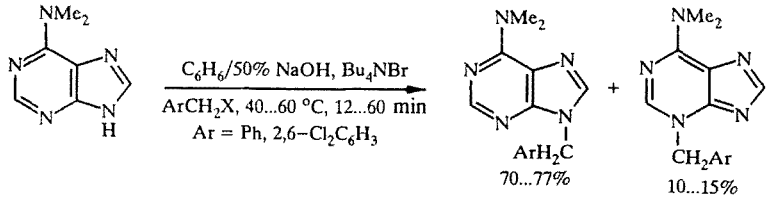
At room temperature in the presence of 18-crown-6, 2-acetylpyrrole is N-alkylated. At elevated temperature, the acetyl group is also alkylated [134].



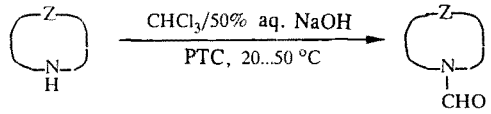
Alkylation of pyrrole is possible in a three-phase system using polyethyleneglycol (low molecular weight) and its ethers bonded to a crosslinked polymer as a catalyst in the presence of t-C_4H_9OK in toluene or tetrahydrofuran. The desired products are obtained in greater than 80% yield [135]. Without solvent, pyrazole is alkylated by such alkylating reagents as methyliodide, ethyliodide, butylbromide, octylbromide, hexadecylbromide, benzylchloride, and allylbromide in the presence of tetrabutylammonium bromide at 0-20°C in 83-98% yield to the corresponding N-alkylpyrazoles. N-Propargylpyrazole was synthesized at 40°C. The yield was only 37% [136].

Depending on the catalyst (tetrabutyl- and tetraoctylammonium and hexyltributylpnosphonium bromides) and reaction conditions, purines are converted to mono-, di-, and trialkyl-substituted purines. The alkylating reagents in these experiments were α-bromo-ω-haloalkanes, 1-bromo-2,2-diethoxyethane, 1-bromo-2-chloroethane, and ethylenebromohydrin. Conditions were found under which 6-substituted purines are regiospecifically alkylated to form the corresponding 9-alkyl derivatives whereas N,9-disubstituted adenines are regiospecifically converted to N,N,9-trisubstituted adenines [137-143].





Saturated N-heterocycles react through PTC with dichlorocarbene to form N-formyl derivatives [144]. The reaction occurs in the biphasic system $CHCl_3-NaOH$ (aqueous, 50%) in the presence of a phase-transfer catalyst. The dichlorocarbene formed is transferred by the catalyst as $R_4N^+CCl_2X^-$ into the organic phase, where dichlorocarbene is incorporated into the N−H bond. In the presence of tetrabutylammonium fluoride, azetidine, pyrrolidine, piperidine, morpholine, 1-H-hexahydroazepine, and 1-methyl-, 1-ethyl-, and 1-phenylpiperazines are N-formylated to the corresponding aldehydes in up to 86% yield [145, 146].



Z = $(CH_2)_n$, $CH_2CH_2OCH_2CH_2$, $CH_2CH_2N(R)CH_2CH_2$,
R = Me, Et, Ph; n = 3, 4, 5, 6

Using N-formylation of pyrrolidine as an example, the effect of the tetrabutylammonium anion on the course of the reaction was studied. It was found that the reaction is 1.7 times faster with fluoride than with chloride and almost eight times faster than with iodide. Tetrabutylammonium chlorate gives the slowest reaction (the rate is 16 times less than with fluoride). The catalyst cation has less effect on the reaction. The reaction rates are similar if tetrabutylammonium is changed to triethylbenzylammonium. The anion effect on the rate of N-formylation may be due to their "different affinity for the interface" and the hydrophilicity. The reactivity of cyclic amines toward addition of dichlorocarbene decreases in the order pyrrolidine > piperidine > 1H-hexahydroazepine > morpholine. The corresponding basicities are 11.27, 11.12, 10.00, and 8.70. Azetidine was the least reactive toward N-formylation even though it has the highest basicity among the studied secondary amines. The reason for this may be the low stability of the intermediate ion that is due to strain in the four-membered ring. The low yields from N-formylation of alkylpiperazines may be caused by poisoning of the catalyst through

reaction with the tertiary N atom and formation of an ylide. 1-Phenylpiperazine, which is much less capable of forming an ylide, is converted into the N-formyl derivative with the same yield as pyrrolidine or piperidine under analogous conditions [145, 146].

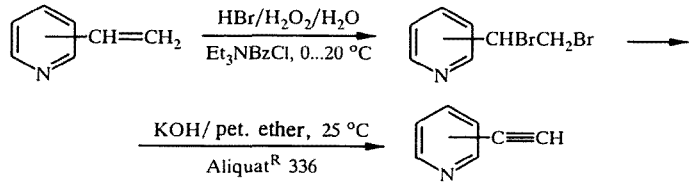
Pyrrolidine is also N-formylated in the presence of betaines of amino acids. Depending on the amino-acid structure and reaction time, the yields of N-formylpyrrolidine were from 24 to 64%. The reaction was performed in $CHCl_3-NaOH$ (50%). The N-formylation of pyrrolidine in the presence of betaines of α-, β-, and γ-amino acids in most instances takes from 3 to 6 hours. The yield of the desired product is highest if the betaine of 1-N-dimethylproline is used as catalyst, in the presence of which the reaction is complete in one hour. Low yields in the series of experiments were obtained if the reaction occurred in the presence of the betaines of N-trimethyl-α-aminobutyric acid, L-thioproline, and the hydrochloride of nicotinic acid betaine [147, 148].

The mechanism of catalysis by a zwitterionic salt [149] supposes binding of dichlorocarbene through interaction with a carboxylate anion and formation of $-N-...C(=O)OCCl_2$, which is more lipophilic and can migrate into the solution. The fact that a dependence between the lipophilicity of the "onium" part of the betaines and their catalytic activity was not found is consistent with this. Increasing the distance between the poles of the dipole in betaines of α-, β-, and γ-amino acids does not increase their reactivity toward dichlorocarbene.

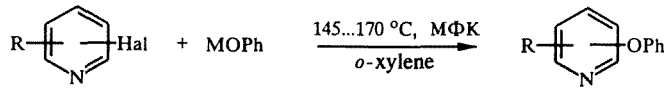
4.2. Reactions of functional groups on heterocycles. Reactions of vinyl-, halo-, carbonyl-, and nitrile-substituted heterocycles are examined below as a function of catalyst and position of the functional group on the heterocycle.

In the presence of triethylbenzylammonium chloride in the biphasic system 30% aqueous H_2O_2-HBr$-CCl_4$, 2-vinyl- and 3-vinylpyridine add Br_2. The yields of 2- and 3-(α,β-dibromoethyl)pyridines are 81 and 82% [150].

Haloethylpyridines may be dehydrohalogenated. In the presence of trioctylmethylammonium chloride (Aliquat® 336) in petroleum ether$-$KOH (s), a mixture of 3-(1,2-dichloroethyl)pyridine and 3-(1-chlorovinyl)pyridine is dehydrohalogenated to give 3-ethynylpyridine in 51% yield. In the analogous reaction of 2-(1,2-dibromoethyl)pyridine, 2-ethynylpyridine is obtained in 13% yield owing to its high lability and large losses in the isolation. Tetraoctylammonium bromide, dodecylbenzyldimethylammonium bromide, hexadecylbenzyldimethylammonium chloride, and tetradecylbenzyldimethylammonium chloride have been used as catalysts [150].



If the halide atoms are directly bonded to a C atom of the ring, they can be replaced by phenoxide under PTC conditions. In a biphasic liquid$-$solid system, halopyridines react with alkali phenoxides. The phase-transfer catalysts in this reaction are quaternary phosphonium salts, tributylphosphine oxide, and crown ethers in addition to phosphonium salts bonded to a polymeric support [151]. If the reaction was performed in xylene with potassium phenoxide (KOPh), the rate was greater than with sodium phenoxide (NaOPh). The results with KOPh are even better if 18-crown-6 and dibenzo-18-crown-6 are used; with NaOPH, 15-crown-5 (owing to the correspondence of the metal ionic radii and the cavities of the crown ethers). Of the studied halopyridines, the least reactive in this reaction was 3-bromopyridine [152, 153].



M = Na, K
R = H, CH_3; Hal = Br, Cl

The halides on C_3 and C_5 in 2,3,5,6-tetrabromopyridine are totally inert. Reaction with KOPh in boiling xylene in the presence of 18-crown-6 replaces only the Br at the 2- and 6-positions. The reaction product is 3,5-dibromo-2,6-diphenoxypyridine. The yield is 70%. Under analogous conditions, pentachloropyridine was converted to 3,5-dichloro-2,4,6-

triphenoxypyridine in 67% yield. Reaction in mesitylene of 2,3,5,6-tetrabromopyridine and dipotassium pyrocatecholate induces cyclization to the tricyclic compound 7,7-dibromo-6-azaphenoxane (in 11% yield) [153].

Reactions of azines containing halides in the side chain were studied using the reaction of the dichloromethyl derivatives and CCl_4 in a system with NaOH (50%) in the presence of catalytic amounts of a quaternary ammonium salt or with solid KOH and 18-crown-6 as catalysts. 2-Trichloromethylpyridine was obtained in 66% yield; 3-trichloromethylpyridine, 27%. At room temperature, dichloromethylpyrazine reacts with analogous reagents to give trichloromethylpyrazine in 51% yield [154].

$$\text{HetCHCl}_2 \xrightarrow[\text{PTC, 20...50 °C, 2...20 h}]{\text{CCl}_4/\text{OH}^-} \text{HetCCl}_3$$

Het = 2- и 3-pyridyl, pyrazinyl

Trichloromethylazines were obtained directly from methylazines, for example, 2-methylpyridine and methylpyrazine, through radical chlorination to the dichloromethylazines and further conversion without isolating the intermediates from the reaction mixture. Thus, CCl_4 in the first step acts as the solvent; in the second, as a reactant [155].

$$\text{HetCH}_3 \xrightarrow[\text{CCl}_4]{\text{N-chlorosuccinimide}} \text{HetCHCl}_2 \xrightarrow[\text{18-crown-6}]{\text{CCl}_4/\text{KOH(s)}} \text{HetCCl}_3$$

Het = 2-pyridyl, pyrazinyl

4.3. Reactions of carbonyl derivatives. Reaction of azinecarbaldehydes and $CHCl_3$ in alkaline solution under PTC conditions forms the azinyl(trichloromethyl)carbinol. Starting with 2-pyridinecarbaldehyde, 3-pyridinecarbaldehyde, and 6-methyl-2-pyridinecarbaldehyde, the corresponding pyridyl(trichloromethyl)carbinols are synthesized in a liquid–liquid system in the presence of triethylbenzylammonium chloride in 25, 20, and 30% yields. In a liquid–solid system, the yields of the desired products from the first two aldehydes were 50 and 28%, respectively. 4-Pyridinecarbaldehyde does not react under the experimental conditions with the trichloromethyl anion since it undergoes the Cannizzaro reaction. 6-Methyl-2-pyridyl-(trichloromethyl)carbinol is obtained in 21% yield in $CHCl_3$–NaOH (50%) in the presence of (8S,9R)-N-cinchonidine chloride (the product exhibited slight optical rotation). If tubocurarine chloride is used as catalyst, there is no reaction [156].

$$\text{Py—CHO} \xrightarrow[\text{0 °C, PTC}]{\text{CHCl}_3/\text{OH}^-} \text{Py—CH(OH)CCl}_3$$

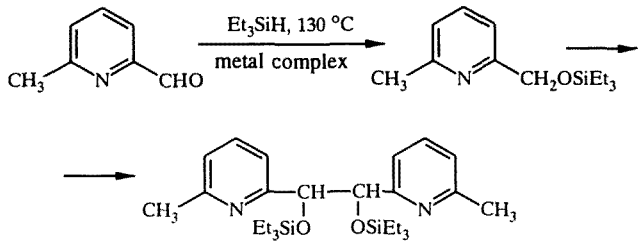
Py = 2- and 3-pyridyl, 6-methyl-2-pyridyl

If metal-complex catalysts are used, pyridinealdehydes undergo hydrosilylation. Complexes of Rh, Ru, and Pd are used as catalysts. With respect to hydrosilylation of 2-pyridinealdehyde with triethylsilane, the activities of the studied catalysts have the order: $Ru(PPh_3)_2(CO)_2Cl_2$ > $Rh(PPh_3)_3(CO)H$ > $Rh(PPh_3)_2(CO)Cl$ > $Ru(PPh_3)_3Cl_2$ > $Pd(PPh_3)_2Cl_2$ > $Rh(PPh_3)_3Cl$. The hydrosilylation rate decreases two hours after the start of the reaction. This is due to inhibition by the resulting ether, which is a stronger electron donor than the starting pyridinealdehyde and irreversibly binds the catalyst.

$$\text{Py—CHO} \xrightarrow[\text{metal-complex catalyst}]{\text{Et}_3\text{SiH, 130 °C, 1...7 h}} \underset{\text{37...70\%}}{\text{Py—CH}_2\text{OSiEt}_3}$$

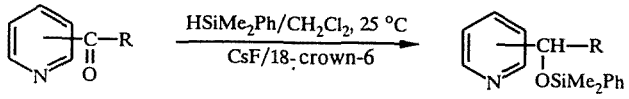
Py = 2-, 3-, 4- pyridyl

On the studied catalysts at 130°C, 6-methyl-2-pyridinealdehyde reacts with triethylsilane to give 6-methyl-2-(triethylsiloxymethyl)pyridine and the threo- and erythro-isomers of the disilyl ether of bis(methylpyridyl)ethanediol. On Ru catalysts, the monoether is formed. On Rh complexes containing CO, the ratio of the mono- and diethers is 1:1.5. 2-Pyrrolecarbaldehyde at 130°C in the presence of Rh catalysts is not hydrosilylated by triethylsilane [157, 158].



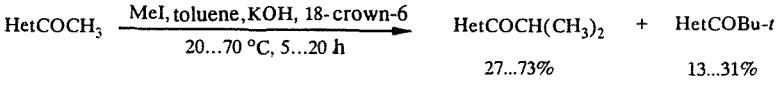
(*threo*- and *erythro*-)

The pyridinealdehydes are more mildly and completely hydrosilylated in the presence of 18-crown-6 and CsF. Dimethylphenylsilane reacts with 2-, 3-, and 4-pyridinealdehyde and 6-methyl-2-pyridinealdehyde at room temperature in dry dichloromethane. The yields of the corresponding dimethylphenylsilyl ethers were 54% (3-isomer) and 67% (2-isomer). The 6-methyl-2-pyridinealdehyde derivative is obtained in 58% yield [159, 160]. The analogous reaction also occurs with methylpyridylketones. The corresponding derivatives are obtained in 60-71% yields [161].



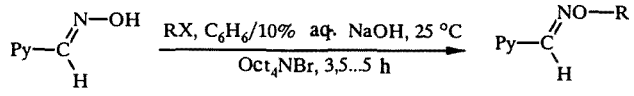
Hydrosilylation was also studied in the presence of metal halides. 3-Acetylpyridine reacts with an equimolar amount of diphenylsilane in the presence of N-benzyl-N-methylephedrinium zincate at room temperature to give C_5H_4NCH-$MeOSiHPh_2$, the hydrolysis of which gives 1-(3-pyridyl)ethanol with 50% optical yield. Besides the dibromodichlorozincate of N-benzyl-N-methylephedrine, the hexachloroplatinate and bromotrichlororhodate were also tested as catalysts [161].

Alkyl−(aromatic heterocyclic) ketones under PTC conditions can be alkylated on the alkyl group. N-Alkylacetylpyrroles at 45°C in a liquid−solid system (alkyliodide−KOH) are alkylated on the keto group. Thus, (isopropyl)(1-alkyl-2-pyrrolyl)ketones were synthesized by reaction with methyliodide. If ethyliodide is used as the alkylating reagent, the reaction temperature should be raised to 70°C. Acetylpyridines at room temperature in toluene (or benzene)−KOH in the presence of 18-crown-6 react with methyliodide to give isopropylpyridylketones or even tert-butylpyridylketones if 2- or 4-acetylpyridines are used [162, 163].



Het = pyrrolyl, 1-methylpyrrolyl, 1-ethyl pyrrolyl
2-, 3-, 4- pyridyl

Pyridinealdoximes (E-isomers) in benzene−NaOH (10%) in the presence of tetraoctylammonium bromide regiospecifically react with alkyl- or benzylhalides to give the corresponding O-ethers. Thus, methyl-, ethyl-, isopropyl-, butyl-, amyl-, and benzyl-O-ethers of the isomeric pyridinealdoximes were synthesized. In these reactions, 3-pyridinealdoxime was much more active than 4-pyridinealdoxime [163].

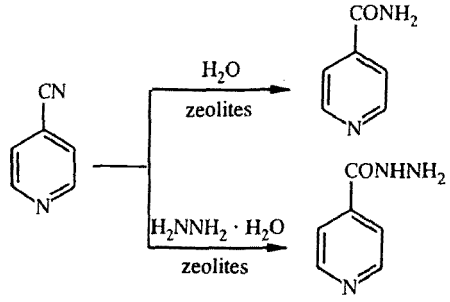


Py = 2-, 3-, 4-pyridyl

R = Me, Et; *i*–Pr, *n*–Bu, *n*–C_5H_{11}, $PhCH_2$; X = Cl, Br, I

Zeolite catalysts were tested in the hydration of 4-cyanopyridine to isonicotinamide. It was found that the acid−base properties of the catalyst substantially affect the course of this reaction. The yield of isonicotineamide reached 90% on NaY and Na-mordenite. Hydrolytic hydrazinolysis of 4-cyanopyridine to the hydrazide of isonicotinic acid occurred on synthetic zeolites. Reaction with hydrazine hydrate in aqueous medium in the presence of zeolites modified with alkali metal ions produced the hydrazide of isonicotinic acid in yields from 41 to 65%. Depending on the alkali metal, the yield increased in

the order Cs < Rb < K < Na. The low yields of the desired product on zeolites modified with K, Rb, and Cs are supposedly caused by the increased side reactions to form such products as isonicotinamide and 2,5-bis(4-pyridyl)-1-triazoleamine. On zeolite NaX under optimal conditions, the yield of the desired product was 60-63% [164, 165].



The examples of catalytic reactions of N-heterocycles that were presented are only a sampling of the synthetic possibilities of both heterogeneous and homogeneous catalysis. This area of catalysis is constantly developing and is important not only to preparative synthesis of several practically valuable products but also for further elucidation of the theoretical principles of the mechanism of catalysis.

CONCLUSION

In the modern concept of catalysis as a chemical phenomenon, the catalytic effect depends not only on the catalyst properties and its ability to participate in redox and acid–base reactions with the substrate but also on the nature and structure of the compound affected by the catalyst. It follows from the examples of oxidations that even small changes in the structure of the molecule to be oxidized cause fundamental changes in the reaction mechanism and catalyst formation and poisoning.

Existing instrumental methods for investigating surface reactions and detecting intermediates and for separating and analyzing complicated multicomponent mixtures should further stimulate interest in catalytic conversions of heterocycles with several catalytically reactive centers in the molecule. These exhibit an increased tendency to form stable complexes with the catalyst or to be strongly adsorbed to the surface. Achievements in elucidating the mechanism of catalytic reactions by using molecular beams, modern laser techniques, and ion beams [166] in addition to the application of quantum chemistry to estimate surface intermediates [167] are making it very easy to establish the actual reaction mechanisms of the most common catalysts with the simplest heterocycles. On the other hand, as G. K. Boreskov noted, "Chemistry presents a practically unlimited number of substances and compositions for inventing catalysts" [168]. The chemist has in his hands a multitude of tools for changing the direction and selectivity of catalytic reactions by changing the metal dispersion [169] or adding compounds to oxide systems in order to change the oxidation state of the principal catalyst components or the surface acid–base properties [170]. The reaction medium also affects the formation of the active catalyst [171], especially with respect to heterocycles. In several instances the medium not only activates but also poisons the catalyst.

Therefore, considering the typical small-scale catalytic production of heterocycles, liquid-phase catalysis using both homogeneous and heterogeneous metal-complex catalysts, ion-exchange resins, and phase-transfer catalysts are especially promising on an industrial scale. Bifunctional catalysts based on metal complexes can be successfully used successively to carry out two types of catalytic reactions. These are those characteristic of the metal complexes (hydrogenation, hydrosilylation) and of the onium salts (PTC) [172-174]. In the synthetic chemistry of heterocycles and their organometallic derivatives, the catalytic conversions of which have recently been of great interest [144, 175, 176], the use of bifunctional catalysts is very promising. Asymmetric synthesis becomes possible if metal complexes are formed with optically active ligands. This is especially important in the production of biologically active compounds and their synthons.

In addition to solving synthetic problems, further development of catalytic reactions of heterocycles also embellishes general concepts concerning the essence of catalytic phenomena and the reaction mechanisms of the catalyst and substrate.

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