SYNTHESIS OF METHYLPYRIDINES IN THE PRESENCE OF Pd COMPLEXES CONTAINING S

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Synthesis of methylpyridines from acetaldehyde and ammonia in the presence of heterogeneous Pd complexes containing S is studied by a pulsed microcatalytic method. The process occurs with selective formation of 4-methylpyridine. The difference in the catalytic activity of the studied complexes is explained on the basis of ^{13}C *NMR spectra.*

Pyridine and its derivatives are widely used in the synthesis of a wide assortment of chemicals for protecting plants (Lontrel, Chloramp, Tordon), dyes, surface-active substances, and pharmaceutical preparations.

Known catalytic methods of preparing pyridine and its derivatives are based on the use of acetylene and ammonia or aldehydes and ammonia in the presence of oxides and salts of various acidity [1]. However, the nonreaction is nonselective. The mixture formed contains a number of pyridine derivatives, the concentration of each of which is less than 30-40%.

According to one of the schemes, the synthesis of methylpyridines from acetaldehyde and ammonia includes chain-growth up to 6 C atoms resulting from di- and trimerization of starting molecules and a subsequent cyclization step. It is known [2] that transition metal complexes selectively catalyze these reactions. Thus, it seemed interesting to test heterogeneous metal-complex catalysts in the studied process.

In the present study, results are presented for the synthesis of methylpyridines from acetaldehyde and ammonia in the presence of Pd complexes containing S of general formula PdZ_2Cl_2 [where Z = dimethylsulfoxide (I), 2,2-diphenyl-4-methylthiacyclohexane (II), and 5-butyl-2-thiapyrrolidone (III)] deposited on aluminum oxide from DMF.

The synthesis of methylpyridines from acetaldehyde and ammonia was carried out in the range 80-160°C. The amount of deposited complex (0.25%), the contact time (1 sec), and the acetaldehyde—ammonia—air ratio 1:4:1 were selected on the basis of previous investigations [3] and held constant.

The principal products of the conversion are pyridine, methylpyridines with predominantly 4-methylpyridine (up to 85%), acetonitrile (up to 12%), aldimine (up to 11%), and a series of unidentified oxidation and amination products, the concentration of which is small (1-2%). The activity of the catalyst was compared for the average of the first 5-7 pulses. According to the results obtained (cf. Fig. 1), the degree of conversion of starting acetaldehyde depends little on the properties of the complex used, changing in the range 94-100% (curves 4-6) and decreasing insignificantly on increasing the temperature (94-96%). Ammonia is completely converted regardless of the experimental conditions.

The studied catalysts are placed in the order I > II > III according to content of heterocycles in the catalysates, regardless of the temperature (Fig. 1, curves 1-3). The temperature dependence of formation of 4-methylpyridine for all catalysts passes through a maximum at 100°C. The reduction of the yield of 4-methylpyridine on increasing the temperature is probably due to the increasing extent of parallel formation reactions of acetonitrile and oxidation and amination products. Between 140-160°C the temperature dependences of heterocycle formation for all three samples approach each other.

The concentration of acetonitrile in the reaction products increases as the temperature is increased from 2-5% to 10-12% on all studied catalysts, respectively. This agrees with previous results [4] for the synthesis of methylpyridines on catalysts containing N and P, in the presence of which increasing the temperature and contact time resulted in increased formation of acetonitrile.

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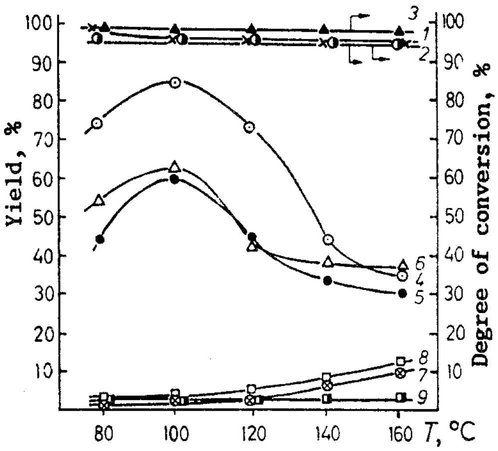

Fig. 1. Temperature dependence of degree of conversion of acetaldehyde (1-3) and formation of 4-methylpyridine (4-6) and acetonitrile (7-9) in the presence of Pd complexes: complex I (1, 4, 7), complex II (2, 5, 8), complex III (3, 6, 9).

It is noteworthy that the content of aldimine identified in the catalysts increases in the range 80-160°C from 1.5 to 7.5% for samples I-III. According to one of the schemes for the process, aldimine is an intermediate in the synthesis of methylpyridines from acetaldehyde and ammonia. The increase of its concentration in the gas phase with a simultaneous decrease of activity for methylpyridines indirectly confirms this fact.

The difference in activity of the studied catalysts is apparently controlled by the different donor—acceptor properties of the ligands containing S, in particular the different degree of electron density transfer from the latter to the metal. Chemical shifts in the ^{13}C NMR spectra of the ligands and the corresponding complexes, presented previously [5], can measure of the change of electron density on the ligand. As the ^{13}C NMR spectra indicate, the degree of transfer of nonbonding electrons to Pd increases markedly on going from complexes II and III to I. This is practically the same as the increase of *trans*-effect in the studied series. As a result, exchange of ligands found on the same coordinate with them for starting material is accelerated and the yield of desired product is increased.

EXPERIMENTAL

The Pd complexes used were synthesized according to the literature methods [6-8]. The compositon and structure of the complexes were established on the basis of elemental and thermogravimetric analyses and IR and ^{13}C NMR spectra.

The datalysts were prepared by constructing the complex on the surface of hydroxylated aluminum oxide. The starting compound for the construction was K_2PdCl_4 and a given amount of ligand dissolved in DMF. Samples were dried at 160°C for 1 h.

The catalytic properties of the prepared Pd complexes for synthesizing methylpyridines were studied on a microcatalytic injection apparatus with pulsed supply of starting material. Products were analyzed chromatographically on a packed steel column of 6 m length and 3 mm internal diameter. Reoplex-400 5% deposited on Inerton—Super was used as the stationary liquid phase. A flame detector with programmed temperature and temperature increase rate 4°C/min was used. The analysis temperature was 50-160°C.

The starting acetaldehyde was technical grade of 98% purity from Saratov Production Association Nitron. Ammonia from a cylinder had the same purity. The reaction mixture contained 16.6% air.

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SYNTHESIS AND PROPERTIES OF HETEROCYCLIC ANALOGS OF 4-AZIDOCHALCONE

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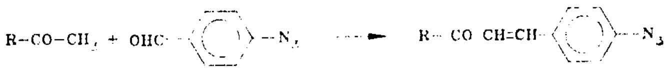
A study has been made of the spectral and photochemical properties of a series of heterocyclic analogs of 4-azidochalcone, specifically the pyridine, quinoline, isoquinoline, and quinoxaline derivatives. It has been shown that the absorption spectra of most of the 4-azidocinnamoylarenes are shifted bathochromically in comparison with 4-azidochalcone. The quantum yields of photodissociation of the compounds that were investigated were found to vary within the limits 0.70 ± 0.15. With steric hindrance for the planar conformation of the molecule, a hypsochromic shift of the absorption spectra is observed, along with a slight decrease of the quantum yield.

Aromatic azides including a propenone grouping —CO—CH=CH— in the overall conjugation chain are finding extensive applications as initiators of photocrosslinking of polymeric molecules [1, 2]. The most active compounds often prove to be those with a p-azidocinnamoyl group [3]. With the aim of determining the influence of the nature of a heterocyclic moiety and the extent of the conjugated system on the spectral and photochemical properties of the aromic azide, we have synthesized and studied a series of analogs of 4-azidobenzaldehyde with various aromatic and heterocyclic methyl ketones:



I–VIII

R = 2-pyridyl (I), 3-pyridyl (II), 4-pyridyl (III), 2-quinolyl (IV), 4-quinolyl (V), 1-isoquinolyl (VI), 2-quinoxalyl (VII), 3-methyl-2-quinoxalyl (VIII)

In the traditional procedure [4], an aqueous solution of NaOH is added to a methanol solution of the mixed aldehyde and ketone. We found that the use of this sequence in mixing the reactants often leads to self-condensation of the ketone (compare [5]) and to much lower yields of the desired azidochalcone. To avoid this effect, we adopted a procedure in which a solution of the ketone was added slowly to a stirred solution of the aldehyde with caustic; in this manner we obtained a series of 4-azidocinnamoylarenes I-VIII (Table 1).

In the PMR spectra of the azides, signals of olefinic protons are observed in the form of two doublets at 7.0/8.0 (α) and 7.3/8.5 (β) with J = 15/16 Hz, indicating the *trans* configuration of the substituents at the double bond. It is interesting to note the considerable downfield shift of the signal of the β-olefinic proton in the case of the 2-pyridine, 2-quinoline, and 2-quinoxaline derivatives. In these compounds, quite possibly, the β-olefinic proton, as a consequence of the *trans* configuration, may fall into the region of deshielding of the aromatic ring because of the planar conformation of the molecule.

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