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Zeolite-Catalyzed Isomerization of Aromatic Amines to Methyl-Aza-Aromatics

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The scope and mechanism of the isomerization of arylamines to methyl-substituted aromatic heterocycles have been studied. Aniline, toluidines, naphthylamines and *m*-phenylenediamine all reacted to the corresponding *ortho*-methyl-substituted aza-aromatics when exposed to high NH_3 pressure and elevated temperature in the presence of acid catalysts. Zeolites with a three-dimensional pore structure, especially H–ZSM-5, showed the best performance. Optimum reaction conditions are around 600 K and 10 MPa. Two mechanisms which had been proposed earlier for this apparent N-*ortho* C exchange reaction proved untenable. Neither incorporation of the N atom into the aromatic ring nor a mechanism based on an intramolecular Ritter reaction could explain the required high NH_3 pressure or the product distribution. Two new mechanisms are proposed which can explain all observations. In both mechanisms, reaction starts with addition of NH_3 to the arylamine, followed by ring opening. In one mechanism an alkyno-imine intermediate is formed; in the other mechanism an enamino-imine intermediate is formed through a reverse aldol reaction. In both cases ring closure and NH_3 elimination lead to the required aromatic heterocycles. The high NH_3 pressure is explained by the need to add NH_3 to the aromatic ring, and the high temperature by the need to desorb NH_3 from the acid sites. © 1995 Academic Press, Inc.

INTRODUCTION

Introduction of heteroatoms, such as N, S, or O, into hydrocarbon molecules adds substantial value, and new routes for such reactions are of continuous interest to the chemical industry. Of the two main classes of aromatic N-containing hydrocarbons, the arylamines and the aromatic N-heterocycles, the arylamines required industrially are exclusively obtained through synthesis, namely, by nitration of aromatics to nitro-aromatics, followed by hydrogenation to arylamines (1, 2). Because of the lower demand for aromatic heterocycles, coal tar is still an important source for pyridine. However, rising demands for aromatic heterocycles have increased the interest in synthetic routes, and processes in which aldehydes and ketones are condensed with NH_3 to form pyridine and alkylated pyridines have been realized. Thus, acetaldehyde and NH_3 are cyclized to a mixture of pyridine and 2- and 5-substituted- (methyl and ethyl) pyridine, while 2-methylpyridine (α-picoline) is synthesized from acetone and acrylonitrile, and 2,6-dimethylpyridine (2,6-lutidine) from acetone, methanol, and NH_3 (1, 2). Pyridine is synthesized from acetaldehyde, formaldehyde, and NH_3 in a fluid bed reactor over H–ZSM-5 (3).

About a decade ago a process for the conversion of phenol into aniline was patented by Mobil Oil (4). At 783 K and a NH_3 pressure of about 1 MPa, a reasonable conversion to aniline was obtained over an H–ZSM-5 catalyst in a flow reactor. The two main by-products were diphenylamine, from the reaction of phenol with the aniline product, and 2-methylpyridine. It was suggested that the latter product was the result of a subsequent reaction of aniline. In a following patent the conversion of aniline to 2-methylpyridine was described, under reaction conditions similar to those for the phenol to aniline reaction (5). A good selectivity (52%) was obtained at 783 K, 2.9 MPa NH_3, and a NH_3 : aniline molar ratio of 8, although the conversion was not very high (13%). By-products were acetonitrile and condensed aromatic heterocycles, such as quinoline and methylindole. The catalyst deactivated rapidly by coke formation. As possible mechanisms for the formation of 2-methylpyridine, a 7-ring mechanism, with uptake of the nitrogen atom of aniline into the aromatic ring, and a ring opening under nitrile formation, followed by a Ritter reaction, were proposed (6). In this respect it is interesting to note that, as mentioned in a review article about the synthesis of picolines and pyrroles (7), the reaction of cyclohexylamine to aniline and some 2-methylpyridine over heated pumice impregnated with $ZnCl_2$ was already described in the 1940s (8). It may be assumed that the 2-methylpyridine was formed from aniline over the solid acid catalyst, similar to the Mobil Oil reaction of aniline over H–ZSM-5.

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In a patent by workers of the Bayer Company (9), a similar isomerization reaction of an arylamine to an aromatic azaheterocycle was described. They succeeded in transforming *m*-phenylenediamine into 2-amino- and 4-amino-6-methylpyridine in a flow reactor at somewhat lower temperature (673 K), higher NH_3 pressure (19 MPa), and therefore higher NH_3 : arylamine ratio (60) than in the case of aniline. Conversion (74%) and selectivity (56% 2-amino-6-methylpyridine and 15% 2-amino-4-methylpyridine) were substantially better than for aniline.

The isomerization of an arylamine to a N-containing aromatic heterocycle would in principle open a new route to pyridines, quinolines, and the like, starting from aromatic hydrocarbons, via nitro-aromatics and arylamines. We were therefore interested in finding out the potential for this reaction and have studied the scope of the isomerization, its optimum conditions, and its mechanism. A full account of our work is given in this paper, while some preliminary results were published earlier (10).

EXPERIMENTAL

Zeolites

Some of the zeolite catalysts used in the present work (MOR, USY, BETA, ZSM-5) were obtained from CU Chemie Uetikon, Switzerland. Others (ZSM-12, ZSM-23, ZSM-48, Nu-10, and ZSM-5 with large crystallites) were prepared according to methods reported in the literature. Thus, ZSM-23 was prepared (10) by making a solution of 1.75 g $Al_2(SO_4)_3 \cdot 8\ H_2O$, 8.4 g 1,6-diaminohexane (Aldrich, tech.), 4.7 g KOH, 36 g colloidal silica (Ludox-40, Du Pont) in 147 g water and stirring the resulting gel for 0.5 h. Hydrothermal synthesis was carried out in a stirred 500 ml autoclave at 433 K for 3 days. ZSM-48 was made according to a modification (12) of a patent (13). A solution of 14 g waterglass, 1.3 g H_2SO_4, 3.15 g $(CH_3)_4NBr$ (Chemie Uetikon, purum), 13.6 g octylamine (Fluka, tech.), 0.45 g $Al(NO_3)_3 \cdot 9\ H_2O$, and 60.25 g water was prepared under vigorous stirring. Hydrothermal synthesis of the resulting mixture was carried out in a stirred (60 rpm) 100-ml autoclave at 433 K for 28 h.

The synthesis of Nu-10 was carried out according to a patent (14, 15). A synthesis mixture of 14.7 g triethyltetramine (Fluka), 53.3 g colloidal silica (Ludox-40, Du Pont), 1.6 g sodium aluminate, and 11.5 g NaCl in 200 g water underwent a hydrothermal synthesis in a stirred 500-ml autoclave at 453 K for 3 days.

ZSM-5 material with rather large crystallites was prepared according to the method described by Guth *et al.* (16, 17). The gel mixture containing 4.2 g $AlCl_3 \cdot 6\ H_2O$, 1.76 g $(C_3H_7)_4\ NBr$ (CU Chemie Uetikon, purum), 0.38 g NH_4F (Riedel de Haen, purum), 23.1 g silica (Cabosil, Fluka), and 326 g water was stirred for 0.5 h. Hydrothermal synthesis was carried out in a stirred 500-ml autoclave at 453 K for 3.5 days. When stirring was carried out at 30 rpm, crystallites with an average diameter of 50 μm were obtained, whereas at 90 rpm the diameter was 30 μm.

In all cases, the material resulting from the hydrothermal synthesis was washed three times, dried at 393 K, calcined at 773 K for several hours, and activated by threefold exchange with acid and subsequent calcination at 723 K for 3 h. Except for ZSM-23 and Beta, for which 0.1 *M* HCl was used, 1 *M* HCl was used in the ion exchange.

The external surface area of freshly calcined H–ZSM-5 was passivated by treatment with a solution of triphenylsilyl chloride in hexane at 328 K for 1 h. Dry nitrogen was continuously fed through the solution and the emerging HCl was determined by titration. After reaction the resulting material was filtered, and dried at 373 K and the organic groups were removed by calcination in air at 773 K.

Reaction Procedure

The reaction of the arylamines was carried out in a 100-ml spinning basket autoclave (Autoclave Eng.), because it was observed that the catalyst remained at the bottom of the autoclave and that mixing was insufficient when a normal stirred autoclave was used. The spinning basket autoclave contains a basket, consisting of two concentric grids filled with catalyst, and a four-blade stirrer. During reaction both stirrer and basket rotate. The stirrer mixes the reactants and forces them through the basket, thus enabling a good contact between solid catalyst and gaseous reactants.

Before each experiment the catalyst was dried at 423 K for several days and calcined at 723 K for 2 h. The catalyst (0.5 g) was brought into the basket and 2.5 g of the arylamine into the autoclave. Air was removed by flushing with nitrogen and the autoclave was checked for leaks. A controlled amount of ammonia (about 8 g) was transferred from a gas cylinder, which was heated by warm water (35°C), into a conduit between two valves. The ammonia was then sluiced into the autoclave, which was cooled in ice water to 5°C.

Samples taken during reaction and at the end of the reaction were dissolved in tetrahydrofuran and analyzed gas chromatographically with a Hewlett–Packard 5890 II apparatus using a 25-m (0.32 mm i.d.) HP-1 fused silica capillary column (0.52 μm methyl silicone coating). Identification of some products was made by GC–MS analysis (Carlo Erba GC and Hewlett–Packard MS), after purification by distillation at 8 kPa until 523 K.

Characterization

X-ray powder diffraction patterns of the synthesized zeolites were obtained with a Siemens D5000 diffracto-

meter using Ni-filtered CuKα radiation. Infrared spectra of disks of the zeolite samples pressed together with KBr were collected on a Mattson Galaxy spectrometer. The Si, Al, and Na contents of the zeolites were determined by atomic absorption spectroscopy on a Varian Spectr AA-10 instrument, while thermogravimetric and differential scanning calorimetric measurements were performed on a Thermal Sciences STA 1500 instrument to determine the optimal calcining conditions and to determine the amount of coke on catalyst after reaction. Nitrogen adsorption isotherms were obtained using a Micromeritics ASAP-2000M instrument. High-resolution ^{29}Si and ^{27}Al spectra were recorded on a Bruker AMX 400 spectrometer with a spinning frequency in the range 2–3 kHz.

RESULTS

Zeolites

XRD and IR measurements showed that the spectra of the homemade zeolites, as well as the spectra of the zeolites obtained from CU Chemie Uetikon, matched those described in the literature for the pure compounds (16, 18–20). The results of our elemental analysis and textural and scanning electron microscopy data for all zeolites used in the catalytic experiments are presented in Table 1.

Reaction Conditions

Results published thus far on the transformations of aniline and *m*-phenylenediamine suggest that an acid catalyst and a high NH_3 pressure are required (4–6, 9, 10). Indeed calcined MgO, a well-known basic catalyst (21), did not show any activity for the transformation of *m*-phenylenediamine to substituted pyridines. The necessity of the high NH_3 pressure and temperature was investigated by using *m*-phenylenediamine as educt, since its conversion and selectivity to substituted pyridines are much higher than those observed for aniline. Figure 1 shows, for instance, that conversion is about 75% and selectivity to 2-amino-6-methylpyridine is 64% after 4 h of reacting 2.5 g *m*-phenylenediamine with 0.5 g H–ZSM-5 PZ2/15 at 593 K, 8 MPa, and NH_3 : diamine = 28.

Results of pressure and temperature optimizations are given in Figs. 2 and 3, respectively, for the H–ZSM-5 FZ21/G catalyst. They show that at 573 K the selectivity goes through a maximum around 10 MPa and that at 6 MPa there is a temperature optimum around 600 K. Surprisingly, the conversion was only slightly dependent on pressure (Fig. 2) and temperature (Fig. 3). The H–ZSM-5 PZ2/15 catalyst showed the same selectivity and conversion features. The *P–T* regime 7–12 MPa and 573–623 K therefore seems to be best suited for conversion of *m*-phenylenediamine.

TABLE 1

Physicochemical Data of the Catalysts

Type	Origin	Code name	Si/Al before	Si/Al after	SA (m^2/g)	ESA[a] (m^2/g)	PV[a] (ml/g)	Φ[a] (μm)	Activation
Mor	CFU[b]	PM1	5.2	7	492	57	0.20	2	[c]
ZSM-12	LTC[b]		35	35	390	45	0.12	1 × 3	[d]
ZSM-48	LTC		39	39	152	42	0.06	0.05 × 3	[d]
ZSM-23	LTC		49	49	180	48	0.10	2	[e]
Nu-10	LTC		39	42	140	38	0.05	1 × 10	[d]
US-Y	CFU		4.7	6	586	45	0.25	2	[c]
BETA	CFU	FB-2/G	40	45	670	50	0.20	0.5	[f]
ZSM-5	CFU	FZ21G	18	20	360	65	0.10	0.9	[d]
	CFU	PZ2/15	17	20	428	160	0.12	0.05	[d]
	CFU	PZ-8/120	120	120	355	51	0.07	2.5	[d]
	CFU	PZ-6/250	245	250	379	43	0.09	3.5	[d]
	CFU	PZ-12/420	420	424	382	42	0.08	3.5	[d]
	LTC	A1	20	23	415	52	0.20	0.2	[d]
	LTC	T1	26	37	388	19	0.19	25	[d]
	LTC	T2	26	37	379	11	0.18	50	[d]
$SiO_2 \cdot Al_2O_3$	Grace	SiAl		5					

[a] ESA, external surface area; PV, pore volume; Φ, particle size.
[b] CFU, CU Chemie Uetikon AG; LTC, Laboratory for Technical Chemistry, ETH, Zürich.
[c] 1 × 1 *M* HCl.
[d] 3 × 1 *M* HCl.
[e] 3 × 0.1 *M* HCl.
[f] 1 × 0.1 *M* HCl.

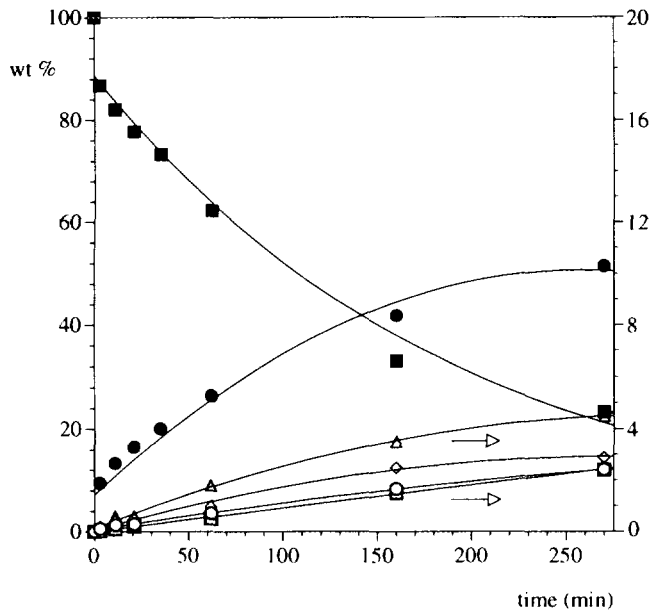


FIG. 1. Conversion of *m*-phenylenediamine at 593 K, 8 MPa, and NH_3: diamine = 28 over H–ZSM-5 PZ2/15.(■) 1,3-phenylenediamine and (●) 2-amino-6-methylpyridine (left-hand scale); (△) condensed aromatics, (◇) acetonitrile, (□) toluene, and (○) aminopyridine (right-hand scale).

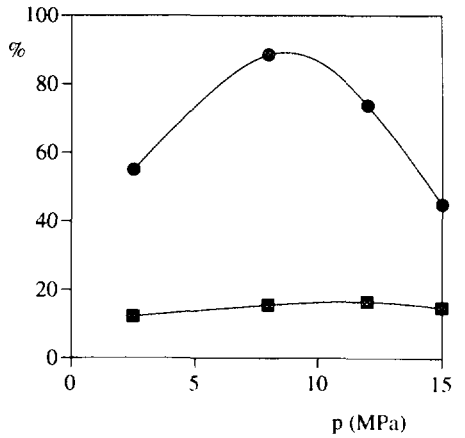


FIG. 2. Conversion of *m*-phenylenediamine (■) and selectivity for 2-amino-6-methylpyridine (●) after 4 h at 573 K as a function of NH_3 pressure over H–ZSM-5 FZ21/G.

That NH_3 is absolutely required for the transformation of arylamines into aza-aromatics was demonstrated by experiments with mixtures of NH_3 and N_2 at a total pressure of 10 MPa at 593 K. As shown in Fig. 4, conversion and selectivity decreased strongly below 6 MPa NH_3 pressure, and no 2-amino-6-methylpyridine was formed when no NH_3 was added to the reaction mixture. Use of other amines (pyridine and triethylamine) instead of ammonia did not produce any substituted pyridines. With trimethylamine, 1% 2-amino-6-methylpyridine was observed, as well as a high conversion to alkylated *m*-phenylenediamines (as with triethylamine).

Also other solid acids transformed *m*-phenylenediamine into 2-amino-6-methylpyridine. Silica–alumina (Si : Al = 5) showed 19% conversion and 64% selectivity under the same conditions as for the zeolitic catalysts described in Table 2, while NH_4Cl led to 74% conversion and 22% selectivity. Four Lewis acids ($AlCl_3$, $FeCl_3$, $SnCl_4$ and $ZnCl_2$) were tested as well. Despite their differences in acid strength, they all showed more or less the same conversion (75%) and selectivity (12–17%), as well as a high selectivity (~50%) to small (C_2–C_4) N-containing molecules.

The results in Table 2 show that zeolites with one-dimensional pore systems (ZSM-12, ZSM-48, ZSM-23, Nu-10, MOR) as well as three-dimensional pore systems (Y, BETA, ZSM-5) catalyze the transformation of arylamine to substituted pyridines. The one-dimensional zeolites showed the lowest selectivity with respect to pyridines, which suggests that either diffusional limitation in the pores plays a role or that the reaction occurs solely on the external surface. This might explain the high selectivity to condensed aromatics (quinoline, indole, and their methylated derivates) for the zeolites with the narrowest pores. Quinoline and indole are most probably formed by ring closure of by-products formed by *ortho*-alkylation of *m*-phenylenediamine. Transmethylation, which needs much space for its bimolecular transition state (22), was especially strong for the ZSM-12 and ZSM-48 zeolites, as shown by the high selectivity for "other" products in Table 2 (mainly methylated *m*-phenylenediamine and demethylated products).

The zeolites with a three-dimensional pore structure had a higher selectivity for substituted pyridines than the one-dimensional ones. Although ZSM-5 has the narrowest

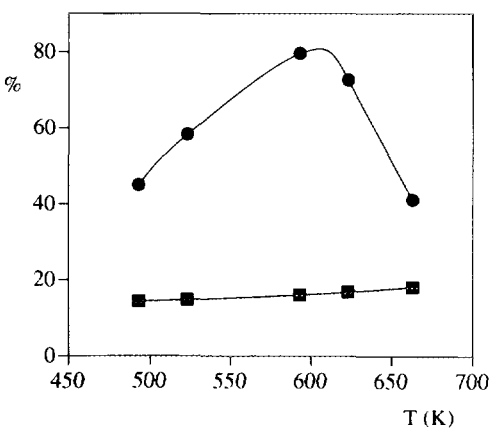


FIG. 3. Conversion of *m*-phenylenediamine (■) and selectivity for 2-amino-6-methylpyridine (●) after 4 h at 6 MPa NH_3 and NH_3: diamine = 25 as a function of temperature over H–ZSM-5 FZ21/G.

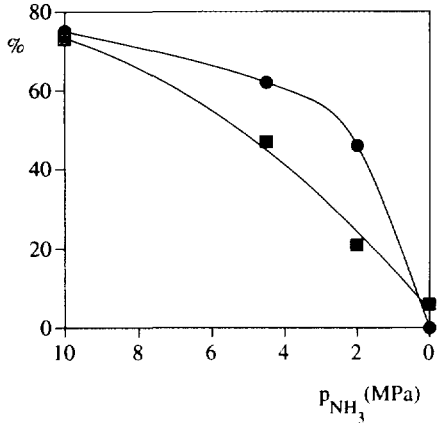


FIG. 4. Conversion of *m*-phenylenediamine (■) and selectivity for 2-amino-6-methylpyridine (●) after 5 h at 593 K, 10 MPa NH_3 + N_2 pressure, and NH_3 : diamine = 30 (at 10 MPa NH_3) over H–ZSM-5 FZ21/G.

pores of the three-dimensional zeolites studied, it had the highest selectivity. This suggests that the reaction takes place mainly inside the pores and that therefore transmethylation and the formation of condensed aromatics are suppressed. Passivation of the external surface area by reaction with triphenylsilyl chloride and subsequent calcination at 773 K did indeed decrease the relative amounts of transmethylation and condensed aromatics (Table 3). The decrease in conversion is probably due to the loss of active external surface area, as well as to blocking of pore mouths.

TABLE 2

Results of the Reaction of *m*-Phenylenediamine with Different Zeolite Catalysts after 5 h at 623 K, 10 MPa NH_3, and NH_3 : diamine = 30.

Zeolite	Conv. (%)	Selectivities (%) AMP	Anil	Cond. arom.	CH_3CN	Others
ZSM-12	12	22	6	7	5	60
ZSM-48	11	23	9	10	5	54
ZSM-23	5	26	10	30	2	32
Nu-10	8	23	12	46	1	17
MOR	10	48	9	18	5	20
USY	19	47	8	7	8	29
BETA	13	63	13	3	4	16
ZSM-5 PZ2/15	66	76	2	4	1	17
$SiO_2 \cdot Al_2O_3$	19	64	8	6	3	19
NH_4Cl	74	22		10	5	>50[a]
$AlCl_3$	75	13		14	7	>50[a]

Note. AMP, 2-amino-6-methylpyridine; anil, aniline; cond. arom., condensed aromatics; others, methylated educts and demethylated products.

[a] Unsaturated NC_2 and NC_4 molecules.

TABLE 3

Results of the Reaction of *m*-Phenylenediamine with H-ZSM-5 Catalysts of Different Si/Al Ratios and Crystallite Sizes after 5 h at 623 K, 10 MPa NH_3 and NH_3 : diamine = 30

Si/Al	Size (μm)	Conv. (%)	Selectivities (%) AMP[a]	Anil	Cond. arom.	CH_3CN	Others
20	0.05	66	76	2	4	1	17
120	2.5	14	62	3	2	1	32
250	3.5	6	66	7	3	0.4	23
424	3.0	3	65	6	9	0.2	19
23	0.2	20	73	3	5	1	18
37	25	6	62	2	2	1	33
37	50	4	66	2	1	0.5	30
20[b]	0.05	24	83	0	0	6	11

[a] AMP, 2-amino-6-methylpyridine.

[b] ZSM-5 passivated with $(C_6H_5)_3SiCl$ and calcined.

In the literature, several zeolite-catalyzed reactions have been described which benefit from the removal of aluminium from the zeolite framework (23, 24). In our laboratory such an increase in conversion was observed in the nitration of benzene (25) and in the alkylation of biphenyl with propene with mordenite as a catalyst (26). In the present case, the transformation of an arylamine to substituted pyridines, conversion decreased with decreasing aluminium content of the zeolite, as the results for the three zeolites with Si/Al ratios of 120, 250 and 420 demonstrate (Table 3). These three zeolites have similar crystal sizes and therefore crystal size effects cannot explain the steady decrease of the conversion with increasing Si/Al ratio. It thus appears that the conversion of arylamines to substituted pyridines depends upon the number of aluminium atoms, that is, upon the number of acid sites. In agreement with this, we found that for a ZSM-5 catalyst in which 98% of the protons had been exchanged for Na ions, the conversion had decreased from 66% for H–ZSM-5 to 4% for NaH–ZSM-5, while the selectivity to 2-amino-6-methylpyridine remained high at 65%.

As the results in Fig. 5 show, conversion proved to be proportional to the reciprocal of the crystallite size. This means either that the reaction occurs mainly at the external surface of the zeolite crystallites or that there is strong diffusional limitation in the zeolite pores. The first possibility must be rejected because, as mentioned above, after surface passivation the catalyst is still active and more selective. Diffusional limitation may explain the linear relationship between conversion and inverse crystal diameter. This follows because, if the Thiele modulus Φ is larger than 3, the effectiveness factor η of the catalyst is

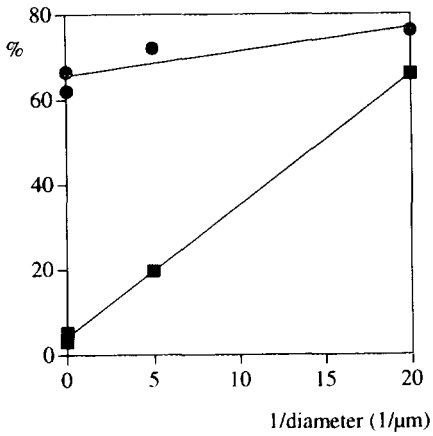
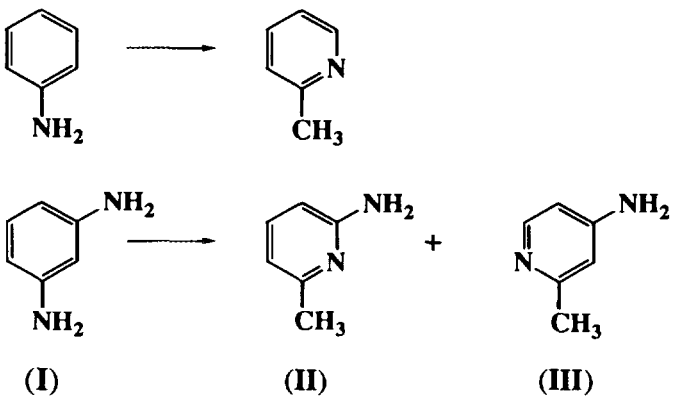


FIG. 5. Conversion of *m*-phenylenediamine (■) and selectivity for 2-amino-6-methylpyridine (●) after 5 h at 623 K, 10 MPa NH_3, and NH_3: diamine = 30 over H–ZSM-5 catalysts with different crystallite sizes (PZ2/15, A1, T1, and T2).

proportional to the inverse of the Thiele modulus ($\eta \approx \Phi^{-1}$), which in turn is proportional to the crystal length ($\Phi = L(k/D)^{1/2}$) (27).

Scope of the Reaction

The only pyridine-type products of the reaction of aniline and *m*-phenylenediamine are those that can be thought of having been formed by an interchange of the N atom by a C atom from the ortho position of the benzene ring (Table 4):



Whereas Chang and Perkins reported (5) conversions of aniline of 10–20% and selectivities to α-picoline of 30–50% at 783 K, 3 MPa, NH_3: aniline = 8 and with H–ZSM-5 as a catalyst in a plugflow reactor at WHSV (aniline) = 1.1 h^{-1}, we obtained somewhat lower conversions after 4 h in a batch reactor at 623 K, 6 MPa, NH_3: aniline = 25, with 0.5 g H–ZSM-5 catalyst and 2.5 g aniline (Table 4). A similar conversion, but with higher selectivity, was reported by Le Blanc and Puppe (9) in their experiment in a flow reactor at 653 K, 19 MPa, and NH_3: aniline = 60.

TABLE 4

Results of the Reaction of Aniline after 5 h at 6 MPa and NH_3: diamine = 25 over H–ZSM-5 (FZ21G)

Temp. (K)	Conversion (%)	Selectivities (%)				
		α-picoline	Arom.	Cond. arom.	CH_3CN	Coke
623	6	55	5	17	4	2
723	4	11	4	28	8	2

Note. Arom., benzene + toluene; cond. arom., condensed aromatics (quinoline, indole, and their methylated products).

In addition to the main product α-picoline, aromatics (benzene and toluene), condensed aromatics (quinoline, indole, and their methylated products), cracking products such as acetonitrile, as well as *N*-methylaniline and toluidines were observed. The amount of coke on the final catalyst was determined as the difference between the decreases in mass in the thermogravimetric analyses in air (burn-off of coke as well as of heavy molecules) and in nitrogen (desorption of heavy molecules).

As reported before (9, 10), and as shown in Tables 2 and 3, much higher conversions and selectivities can be reached in the transformation of *m*-phenylenediamine to pyridine-type products. As shown in Table 2, after 5 h in a batch reactor at 623 K, 10 MPa, with 0.5 g H–ZSM-5 and NH_3: aromatic diamine = 30, 66% conversion of *m*-phenylenediamine and 76% selectivity to 2-amino-6-methylpyridine (**II**) is reached. The most abundant by-products were the higher aromatics, acetonitrile, toluene, and 2-aminopyridine. In their experiments at the higher pressure of 19 MPa, but lower WHSV of 0.02 g/ml · h, Le Blanc and Puppe observed lower conversions, but higher selectivities. Furthermore, they also obtained 2-methyl-4-aminopyridine (**III**) as a product (9).

In order to find out whether the apparent N-*ortho* C exchange pattern in the transformation of aromatic amines to substituted pyridines also holds for other aromatic amines, we studied the reactions of *o*- and *p*-phenylenediamine, toluidines, naphthylamines, and anthracylamines as well. Experiments with *o*- and *p*-phenylenediamine under similar conditions as with *m*-phenylenediamine (600 K, 8 MPa NH_3, 0.5 g H–ZSM-5 and 2.5 g diamine, 5 h) showed almost no isomerization to methyl-substituted pyridines. Conversion for *o*-phenylenediamine was 28% and no pyridine-type molecules could be detected. With *p*-phenylenediamine the conversion was very high (92%), but the selectivity to 2-amino-6-methylpyridine (**II**) and 2-methylpyridine was below 1%. Instead, a very large

TABLE 5

Results of the Reactions of Toluidines after 4 h at 600 K, 8 MPA, and NH_3 : toluidine = 32 over H–ZSM-5 PZ2/15

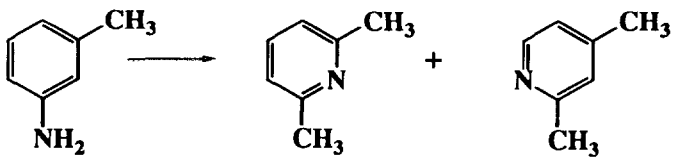
		Selectivities (%)					
Tol	Conv. (%)	Lut coll	Tol isom	Xyl	Anil	Cond. arom.	Other
o	10	5	13	6	13	32	31
m	17	44	36	7	3	1	9
p	20	6	61	10	19	1	3

Note. Lut, lutidine (dimethylpyridine); coll, trimethylpyridine; tol, toluidine (methylaniline); Xyl, xylidine (dimethylaniline); Anil, aniline; cond. arom., condensed aromatics.

number (>50) of products, but no other substituted pyridines, were detected in the gas chromatogram.

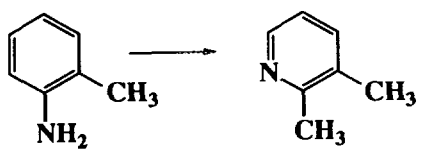
The results of the batch reactions of *o*-, *m*- and *p*-toluidine at 600 K, 8 MPa, NH_3 : toluidine = 32, and with H–ZSM-5 as catalyst, are presented in Table 5. The results show that the conversion is low, just a factor of 2 (*o*-toluidine) to 4 (*p*-toluidine) better than for aniline. A large part of the conversion is, however, due to isomerization of one toluidine to the other two isomers and to transmethylation leading to aniline and xylidines. The yield of substituted pyridines (lutidine and collidine) is therefore about as low as that for the aniline transformation.

Although the yields of substituted pyridines from the toluidines are low, they suffice to show that also in this case they are formed exclusively by N-*ortho* C exchange. For instance, the only substituted pyridines formed from *m*-toluidine are 2,4-lutidine (**V**) and 2,6-lutidine (**IV**), as well as 2,4,6-collidine as a result of subsequent transmethylation (Table 6).



(IV) **(V)**

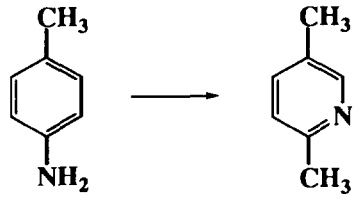
The main pyridine-type product formed from *o*-toluidine, 2,3-lutidine (**VI**), is a result of N-*ortho* C exchange as well:



(VI)

The other two pyridine-type products of *o*-toluidine, 2,4-lutidine (**V**) and 2,6-lutidine (**IV**), are most likely formed by isomerization of *o*-toluidine to *m*-toluidine and subsequent transformation to the 2,4- and 2,6-lutidines.

The pyridine-type products from *p*-toluidine look at first glance to be a complex mixture (Table 6). However, the strong isomerization of *p*-toluidine to *o*- and *m*-toluidine explains the subsequent formation of 2,3-lutidine, and of 2,4- and 2,6-lutidine and 2,4,6-collidine, respectively. The remaining 2,5-lutidine (**VII**) is then the direct result of a N-*ortho* C isomerization of *p*-toluidine:



(VII)

Thus, all three toluidines lead to lutidines and 2,4,6-collidine by the exclusive N-ortho C interchange in combination with isomerization of the toluidines.

Note that the isomer distribution of the toluidines in the reaction of *p*-toluidine showed a higher content of *o*-toluidine than of *m*-toluidine, suggesting that the isomerization has occurred inside the zeolite pores. The isomerization occurs via a 1, 2 methyl-shift mechanism (28, 29), which in the case of *p*-toluidine should lead to more *m*-toluidine than *o*-toluidine. The much slower diffusion of *m*-toluidine as compared to *o*-toluidine out of the pores explains, however, why more *o*-toluidine is observed in the reaction mixture outside the zeolite. This example of disguised kinetics is analogous to that of the isomerization of xylenes, with the slower diffusion of *m*-xylene (30).

The aza-aromatic products of the reactions of α- and β-naphthylamine are presented in Table 7, and those of α- and β-amino-anthracene in Table 8. They are the result of N-ortho C interchange in combination with equilibration between α- and β-naphthylamine. Thus 1-methylisoquinoline (**IX**) is the direct product from α-naphthylamine (**VIII**)

TABLE 6

Lutidines, Collidine, and Toluidine Isomers Formed in the Reactions of Toluidines at 600 K and 8 MPa

	Selectivities (%)							
	Lutidines					Toluidines		
Toluidine	2,3	2,4	2,5	2,6	2,4,6-Collidine	*o*	*m*	*p*
o	2.9	0.5	0	1.4	0	—	12	1
m	0	12.8	0	6.5	25	7	—	29
p	0.2	1.0	1.2	1.5	1.7	43	18	—

TABLE 7

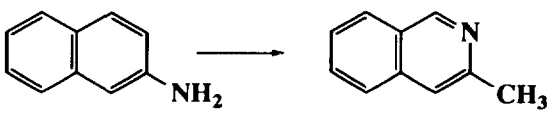
Results of the Reactions of Napthylamines at 10 MPa and NH_3 : amine = 18

Naphthyl-amine	Catalyst	T (K)	Conv. (%)	Selectivities (%)[a] 1-Me-IQ	3-Me-IQ	2-Me-Q	Isom.	Cond. arom.
α	ZSM-5	573	6	12			0	42
α	ZSM-5	673	16	28			25	29
α	BETA	573	28	27	2		25	21
α	BETA	623	40	16	4	2	35	11
α	Pass β[b]	593	9	71			7	5
β	BETA	593	19	3	15		45	14
β	BETA	623	50	2	7	1	45	18

[a] 1-Me-IQ, 1-methylisoquinoline; 3-Me-IQ, 3-methylisoquinoline; 2-Me-Q, 2-methylquinoline; Isom., other naphthylamine isomer.
[b] Pass, passivated.

(VIII) **(IX)**

and 3-methylisoquinoline (**XI**) is the direct product of β-naphthylamine (**X**):



(X) **(XI)**

Isomerization of α- to β-naphthylamine explains why 3-methylisoquinoline (**XI**) is a by-product in the reaction of α-naphthylamine. Analogously, 1-methylisoquinoline (**IX**) is a by-product in the reaction of β-naphthylamine. It should be noted that almost no 2-methylquinoline was produced.

As the results in Table 7 show, higher conversions were obtained with the 12-ring zeolite Beta than with the 10-ring zeolite ZSM-5. This may be due to diffusion limitations of the substituted naphthalenes in the 10-ring pores. Therefore, the experiments with aminoanthracene (Table 8) and other substituted naphthalenes (Table 9) were performed with zeolite H-BETA.

Chang and Perkins discovered the isomerization of aniline to α-picoline when they allowed phenol to react with high-pressure ammonia in a flow reactor (4). In addition to aniline they observed α-picoline. Also Le Blanc and Puppe reported that a phenol could be used instead of an arylamine (9). At 593 K and 19 MPa they obtained 2-amino-6-methylpyridine from resorcinol (*m*-dihydroxybenzol). We have therefore tried to convert α-naphthol, β-thionaphthol, 1-chloronapthalene, and 1-bromonaphthalene to aza-aromatic products; however, we did not have much success, as the results collected in Table 9 demonstrate. Although α-naphthol had reacted with high conversion, the reaction had stopped more or less at the α-naphthylamine stage. Only 3% selectivity to 1-methylisoquinoline was obtained. The other substituted naphthalenes, β-thionaphthol, 1-chloronapthalene, and 1-bromonaphthalene, showed a high conversion also, not to the corresponding naphthylamine, but rather mainly to naphthalene. Only minor amounts of methylisoquinoline were

TABLE 8

Results of the Reactions of Anthracylamines after 5 h at 603 K, 10 MPa, NH_3 : amine = 14 and over H-BETA

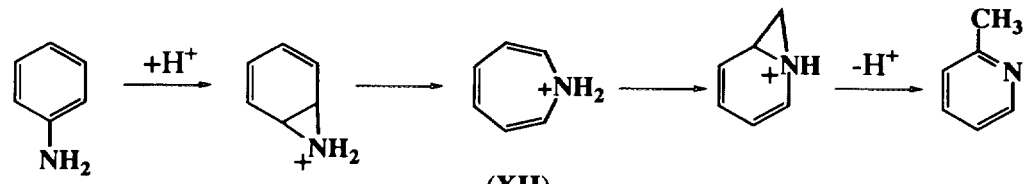
Anthracyl amine	Conv. (%)	Aza aromatic	Selectivities (%) Anthracene	CH_3CN	Others	Isomer
α	41	29[a]	4	19	24	0
β	39	17[b]	23	0.2	7	6

[a] 1-methyl-2-aza-anthracene.
[b] 2-aza-3-methylanthracene.

formed. Attempts to cause chlorobenzene to react with ammonia (8 MPa) at 573 K in the presence of H–ZSM-5 were unsuccessful. No conversion could be detected.

DISCUSSION

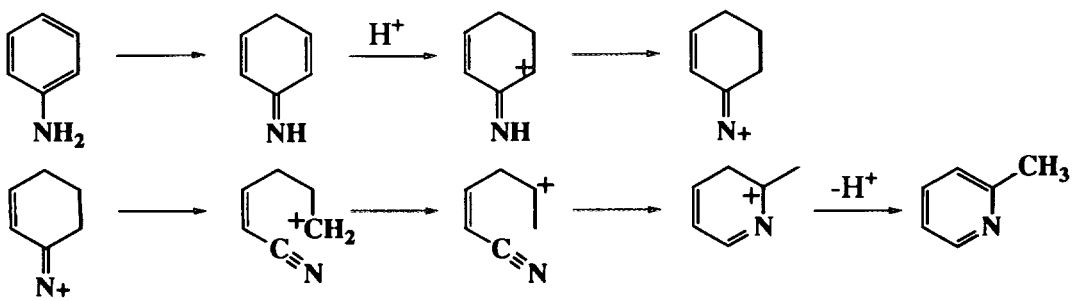
In all cases the aromatic amines isomerized to aza-aromatic compounds with a methyl substituent ortho to the N atom when an acid catalyst, a relatively high temperature and a high NH_3 pressure were applied. The first question to be answered is what is the mechanism of this curious isomerization reaction? Chang and Perkins proposed that the reaction of aniline to α-picoline occurs via ring enlargement to an aza-7-ring (**XII**), from which a carbon atom is extruded (4, 6):



(XII)

This reaction sequence might seem a plausible mechanism for the formation of α-picoline from aniline. However, the 7-ring mechanism is incapable of explaining why the toluidines, *m*-phenylenediamine, naphthylamines, and anthracylamines react exclusively via N-*ortho* C exchange of the N atom in the aromatic amine with a ring carbon atom in the ortho position. Assuming that carbon extrusion from the aza-7-ring (**XII**) takes place adjacent to the aza atom, as suggested by the exclusive formation of α-picoline, the predicted products for *m*-toluidine are 2,3-, 2,4-, and 2,5-lutidine (2,4- and 2,6-lutidine are observed, Table 6). For *m*-phenylenediamine the predicted products are 2-methyl-3-aminopyridine, 2-methyl-4-aminopyridine, and 2-methyl-5-aminopyridine, whereas 2-methyl-4-aminopyridine and 2-amino-6-methylpyridine are observed. Also for the reaction of α-naphthylamine the wrong isomer, 3-methylisoquinoline instead of 1-methylisoquinoline (Table 7), is predicted. In addition to not predicting the reaction products, the 7-ring mechanism does not give an explanation for the need of the high NH_3 pressure either.

Another mechanism proposed by Chang and Perkins (6) is based on an intramolecular Ritter reaction, the reaction of a carbenium ion with the N atom of a cyano group:



(XIII)

The necessity for a nitrenium ion (**XIII**) and the high strain in the intramolecular Ritter reaction step make this mechanism very unlikely. Also, the formation of linear compounds such as unsaturated nitriles would be expected in the pentasil-type zeolite, because of steric constraints in the transition state. In addition, the mechanism does not explain the need for a high NH_3 pressure and predicts the wrong products. Thus only 2-methyl-6-aminopyridine (**II**) is predicted from *m*-phenylenediamine, 2,5-dimethylpyridine (**VII**) from *o*-toluidine, only 2,6-dimethylpyridine (**IV**) from *m*-toluidine, 3-methyl-isoquinoline (**XI**) from α-naphthylamine, and 1-methylisoquinoline from β-naphthylamine.

Another mechanism which, instead of the Ritter reaction, involves an intramolecular reaction of an enamino group with a C≡C triple bond is, however, capable of explaining the N-*ortho* C isomerization in most of the reactions studied. In this mechanism ammonia is added

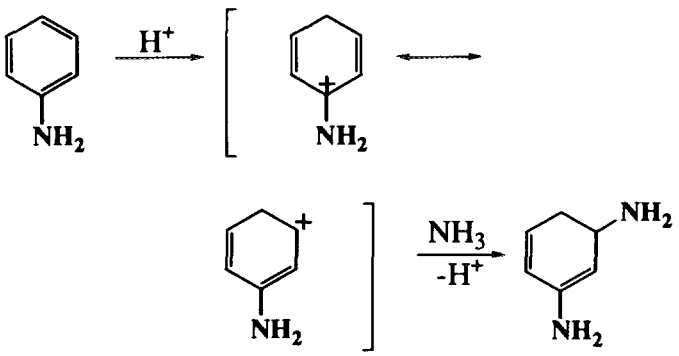
TABLE 9

Results of the Reactions of Substituted Naphthalenes (X-$C_{10}H_7$) after 5 h at 573 K, 10 MPa, and NH_3 : X-$C_{10}H_7$ = 17 over H-BETA

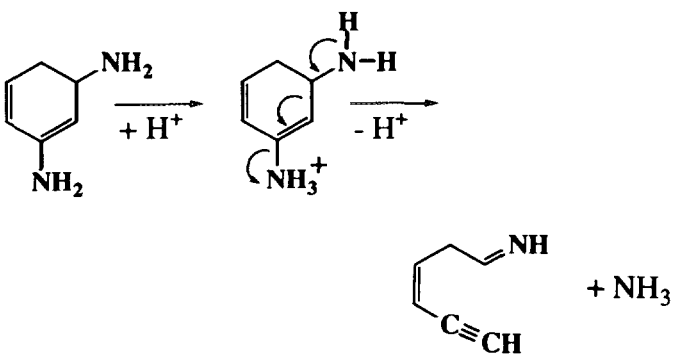
		Selectivities (%)		
X	Conv. (%)	Naphthylamine	Naphthalene	Aza-arom.
α-OH	99	90[a]	0	3[b]
β-SH	97	10[c]	87	0.7[d]
α-Cl	94	1[a]	93	0
α-Br	99	1[a]	97	0.1[b]

[a] α-naphthylamine.
[b] 1-methylisoquinoline.
[c] β-naphthylamine.
[d] 3-methylisoquinoline.

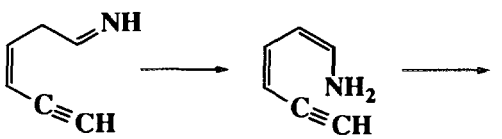
to the aromatic ring in the meta position first:



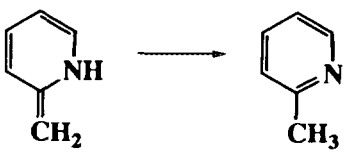
This acid-catalyzed reaction sequence is analogous to the one suggested by Rieche and Seeboth to explain the Bucherer reaction (31). In a subsequent step the ring is opened, the original amino group is extruded and a C≡C triple bond is formed:



A similar 1,3 substitution (addition on the 3 position and elimination on the 1 position) has been proposed by Van der Plas and co-workers for the reaction of 4-chloro-2-alkylpyrimidine with KNH_2 in ammonia to give 4-methyl-2-alkyl-1,3,5-triazine (32, 33), and proof for the existence of open-chain polyunsaturated compounds in that reaction has been given (34). The alkyno-imine (**XIV**) intermediate formed can undergo a ring closure to α-picoline:

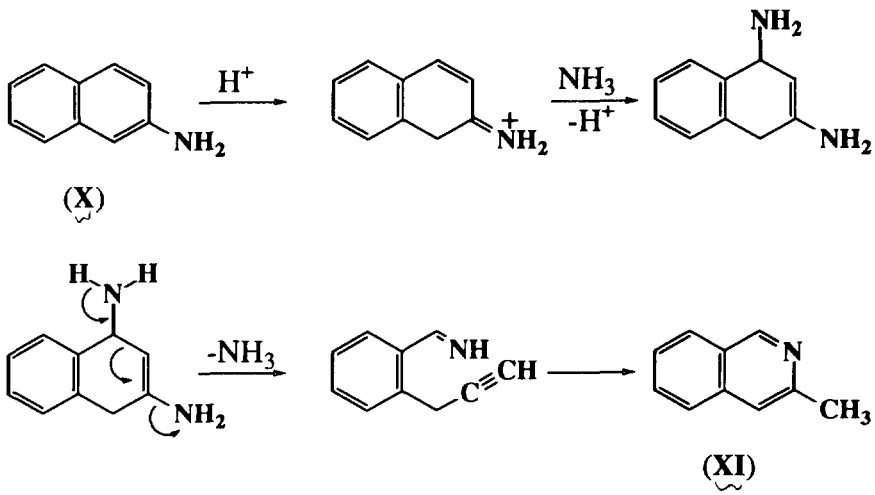


(XIV)



This mechanism explains that an acid catalyst and a high ammonia pressure are required for the formation of the ammonia adduct and that the isomerization of the arylamine occurs via N-*ortho* C exchange. However, it is clear why one should speak of *apparent* N-*ortho* C exchange, since actually in this mechanism it is the N atom from NH_3, and not the N atom from the amino group, which ends up in the ring. The relatively high reaction temperature can be explained by this mechanism by the necessity of having both a high ammonia pressure and acid catalytic sites. At low temperature the acid sites bind ammonia strongly and only at high temperature will some acid sites become free by desorption of ammonia. In a future publication we will show that, indeed, when using zeolites with a lower acid strength, the NH_3 is less strongly bonded and can desorb already at lower temperature, so that the reaction can be performed more selectively at lower temperature (35).

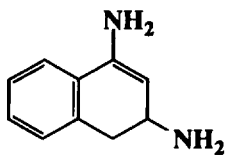
The only reaction which needs some adaptation to be explained by this mechanism is the transformation of β-naphthylamine (**X**) to β-methylisoquinoline (**XI**):



(X)

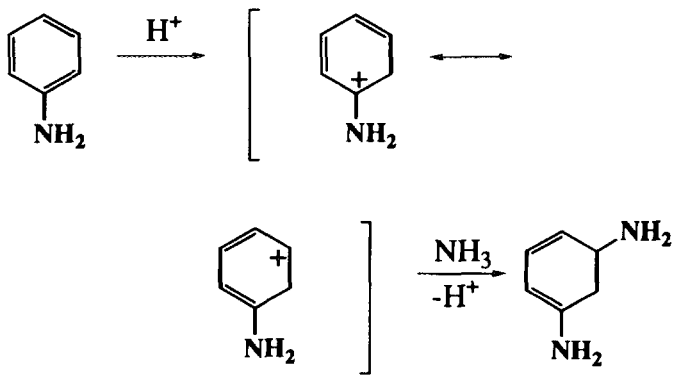
(XI)

A problem in this mechanism is that the ammonia adduct, which is required for the ring opening and subsequent ring-closure reactions, contains an isolated double bond which is not conjugated to the benzene ring. This double bond should shift rapidly to give

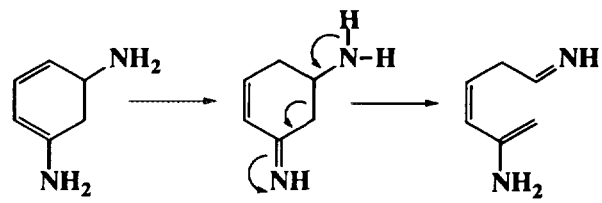


which can ring open and subsequently close the ring by the intramolecular reaction of the imino group with the C≡C triple bond, but in that case the product would be 1-methylisoquinoline and not 3-methylisoquinoline.

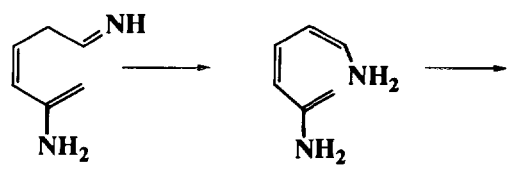
However, another mechanism can explain all the observed reaction products, including the product from β-naphthylamine. This mechanism has in common with the foregoing the fact that first an ammonia adduct of the arylamine is formed as an intermediate:

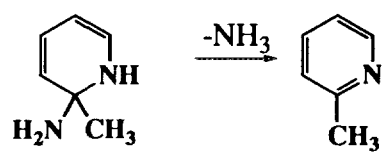


but ring opening occurs through a reverse aldol-type reaction:

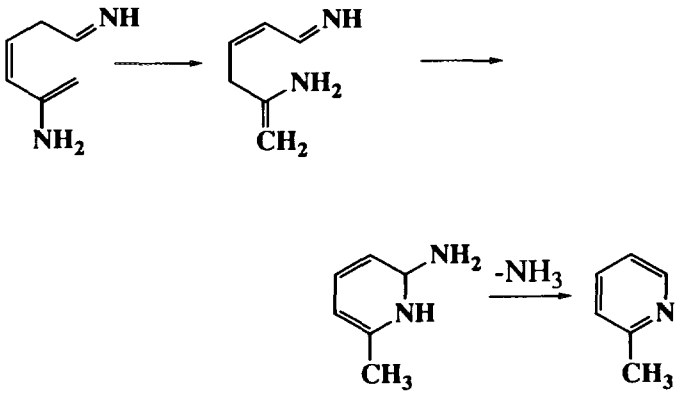


Ring closure occurs by addition of the newly introduced amino group to a C=C-double bond:



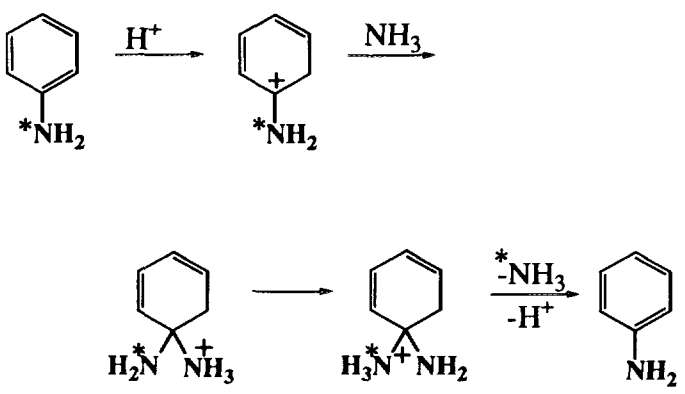


or by addition of the original amino group to an imino group:



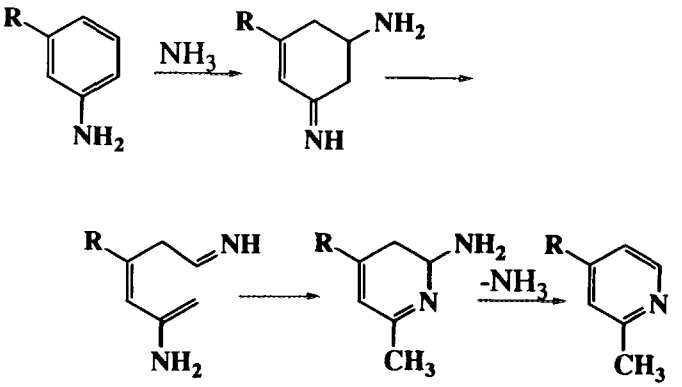
In both cases, the aza-aromatic is formed by elimination of NH_3 in the final step.

The ordering of the carbon atoms is the same in both cases, and only the origin of the nitrogen atom is different. In the first type of ring closure it is the nitrogen atom of the added NH_3 which ends up in the ring, whereas in the second type of ring closure the nitrogen atom of the original arylamine becomes the aza-atom. We thought that labelling the nitrogen atom of the arylamine would allow us to find out which nitrogen atom becomes the aza-atom. Reaction of commercially available ^{15}N-aniline with normal NH_3 was inconclusive, however, since after 4 h at 623 K and 9 MPa with $^{14}NH_3 : C_6H_5{-}^{15}NH_2 = 30$ the reaction mixture contained not only 2% α-picoline (^{14}N), but also 95% ^{14}N-aniline. Apparently an almost complete N-exchange had occurred between $^{14}NH_3$ and ^{15}N-aniline, catalyzed by the solid acid.



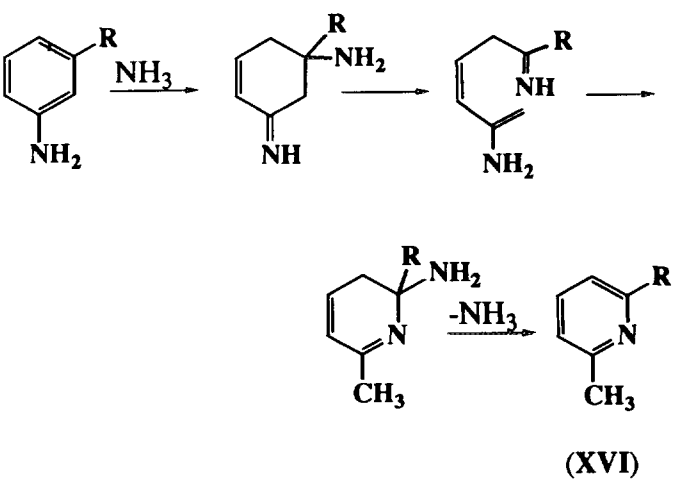
This $^{15}N{-}^{14}N$ exchange between aniline and NH_3 precluded a conclusion about the origin of the aza atom. In the future we will try to perform the reaction with ^{15}N labelled *m*-phenylenediamine and $^{14}NH_3$. Hopefully in that case the transformation of the arylamine into the substituted pyridine will be faster than the $^{15}N{-}^{14}N$ exchange of *m*-phenylenediamine.

The above mechanism, with opening of the arylamine ring through a reversed aldol-type reaction, predicts the formation of 4-substituted-2-methylpyridines (**XV**) from *meta*-substituted aniline (e.g. *m*-toluidine and *m*-phenylenediamine):



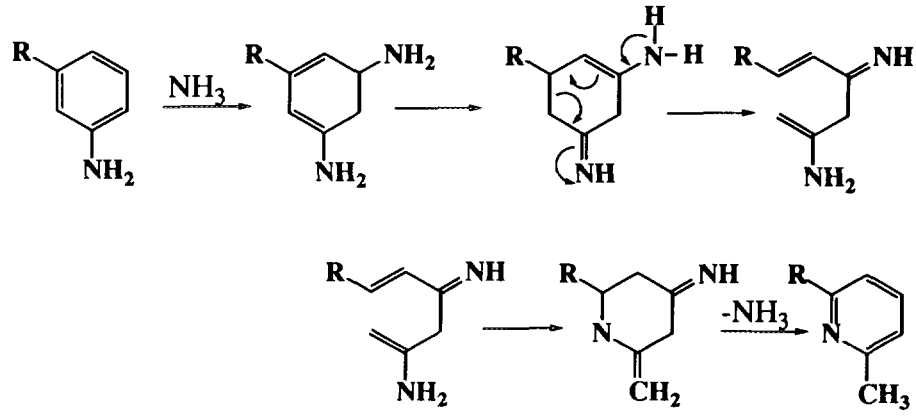
(XV)

To explain the formation of 6-substituted-2-aminopyridines (**XVI**) ipso addition of NH_3 has to be assumed:



(XVI)

or, alternatively, ring opening might take place via a reversed Michael-type reaction:



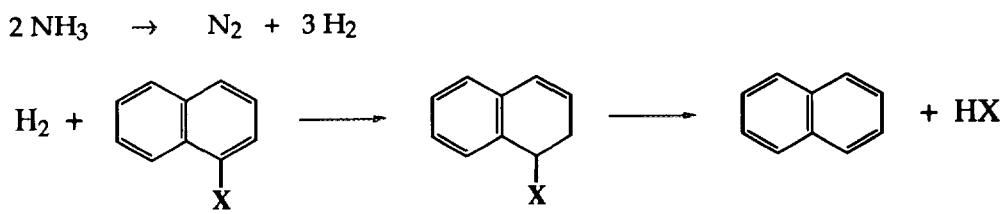
(XVI)

The formation of 2,3-lutidine (**VI**) from *o*-toluidine and 2,5-lutidine (**VII**) from *p*-toluidine can be explained with the reverse aldol-type reaction, as well as with a reverse Michael-type reaction. However, the formation of 1-methylisoquinoline (**IX**) and 3-methylisoquinoline (**XI**) from α- and β-naphthylamine, respectively, can be explained only by the reverse aldol-type reaction. The improbability of addition of NH_3 to a bridge-head carbon atom explains why no 2-methylquinoline is formed directly from β-naphthylamine.

The 1,3 NH_2 substitution, with ring opening to an alkyno-imine (**XIV**) and ring closure, and the reverse aldol and reverse Michael reactions require that addition of NH_3 to the aromatic ring takes place. This is much easier for naphthylamine than for aniline, since the energy of aromatic stabilization per ring is smaller in naphthalene than in benzene. This explains the higher conversions for the naphthylamines. The conversion of aniline is limited by thermodynamics, since aniline is more stable (ΔG_f^{298} = 10 kJ/mol) than α-picoline (36–38). The high conversions which were obtained with *m*-phenylenediamine suggest that for this molecule the isomerization reaction is exothermic. This would imply that conversion might be raised by going to lower temperatures if an active enough catalyst could be found. The other advantage of a lower reaction temperature would be that the transalkylation and methyl-shift side reactions would be suppressed. Because thermodynamic data are available only for the aniline–picoline couple, we plan to perform ab initio calculations of the energies of some of the other arylamine-methyl-aza-aromatic couples which we investigated.

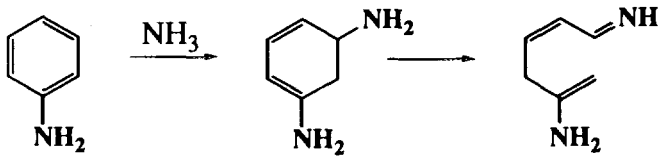
Although we carefully looked for dimethylpyrimidine products, we never observed them in the *m*-phenylenediamine reaction, or in the reaction of 2-methyl-6-aminopyridine, which we carried out as a check. This suggests that 2-methyl-6-aminopyridine is more stable than dimethylpyrimidine and that the reaction stops after the first N-*ortho* C exchange reaction. That a pyrimidine is formed by reacting 2,6-dibromo-pyridine with KNH_2 (39), and that triazines are formed by reacting bromo-substituted pyrimidines with KNH_2 in liquid NH_3 (32, 33), is due to the presence of a bromo leaving group (40).

Whereas the hydroxyl groups of naphthol and phenol were converted to the corresponding amino groups under high NH_3 pressure and in the presence of an acid catalyst, the sulfhydryl and halogen substituents were removed from naphthalene under the same conditions. An explanation for the SH and *X* removal might be that hydrodesulfurization and hydrodehalogenation have occurred with the help of hydrogen formed via decomposition of NH_3 at the steel reactor wall. Hydrodesulfurization of thionaphthol is known to be a fast reaction.

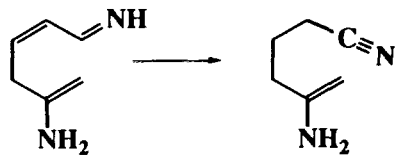


In accordance with this explanation, chlorobenzene was unreactive under reaction conditions.

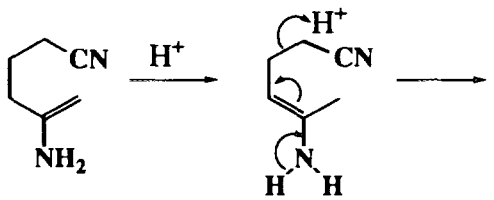
Acetonitrile and other small nitrogen-containing molecules are by-products in all reactions studied. An explanation for the formation of such products might go along lines similar to that of the main aza-aromatic isomerization product. Once a ring-opened intermediate is formed after NH_3 addition,



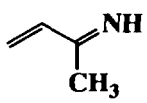
it may isomerize to a nitrile,



which can undergo fragmentation (a reverse Michael reaction),



CH_3CN +



(XVII)

giving acetonitrile and the imine of methyl vinylketone (**XVII**).

Besides decomposition to small molecules, isomerization by a methyl shift and transmethylation are side reactions which suppress the selectivity of the desired arylamine to aza-aromatic reaction. By their occurrence, these reactions are proof that acid sites are present under reaction conditions, since methyl shifting and transmethylation require acid sites. Because of the rather high temperature needed for the reaction of arylamine to substituted pyridine, these side reactions are quite fast and may substantially lower the selectivity of the required reaction. Isomerization by methyl shifts has been reported to be more important for toluidines than for picolines (29), suggesting that in our case this reaction is more important for the arylamine reactants than for the aza-aromatic products. Transmethylation may occur with reactants as well as with products. Methyl-group isomerization and transmethylation may lead to many side products and to a complex reaction mixture, which is difficult to separate. Lowering of the reaction temperature, by the use of less acidic zeolite, should diminish the deleterious effects of these side reactions. Furthermore, pore size restrictions should suppress a transmethylation, since its transition state consists of a bimolecular complex (22).

CONCLUSIONS

Besides the reactions of aniline to α-picoline and of *m*-phenylenediamine to 2-methyl-6-aminopyridine and 2-methyl-4-aminopyridine, we found that also toluidines, naphthylamines, and anthracylamines react according to the same N-*ortho* C exchange reaction when subjected to a high NH_3 pressure and elevated temperature in the presence of an acid catalyst. Zeolites with a three-dimensional pore structure, especially H–ZSM-5, performed best, which is explained by a decrease of the number of possible intermolecular reactions of the highly unsaturated intermediates to condensed aromatics, which block the pores. Passivation of the outer surface of the zeolites did indeed have a positive influence on the selectivity. Optimization of the process conditions showed that rather drastic conditions, about 600 K and 10 MPa NH_3, are required. Without NH_3 no reaction of arylamines to aromatic heterocycles takes place at all.

These experimental facts cannot be explained by the two mechanisms which had been proposed before. Neither the required high NH_3 pressure nor the right reaction products are explained by the 7-ring mechanism and by the mechanism which involves an intramolecular Ritter reaction step. Two new reaction mechanisms are capable of explaining all observations. In both mechanisms, NH_3 is added to the aromatic ring of the arylamine first. This explains the required high NH_3 pressure and the easier reaction with naphthylamine. In a subsequent step, a ring opening takes place, either to an alkyno-imine or an enamino-imine intermediate. Intramolecular reaction of the C,C triple bond with the imino group, or of the enamine with the imino group, leads to ring closure. NH_3 elimination then gives the methyl-substituted aromatic heterocycles. In both mechanisms acid catalysis is required. This, in conjunction with the required high NH_3 pressure, explains why a relatively high reaction temperature is needed. At low temperature all acid sites are occupied by NH_3, and only at elevated temperature will enough NH_3 desorb and will acid sites become available for catalysis. Unfortunately, a high temperature also favors acid-

catalyzed side reactions such as methyl shift and transmethylation. These lead to many side products and to separation problems. Our future efforts will therefore concentrate on less acid catalysts (35), which will adsorb NH_3 less strongly and therefore will not require high temperatures for NH_3 desorption. The use of a plug-flow reactor, instead of autoclaves, might also diminish side reactions. Another question which remains to be answered by future research is that of which of the two alternative mechanisms is operative. This can be answered only by isotopic labelling of carbon atoms. The question of whether the amine or the ammonia N atom is incorporated into the aromatic heterocycle will be answered only if the scrambling of the N atoms can be slowed down.

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