HYDROGENOLYSIS OF NITROGEN-CONTAINING COMPOUNDS ON A COBALT–MOLYBDENUM CATALYST

Mirko Černý

Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague-Suchdol

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A sulphidized cobalt–molybdenum catalyst on Al_2O_3 has been used to study hydrogenolysis of pyridine, piperidine, quinoline and their methyl derivatives. In reaction mixtures were identified the compounds which contribute to the knowledge of the mechanism of hydrogenolysis. The cleavage of 2-methylpiperidine ring takes place between the nitrogen atom and the methylene groups and not between the nitrogen atom and the carbon substituted with the methyl group. The amount of hydrogenolysis products decreases in the series pyridine, 2-methylpyridine, 2,6-dimethylpyridine and 2,4,6-trimethylpyridine, *i.e.* with the increasing number of the methyl groups bonded to the ring.

The removal of nitrogen- and sulphur-containing compounds from individual fractions by means of hydrodesulphuration and hydrodenitrogenation plays an important role in the industraial processing of petroleum and petroleum products. The above compounds act not only as catalytic poisons for the majority of the catalysts, but affect unfavourably also the quality of final products. Nitrogen-containing substances belong to various types, from simple amines and pyridine, quinoline, isoquinoline, indole, pyrrole and carbazole derivatives to heterocycles containing two or more nitrogen atoms and oxygen- and sulphur-containing heterocyclic compounds. In addition to hydrodenitrogenation of petroleum fractions, hydrogenolysis of the well defined starting compounds has been studied in many laboratories. These studies have been carried out not only to analyse reaction mixtures but also to examine the kinetics of the reaction and to elucidate its mechanism.

Hydrogenolysis of pyridine and piperidine with the use of the reduced cobalt–molybdenum catalyst in a flow reactor was studied by Sonnemans[1-5]. The sulphidized cobalt–nickel–tungsten–molybdenum catalysts were employed by Satterfield[6-8], Mc Ilvried[9] and by other authors[10-12]. Of the other catalysts, Raney nickel[13], WS_2 (ref.[14]), MoS_3(ref.[15]) and MoS_2 (refs [16,17]) were used to hydrogenolyse pyridine in an autoclave. As found by the above authors, the products of hydrogenolysis of pyridine contained ammonia, 1-methylpiperidine, 1-ethylpiperidine, 1-propylpiperidine, 1-butylpiperidine, 1-pentylpiperidine, 1-cyclopentylpiperidine, 1,5-dipiperidinopentane, pentylamine, dipentylamine, tripentylamine, cyclopentylamine and butyronitrile. Of the hydrocarbons, pentane, pentenes, cyclopentane, cyclopentene, decane and 1,5,9-decatriene were found to be present in the reaction mixture.

The complex course of the reaction is indicated also by the fact that the amount of the still unidentified compounds formed during hydrogenolysis of pyridine rapidly increases with increasing temperature and at 340°C it amounts to 77% (refs[16,17]). The complete hydrodenitrogenation of pyridine, *i.e.* its cleavage to pentane and ammonia, takes place, however, only on prolonged heating to temperatures around 400°C (ref.[18]).

Hydrogenolysis of quinoline was studied with the use of MoS_2 and MoS_3 (refs[16,19–21]) or cobalt, nickel and molybdenum oxides (refs[22–26]) as catalysts. Compared to pyridine, higher temperatures and longer reaction times are needed to hydrogenolyse quinoline. In addition to the compounds formed by hydrogenation of quinoline, the reaction products were also aniline, 2-methylaniline, 2-ethylaniline, 2-propylaniline, N,N-dimethylaniline, N-ethylaniline, the derivatives of indole, benzene, toluene, ethylbenzene, propylbenzene, methylcyclopropane, alkylquinolines, isoquinoline, γ-phenylpropylamine and a number of unidentified substances.

Within the framework of the broader study of the action of a cobalt–molybdenum catalyst the aim of the present work was to examine in more detail the course of the cleavage of six-membered rings containing nitrogen and the effect of the methyl substituents upon this cleavage. The model compounds chosen for this study were pyridine, piperidine, 2-methylpyridine, 2,6-dimethylpyridine, 2,4,6-trimethylpyridine, quinoline and 2-methylquinoline. Reaction mixtures were analysed by gas–liquid chromatography using various stationary phases and authentic samples and by mass spectrometry combined with gas chromatography. In this case several compounds have been identified which contribute to the knowledge of the mechanism of the hydrogenolysis studied.

TABLE I

Composition of Reaction Mixture After Hydrogenolysis of Pyridine (in %)
A in decane, 255°C, 3 h; B in cyclohexane, 255°C, 4·5 h.

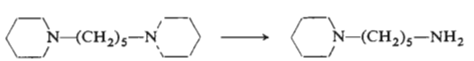
Substances	A	B
Pyridine + piperidine + 1-methylpiperidine	91	84
1-Ethylpiperidine	4	7
1-Propylpiperidine	2	3
1-Pentylpiperidine	2	4
1-Cyclopentylpiperidine	1	2
1-Butylpiperidine	0·1	0·2

Hydrogenolyses of pyridine were made both in inert solvent and in its absence (only with the present catalyst). Decane and cyclohexane were tested as solvents. With regard to their critical temperature (T_c = 281°C) cyclohexane could be used only to 250°C; by contrast to it, decane, the critical temperature of which is 346°C, made it possible to use temperatures around 300°C. After hydrogenolysis in solvents, basic compounds were separated by usual procedure from neutral portions and analysed gas chromatographically. The composition of the reaction mixture after hydrogenolysis of pyridine is given in Table I.

When hydrogenolysis of pyridine itself was made without solvent, the great amount of hydrogen was consumed by hydrogenation of pyridine ring and the hydrogenolysis proceeded only to a small extent. In addition to the unreacted pyridine, the reaction mixture contained piperidine and a small amount of substances formed by hydrogenolysis. With respect to the fact that the first step of hydrogenolysis of pyridine is its hydrogenation to piperidine, the latter substance has been used as the starting compound to obtain the greater amount of side products.

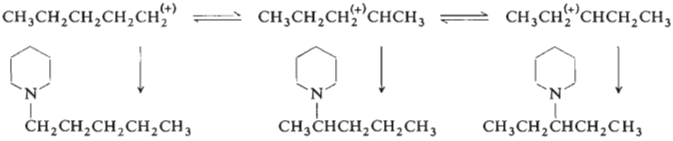
Hydrogenolysis of piperidine was carried out in the absence of solvent by heating piperidine (which was purified *via* picrate) to 300°C for 9 h in the presence of 10% of the catalyst. Under these conditions the sufficient amount of reaction products was produced by the reaction. These were separated by distillation. Individual fractions boiling from 95 to 175°C/2·0 kPa were analysed by gas chromatography, using the column packed with poly(ethylene glycol), poly(ethylene glycol adipate), a methyl phenyl silicone oil and a silicone elastomer. By comparison with authentic sample the following substances have been found and proved to be present in the reaction mixture: pentane, decane, unreacted piperidine, 1-methylpiperidine, 1-ethylpiperidine, 1-propylpiperidine, 1-butylpiperidine, 1-pentylpiperidine, 1-(2-pentyl)-piperidine, 1-cyclopentylpiperidine, 1-(5-aminopentyl)piperidine, 1,5-dipiperidinopentane and 1-(3-pentyl)piperidine.

The following new compounds, so far not reported to be formed by hydrogenolysis of pyridine and piperidine, have been found: 1-(5-aminopentyl)piperidine, 1-(2-pentyl)piperidine and 1-(3-pentyl)piperidine.The first compound is most likely produced by hydrogenolysis of 1,5-dipiperidinopentane according to the equation (*A*).



(*A*)

As to the other two compounds, their formation can be ascribed to reactions of carbonium ions having the charge located on carbons in positions 2 and 3. Both cations can result from isomerisation and can react with piperidine as depicted in Scheme 1.



SCHEME 1

The relative amounts of these three isomers are shown in Fig. 1. Compared to 1-pentylpiperidine, both isomers mentioned are present in very small amounts only.

Mass spectrometry combined with gas chromatography was used to analyse one fraction (Fig. 2). As it is seen, along with the compounds found and identified, the reaction mixture contains also a number of substances which remain still to fully identify. Although for some compounds their molecular weight was determined from their mass spectrum, the unequivocal determination of their structure requires the synthesis of the proposed compound and its comparison with the sample of the reaction mixture by gas chromatography with the use of several different stationary phases, in order to eliminate interfering effects of the substances with identical or very similar retention times. As shown in Fig. 2, at least seven compounds having molecular weight 153 ($C_{10}H_{19}N$) are present in the reaction mixture. It seems very probable that these compounds are piperidine isomers substituted by the C_5H_9 alkenyl in position 1. Of the expected isomers 1-(4-pentenyl)piperidine had been

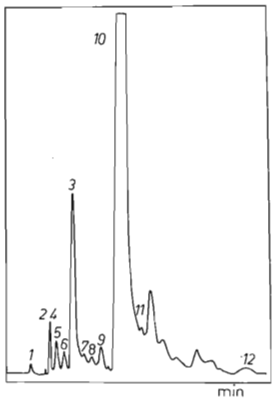


FIG. 1

Fraction *3* from Hydrogenolysis of Piperidine Purified *via* Picrate

Column packing-poly(ethylene glycol adipate), 120°C. *1* Pentane, *2* decane, *3* piperidine, *4* 1-methylpiperidine, *5* 1-ethylpiperidine, *6* 1-propylpiperidine, *7* 1-butylpiperidine, *8* 1-(3-pentyl)piperidine, *9* 1-(2-pentyl)-piperidine, *10* 1-pentylpiperidine, *11* 1-(4-pentenyl)piperidine, *12* 1-cyclopentylpiperidine

synthesized, but its presence in the reaction mixture was not convincingly proved. Of the compounds with molecular weight 155 ($C_{10}H_{21}N$), 1-(2-pentyl)piperidine and 1-(3-pentyl)piperidine were prepared. These were found to be present in the reaction mixture.

Since the reaction mixture was divided by distillation only into five fractions which were collected over a broad boiling point region, some compounds were present in individual fractions in so small amounts that their reliable identification was rather tedious. Moreover, the presence of some compounds in greater amounts, *e.g.* of piperidine, made the separation difficult. To solve some controversial questions and to make isolation of some compounds possible, hydrogenolysis of piperidine was made using tenfold amount of the substances and the mixture was divided into 23 fractions. The analysis of fraction 12 which contained nearly exclusively one compound (contaminated only by a small amount of impurities) showed that this sub-

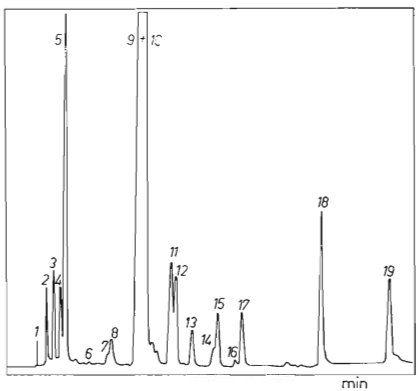


FIG. 2

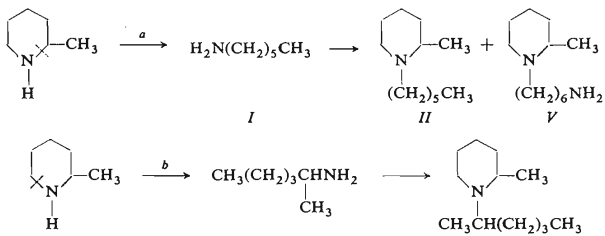
Fraction *3* from Hydrogenolysis of Piperidine Purified *via* Picrate

Column packing-poly(ethylene glycol) + KOH. *1* Pentane; *2* 1-methylpiperidine; *3* M^+ 113, 98, 83, 85 1-ethylpiperidine; *4* M^+ 142, 43, 57, 41, 83, 85 decane; *5* M^+ 85, 84, 56, 57, 42 piperidine, *6* 1-butylpiperidine; *7* M^+ 151, 94, 95; *8* M^+ 155, *112*, 41, 55 1-(2-pentyl)piperidine; *9* M^+ 155, 98; *10* M^+ 155, *98* 1-pentylpiperidine; *11* M^+ 153, *98*, 41, 83, 55, 42; *12* M^+ 153, 41, 83, 55, 98, 97; *13*, M^+ 153, *124*, 41, 96, 110 1-cyclopentylpiperidine; *14* M^+ 153, *96*, 41, 55, 97, 98; *15* M^+ 153, 96, 41; *16* M^+ 153, 96, 41, 55; *17* M^+ 153, 96, 41; *18* M^+ absent, 55, 41, 98, 79, 84 1-(5-aminopentyl)-piperidine); *19* M^+ 238, 98, 124, 154 1,5-dipiperidinopentane. The first peak is the base peak of the spectrum. If written in italics it is the most intense peak of the spectrum and the intensity of the other peaks is less than 20% of the intensity of the base peak.

stance has the formula $C_{10}H_{22}N_2$. One of the possible and expected compounds of this formula is 1-(5-aminopentyl)piperidine. This substance was therefore synthesized and its presence in the reaction mixture was established by gas chromatography.

As found by the evaluation of the chromatograms of individual fractions, the reaction mixture after hydrogenolysis of piperidine contained approximately 53% of piperidine, 19% of 1,5-dipiperidinopentane, 7% of 1-pentylpiperidine and 3% of 1-(5-aminopentyl)piperidine. The other defined compounds were present in amounts not exceeding 1%.

Hydrogenolysis of 2-*methylpyridine.* Hydrogenolysis of 2-methylpyridine gives first the hydrogenation product, 2-methylpiperidine, which then undergoes the cleavage involving piperidine ring. This cleavage can take place either between the nitrogen atom and the carbon substituted with the methyl group (pathway *a*) or between the nitrogen and the methylene group (pathway *b*) or in both positions simultaneously. This situation is depicted in Scheme 2.



SCHEME 2

As it is evident from the equations shown, this leads to 1-hexylamine (*I*) or 2-hexylamine (*III*) which by disproportionation reactions with 2-methylpiperidine can yield 1-hexyl-2-methylpiperidine (*II*), 1-(2-hexyl)-2-methylpiperidine (*IV*) and 1-(6-amino-1-hexyl)-2-methylpiperidine (*V*). These compounds, formation of which was expected by analogy with the hydrogenolysis of piperidine, were therefore synthesized. Gas chromatographic analysis of the reaction mixture after hydrogenolysis of 2-methylpyridine confirmed the presence of substance *IV* and the absence of substances *II* and *V*. Amines *I* and *III* were poorly separated on the columns used. The results obtained convincingly show that the cleavage of the piperidine ring proceeds in the sterically unhindered site, between the nitrogen atom and the methylene group *via* pathway *b*, to form 2-hexylamine which then reacts further.

Hydrogenolysis of quinoline was carried out in a similar way as hydrogenolysis of pyridine, either in decane or without solvent, both in the presence of the catalyst. In these experiments the effect of temperature and time upon the course of the hydrogenolysis were examined. It was found that at 250–260°C the exclusive hydrogenation of the pyridine ring took place after 7 h to produce 1,2,3,4-tetrahydroquinoline. At 300–305°C 88% of this compound and 12% of hydrogenolysis products were obtained. On prolonging the reaction time from 7 to 32 h, the proportion of the products of both types changed to 77 and 23% respectively. By using model compounds, the reaction mixture was found to contain as the main products those of hydrogenation, *i.e.* 1,2,3,4-tetrahydroquinoline and decahydroquinoline. Hydrogenolysis products were identified as 2-methylaniline, 2-propylaniline and propylbenzene. 2-Ethylaniline has not been convincingly proved. These results were also confirmed by gas chromatography combined with mass spectrometry. Moreover, this method allowed to detect the presence of a compound with M^+ 161 (most likely 5,6,7,8-tetrahydroquinoline containing the ethyl group in positions 5,6,7 or 8), methylnaphthalene and of an aromatic hydrocarbon with M^+ 120 (1,2-or 1,3-methylethylbenzene). Since these compounds have not been proved by chromatography on two different columns their presence in the reaction mixture is not quite sure. The disadvantage of all these experiments was the limit temperature of 300°C which could not be further increased and which for the reaction time given did not ensure the high conversion of hydrogenolysis.

Hydrogenolysis of 2-*methylquinoline* in decane at 250°C yielded after 4 h *cis*- and *trans*-2-methyl-1,2,3,4-tetrahydroquinoline as the main product which contained a small amount of the unreacted starting compound. After raising the temperature to 300–310°C and prolonging time to 31 h, the reaction mixture contained *cis*- and *trans*-1,2,3,4-tetrahydroquinoline (50%) and *cis*- and *trans*- 2-methyldecahydroquinoline (37%) as the main products, along with the unreacted 2-methylquinoline (5%). The products of hydrogenolysis were 2-butylaniline (3%) and the two, still unidentified, compounds in 5% amounts.

The effect of methyl groups upon the hydrogenolysis of pyridine ring. Hydrogenolysis of pyridine ring proceeds the slower, the higher is the number of the methyl groups. The effect of methyl groups upon hydrogenolysis of pyridine has not yet been studied. It could be, however, expected that the dependence would be similar. The course of the hydrogenolysis was followed similarly as in all the other hydrogenolysis experiments. The method of competition reactions could not be used. In this case it was found that the reaction mixture after hydrogenolysis of a mixture of two substances does not contain only the sum of the compounds formed by hydrogenolysis of the starting compounds but also new substances which are formed by mutual interaction of the reaction products formed. Similarly, hydrogenolyses of

several samples placed in open ampoules in a closed autoclave could not be made, because of the evaporation of the solvent and the sample at higher temperatures.

The effect of methyl groups upon hydrogenolysis of pyridine ring was followed in the series pyridine, 2-methylpyridine, 2,6-dimethylpyridine and 2,4,6-trimethylpyridine, using the above mentioned catalyst. The experiments were carried out at a temperature of 300°C. The reaction mixture after hydrogenolysis was analysed to determine the amount of the starting compound with the pyridine ring and the substance with the hydrogenated pyridine ring as well as to determine the proportion of these two compounds with respect to the other bases formed during hydrogenolytic cleavage of the piperidine ring.

As to the hydrogenolysis of pyridine, the reaction mixture contained 17% of pyridine, 60% of piperidine and 23% of higher boiling products. In the case of 2-methylpyridine the amount of basic substances formed during hydrogenolysis decreased to 8% and the starting compound and its hydrogenated product were present in 40 and 52% respectively. In hydrogenolysis of 2,6-dimethylpyridine the effect of methyl groups was even more distinct. The hydrogenolysis produced 3% of basic compounds and the reaction mixture contained the unreacted starting compound as predominant substance. In the case of 2,4,6-trimethylpyridine, the reaction mixture contained 74% of pyridine derivatives, 25% of piperidine derivative and only 1% of the substance formed by hydrogenolysis (Table II). From these results it becomes evident that the presence of methyl groups on the pyridine ring in the above positions slows down both the hydrogenation to piperidine derivative and the cleavage of the piperidine ring leading to other basic compounds.

TABLE II

Composition of Bases after Hydrogenolysis of Pyridine and its Derivatives

Starting compound	Starting compound after reaction %	Hydrogenation product %	Bases formed by hydrogenolysis %
Pyridine	17	60	23
2-Methylpyridine	40	52	8
2,6-Dimethylpyridine	62	35	3
2,4,6-Trimethylpyridine	74	25	1

EXPERIMENTAL

Model Compounds

Piperidine (Reachim) was redistilled before using for larger scale hydrogenolysis. It was purified *via* picrate. After threefold crystallization of the picrate from ethanol the base released was distilled and the fraction boiling at 105·5°C was collected and used.

1-(4-*Pentenyl*)*piperidine*. Piperidine (10·4 g) and 4-pentenyl bromide (12·6 g) were mixed and after the exothermic reaction subsided the reaction mixture was allowed to cool. Then it was dissolved in water, the solution was acidified and the unreacted bromide was extracted with ether. The solution was then made alkaline with KOH solution and the base was extracted with ether, the ether layer was dried over KOH pellets and then distilled to give 6·85 g of the product boiling at 194—195°C.

1-(3-*Pentyl*)*piperidine*. A mixture of 3·5 g of piperidine and 6·7 g of 3-bromopentane, obtained from the corresponding alcohol by its reaction with triphenylphosphine in dimethylformamide[27,28], was heated at 120°C for 8 h. After cooling, the reaction mixture was dissolved in water, acidified and extracted with ether. The bases released by alkalization were extracted with ether, dried over KOH and distilled to give 1·8 g of the product boiling at 184—196°C. Its purity was checked by gas chromatography.

1-(2-*Pentyl*)*piperidine* was obtained similarly. B.p. 58—62°C/1·6 kPa.

1-(5-*Amino*-1-*pentyl*)*piperidine*. Reaction of phthalimide with 1,5-dibromopentane yielded N-(5-bromopentyl)phthalimide[29] which by treatment with piperidine[30] gave the product (b.p. 123—124°C/2·3 kPa) in 61% yield.

2-*Hexylamine*. Reaction of methyl ethyl ketone with hydroxylamine produced the corresponding oxime[31] which was hydrogenated on Raney nickel W—6 in anhydrous ethanol[32]. B.p. 114—115°C.

2-*Methylpiperidine* was obtained in 86% yield by the reduction of 2-methylpyridine with sodium in butanol. B.p. 116—118°C.

1-*Hexyl*-2-*methylpiperidine*. 2-Methylpiperidine (3·3 g) and hexyl bromide (6·1 g) were mixed and the mixture was heated to 150°C for 3 h. On increasing the temperature to 100°C the hydrobromide started to precipitate as white crystals which then melted on increasing further the temperature. After dilution with the same volume of water, the reaction mixture was refluxed for 1 h, then acidified with dilute hydrochloric acid. Neutral substances were extracted with ether and the base was released from the aqueous solution of potassium hydroxide and extracted with ether. After drying over solid KOH, distillation afforded 3·23 g of the product, b.p. 114 to 116°C/2·7 kPa. For $C_{12}H_{25}N$ (183·3) calculated: 78·62% C, 13·74% H; found: 78·33% C, 13·76% H. The purity of this substance was checked by gas chromatography; the product contained small amounts of impurities.

1-(2-*Hexyl*)-2-*methylpiperidine*. 2-Hexanol, prepared by the reaction of butylmagnesium bromide with acetaldehyde, was reacted with bromine and triphenylphosphine in dimethylformamide[27,28]. The product (b.p. 134—138°C) consisting of 2-bromohexane, was shown by gas chromatography to contain also the unreacted starting alcohol and 3-bromohexane.The IR spectrum (KBr discs) confirmed the presence of butyl (a strong band at 731 cm^{-1}), ethyl (a weak band at 785 cm^{-1}) and propyl (a medium band at 745 cm^{-1}) groups. This mixture of bromides containing the unreacted alcohol (10·55 g) and 17·45 g of 2-methylpiperidine was refluxed for 24 h. After that time the mixture was dissolved in water, acidified with hydrochloric acid and extracted with ether. The aqueous solution was made alkaline and extracted with

ether. The ether extracts were dried over KOH pellets. Distillation through a short distillation column gave 4·78 g of the base, b.p. 83—85°C/1·1 kPa, which was shown by gas chromatography to be a mixture of 1-(2-hexyl)-2-methylpiperidine and 1-(3-hexyl)-2-methylpiperidine.

1-(6-*Aminohexyl*)-2-*methylpiperidine*. Phthalimide (7·35 g), 1,6-dibromohexane (31·8 g), grounded K_2CO_3 (3·8 g) in 40 ml of xylene was refluxed for 6 h. The residue after steam distillation was recrystallized from ethanol and light petroleum (m.p. 53—54°C). N-(6-bromohexyl)-phthalimide (2·7 g) so obtained and 0·9 g of 2-methylpiperidine were heated on a steam bath for 5 h. The reaction mixture was dissolved in hot water, filtered off from an oily portion and after partial evaporation under reduced pressure the residue was mixed with 15 ml of concentrated hydrobromic acid and the mixture was heated to boiling point for 2 h. After cooling and dilution with water, the precipitated phthalic acid was filtered off and the aqueous solution was evaporated to dryness. The free base was released by adding KOH. Distillation gave 0·82 g of the product, b.p. 143—148°C/1·9 kPa. For $C_{12}H_{26}N_2$ (198·36) calculated: 72·66% C, 13·21% H; found: 72·45% C, 13·08% H.

1,2,3,4-*Tetrahydroquinoline* was prepared by the reduction of quinoline with tin in hydrochloric acid.

The other model compounds were kindly gifted by Dr V. Galík and Dr Z. Kafka, Prague Institute of Chemical Technology, Prague. The IR spectra were measured by Dr R. Řeřicha of this Institute on UR 20 spectrophotometer (Zeiss, Jena).

Gas chromatographic analyses were carried out on Chrom 3 instrument equipped with a flame-ionisation detector, using the following columns: *a*) 4% poly(ethylene glycol) + 3% KOH on Chromosorb W (30—60 mesh), 2 m column; *b*) 12% poly(ethylene glycol adipate) on Chromaton N (0·2—0·25 mm), 4 m column; *c*) 10% methyl phenyl silicone oil on Chromaton N (0·2—0·25 mm) 3 m; *d*) 10% silicon elastomer Sil E 302 on Chromaton N (0·2—0·25 mm), 2 m column, *e*) 9·2% Apiezon L on Chromaton N (0·2—0·25 mm).

Mass spectra of the compounds present in the reaction mixture were measured by Dr K. Ubik, Institute of Organic Chemistry and Biochemistry Czechoslovak Academy of Sciences, Prague, on AEI MS 902 mass spectrometer combined with Pye 104 gas chromatograph (a flame ionisation detector, programmed temperature). The column (1·5 m long) was packed with the poly-(ethylene glycol) + KOH stationary phase. Helium was used as a carrier gas.

The catalyst was prepared by impregnation of γ-alumina by ammonium molybdate and cobalt(II) nitrate, dried and calcinated at 650°C for 5 h. The $CoO : MoO_3 : Al_3O_3$ ratio was 1 : 2 : 30. Sulphidation of the catalyst was carried out by heating it in a stream of $H_2 + H_2S$ at 450°C until the sulphur content was 1·4%. The catalyst was kindly gifted by Dr V. Vyskočil of this Institute.

Hydrogenolysis of Pyridine

a) Pyridine (2 g) was dissolved in 20 g of n-decane and after addition of 0·5 g of the catalyst the base was hydrogenated at 250—260°C for 3 h in an autoclave. The hydrogen pressure increased from the initial 8·5 MPa to 13·5 MPa. After cooling and discharge of hydrogen (pressure 7·5 MPa) the contents were freed of the catalyst by filtration and then shaken with 3 ml of dilute hydrochloric acid. The bases were released from the hydrochloride solution by 50% KOH solution and then (0·9 g) they were analysed by gas chromatography, using the columns filled with a methyl phenyl silicone oil and Sil E 302 elastomer.

b) Hydrogenolysis was carried out in cyclohexane at 250—260°C for 4·5 h. The pressure in the autoclave increased from 7·9 MPa to 15·6 MPa; after cooling it dropped to 5·4 MPa. The composition of the reaction mixture from both experiments is presented in Table I.

c) Pyridine (25·5 g) and the catalyst (2·0 g) were subjected to hydrogenation (250°C, 30 min). Then the temperature was raised to 300°C during 1 h and heating was continued for another 7 h. The hydrogen pressure increased from 8·6 MPa to 16·0 MPa and then it decreased again to 6·5 MPa. After cooling it was 1·0 MPa. The reaction mixture contained piperidine and the unreacted pyridine. 1-Pentylpiperidine was found to be present in only small amounts (by g.l.c.).

Hydrogenolysis of Piperidine

a) Piperidine (21·45 g) purified *via* the picrate and 2·15 g of the catalyst were heated at 300 ± 4°C for 9 h in an autoclave. The initial hydrogen pressure was 5·0 MPa, at maximum temperature it increased to 12·0 MPa. After cooling, the reaction mixture was separated from the catalyst by decantation and filtered. Distillation yielded the following fractions: *1* b.p. 95—108°C (4·0 g); *2* b.p. 108—110°C (2·15 g); *3* b.p. 110—205°C (2·5 g); *4* b.p. 80—168°C/2·0 kPa; *5* b.p. 170 to 174°C/2·0 kPa (2·45 g). Distillation residue weighed 2·8 g. Individual fractions were chromatographed, using the columns filled with poly(ethylene glycol) and poly(ethylene glycol adipate) (Figs 1 and 2).

b) Piperidine (66·7 g) and 5·4 g of the catalyst were subjected to hydrogenolysis in an autoclave. The initial hydrogen pressure was 6·1 MPa. Temperature 300°C, time 8·5 h, hydrogen pressure increased to 16·0 MPa. The contents were allowed to cool overnight by which the hydrogen pressure dropped to 5·8 MPa. The liquid portion was decanted and the autoclave was charged with 58·2 g of piperidine and 4·4 g of the catalyst; the reaction mixture was again heated at 300°C for 7 h. After cooling, the liquid layer was decanted and 126 g of piperidine were added. The mixture was heated at 300°C for 7 h. The initial hydrogen pressure was 5·7 MPa. The part of hydrogen was necessary to discharge during the reaction, in order that the pressure not exceed the maximum safe value. The liquid portion was filtered through a G4 porous glass under pressure. A total of 218 g of a colourless filtrate were obtained which was distilled through 32 cm column filled with metallic spirals and the following fractions were collected: *1* b.p. up to 40°C (0·45 g); *2* b.p. 40—90°C (3·95 g); *3* 103—104°C (104·4 g); *4* 104—105·5°C (6·41 g); *5* 105·5—120°C (2·52 g); *6* 120—160°C (1·0 g); *7* 160—190°C (1·5 g); *8* 190—191°C (5·44 g); *9* 75—77°C/1·7 kPa (7·63 g); *10* 77—85°C/1·7 kPa (2·0 g); *11* 85—115°C/1·7 kPa (2·5 g); *12* 115—117°C/1·7 kPa (4·13 g); *13* 117—152°C/1·7 kPa (2·32 g); *14* 152—168°C/1·7 kPa; *15* 168—170°C/1·7 kPa (16·66 g); *16* 168—170°C/1·7 kPa (6·78 g); *17* 138—140°C/293 Pa (12·85 g); *18* 140—155°C/293 Pa (4·28 g); *19* 109—116°C/26 Pa (5·22 g); *20* 116—132°C/26 Pa (3·20 g); *21* 130—164°C/13 Pa (5·44 g); *22* 164—190°C/13 Pa (6·50 g); *23* 190—220°C/13 Pa (1·72 g). Distillation residue together with loses amounted to 6·05 g. Fractions 19 and 23 were distilled from mantel flask without using the column.

Individual fractions were analysed by gas chromatography using the columns filled with a methyl phenyl silicone oil, poly(ethylene glycol adipate) and poly(ethylene glycol). The amounts of individual substances in the fractions were determined only aproximately from peak areas by planimetration without using correction factors. Analysis of the fraction 12: for $C_{10}H_{22}N_2$ calculated: 70·53% C, 13·02% H; found: 70·50% C, 12·91% H.

Hydrogenolysis of 2-Methylpyridine

a) A solution of 2 g of 2-methylpyridine in 20 g of decane was hydrogenated in the presence of 0·5 g of the catalyst at 250°C for 7 h. The initial hydrogen pressure (8·8 MPa) increased to 15·5 MPa. After cooling it was 7·3 MPa. The treatment of the reaction mixture was the same as in the case of pyridine hydrogenolysis. 2-Methylpiperidine was found as the main product by gas chromatography.

b) A mixture of 20 g of 2-methylpyridine and 2 g of the catalyst were hydrogenated at 300°C for 11 h. The initial hydrogen pressure was 8·0 MPa. During the reaction the amount of hydrogen was twice refilled after cooling the autoclave. The pressure during the hydrogenation changed within 10·0—15·5 MPa. After cooling and separation of the catalyst by filtration, a total of 15·2 g of the product were obtained which was divided into the following fractions: *1* b.p. 70—130°C (4·4 g); *2* b.p. 130—133°C (3·8 g); *3* b.p. 101—190°C/2·0 kPa (3·3 g). All the fractions were analysed by gas chromatography. By using Sil E 302 elastomer it was found that 1-hexyl-2-methylpiperidine could not be, however, excluded. The latter compound was confirmed with the aid of the column packed with a methyl phenyl silicone oil phase. This phase was also used to prove the absence of 1-(6-aminohexyl)-2-methylpiperidine.

Hydrogenolysis of Pyridine, 2-Methylpyridine, 2,6-Dimethylpyridine and 2,4,6-Trimethylpyridine

a) Hydrogenolysis of 1 g of pyridine and 1 g of 2-methylpyridine in 20 g of decane in the presence of 0·5 g of the catalyst at 250°C for 4 h yielded a mixture of substances which was found by gas chromatography not to be the sum of the compounds formed by hydrogenolysis of pyridine and its 2-methyl derivative themselves. It contained also some unidentified substances which were most likely formed by mutual interaction of the cleavage products arising from the starting compounds.

b) Mixtures of 0·55 g of pyridine + 0·1 g of the catalyst and 0·55 g of 2-methylpyridine + 0·1 g of the catalyst were placed into two open ampoules and introduced into an autoclave. Then the autoclave was sealed and filled with hydrogen, the contents were heated to 300—350°C for 8 h. After cooling it was found that both compounds evaporated to the autoclave.

c) The starting compound (2 g) was dissolved in 10 g of decane, 0·2 g of the catalyst was added and the mixture was hydrogenated at 295—305°C for 5 h. After cooling, the reaction mixture was acidified with 3 ml of dilute hydrochloric acid (1 : 1), the aqueous layer was separated and shaken with ether. After evaporation of the aqueous layer to dryness, the residue was dissolved in 1 ml of water, made alkaline by adding 2 g of 50% KOH solution. The bases so released were separated, dried over solid KOH and analysed by gas chromatography. The results obtained are presented in Table II.

Hydrogenolysis of Quinoline

a) A mixture of 2 g of quinoline and 10 g of decane was hydrogenated in the presence of 0·5 g of the catalyst at 250—260°C for 7 h. The reaction yielded the pure 1,2,3,4-tetrahydroquinoline. The initial hydrogen pressure was 8·6 MPa, during the hydrogenation it increased to 14 MPa. After cooling it was 7·6 MPa.

b) After heating to 300—305°C for 7 h the reaction mixture contained 88% of 1,2,3,4-tetrahydroquinoline and a mixture of substances which formed three peaks with approximate amounts 3·5 and 4%.

c) Prolongation of the reaction time to 32 h led to the decrease in the content of 1,2,3,4-tetrahydroquinoline to 76% and the amount of side products increased to 10, 12 and 1%. The reaction mixture did not contain 2-methyl- and 2-ethylaniline.

d) A mixture of 19·8 g of quinoline and 2 g of the catalyst was heated to 250°C. The hydrogen consumed by hydrogenation was gradually refilled to 8·6 MPa pressure directly from the pressure cylinder. All the quionoline was hydrogenated after heating the mixture for 2 h. The auto-

clave was pressurized after cooling by hydrogen to 8·6 MPa and heated to 300°C for 15 h. After cooling, the hydrogen pressure dropped to 7·0 MPa. The reaction mixture was freed of the catalyst by filtration and distilled. Two fractions were collected: *1* b.p. 220–240°C (11·5 g) and *2* 115–120°C/1·7 kPa (0·9 g). The distillation residue weighed 4·4 g. The analysis of the main fraction performed with the use of a methyl phenyl silicone oil and Apiezon L revealed the presence of the following compounds: 1,2,3,4-tetrahydroquinoline (75%), quinoline (5%), 2-propylaniline (5%), 2-ethylaniline + decahydroquinoline (12%), aromatic hydrocarbons (3%) and 2-methylaniline (traces). The composition of the reaction mixture is semiquantitative since correction factors have not been used to estimate peak areas.

Hydrogenolysis of 2-Methylquinoline

a) A solution of 2 g of 2-methylquinoline in 20 g of decane was hydrogenated in the presence of 0·5 g of the catalyst at 300–310°C for 31 h. The work-up of the reaction mixture afforded a mixture of bases which according to gas chromatography had the following composition: *cis*- + *trans*-2-methyl-1,2,3,4-tetrahydroquinoline (50%), 2-methylquinoline (5%), *cis*- + + *trans*-2-methyldekahydroquinoline (37%), 2-butylaniline (3%) and two unidentified compounds (5%).

b) Hydrogenation of the above mixture at 250°C for 4 h yielded only *cis*- + *trans*-2-methyl--1,2,3,4-tetrahydroquinoline.

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