HYDROGENOLYSIS OF NITROGEN-CONTAINING COMPOUNDS ON COBALT–MOLYBDENUM CATALYSTS

Mirko ČERNÝ
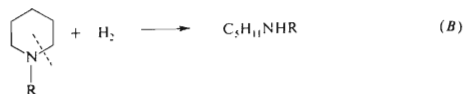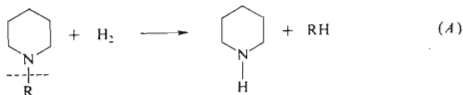
Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchdol

Hydrogenolysis of N-(1-hexyl)piperidine, N-(1-pentyl)piperidine and 1-pentyl-1-hexylamine on sulphidized CoO–MoO$_3$ catalysts has been investigated. The primary reaction in the hydrogenolysis is the cleavage of the bond between the nitrogen atom and the methylene group of the alkyl substituent or of the methylene ring. Alkylation and transalkylation reactions on the nitrogen play also a role.

Hydrogenation and hydrogenolysis of nitrogen-containing heterocyclic compounds with pyridine, piperidine or quinoline ring and derivatives thereof are still of research interest, especially in relation to their occurrence in petroleum and petroleum fractions. In addition to analytical studies which are devoted to the composition of the reaction mixture after hydrogenolysis of pure model compounds, there are studies dealing with kinetics of the reaction and reaction mechanism of cleavage reactions[1−5].

In a previous communication it was found[6] that the cleavage of piperidine ring of 2-methylpiperidine takes place between the nitrogen atom and the methylene group and not between the nitrogen atom and the carbon substituted with the methyl group. Reactions of N-(1-alkyl)piperidines have not been however examined in detail. In these compounds the primary hydrogenolytic cleavage can proceed either between their nitrogen and methylene group of the alkyl substituent or between nitrogen atom and the neighbouring methylene group of piperidine ring according to equation (*A*) and (*B*), respectively. As it is seen from the equations, reaction products may be piperidine, a hydrocarbon and a secondary amine.

$$\text{(piperidine, N-R)} + H_2 \longrightarrow \text{(piperidine, N-H)} + RH \qquad (A)$$

$$\text{(piperidine, N-R)} + H_2 \longrightarrow C_5H_{11}NHR \qquad (B)$$

Hydrogenolysis of N-(1-pentyl)piperidine on CoO–MoO₃ catalysts was studied by Sonnemans and coworkers[3,4]; they found that the reaction mixture contains piperidine, pentane, decane, pentylamine, dipentylamine and ammonia. The composition reported does not allow, however, to ascertain the sequence of the cleavage of individual bonds in this compound due to the same number of carbon atoms in the alkyl group and in the piperidine ring. This means that no decision can be made concerning pentane formation that can proceed *via* hydrogenolytic cleavage of the alkyl group or of the piperidine ring. Furthermore, the reaction mixture after hydrogenolysis of pyridine or piperidine contains, along with other substances, also N-(1-alkyl)piperidines which are formed by acid-catalysed alkylation of piperidine by species formed by decomposition of the piperidine ring. Among these N-(1-alkyl)piperidines, the prevailing one is N-(1-pentyl)piperidine. In order to clarify this question it was necessary to choose such a N-(1-alkyl)piperidine which is not formed by hydrogenolysis of piperidine and to carry out the reaction in the region of low conversions, to avoid further reactions of the primary products formed to secondary ones. N-(1-Hexyl)piperidine was found to be suitable compound for these purposes. Its reaction on a sulphidized CoO–MoO₃–Al₂O₃ catalyst in the presence of hydrogen at 300°C yields the reaction mixture which contains 1-pentylamine, 1-hexylamine, di-1-pentylamine, di-1-hexylamine and N-(1-pentyl)piperidine, in addition to pentane, hexane, piperidine and 1-pentyl-1-hexylamine.

The piperidine found among reaction products as well as the mutual ratio of hexane to pentane (10 : 1) indicated the prevailing cleavage according to equation (A). The presence of 1-pentyl-1-hexylamine speaks for the cleavage according to equation (B). To examine further the behaviour of secondary amines under hydrogenolytic conditions, we studied the reaction of 1-pentyl-1-hexylamine in the presence of piperidine and the catalyst. Under identical reaction conditions (the same reaction time, temperature) 31% of 1-pentyl-1-hexylamine reacted to give 1-pentylamine, 1-hexylamine, di-1-pentylamine and di-1-hexylamine. A total of 28% of the present piperidine was converted into N-(1-pentyl)- and N-(1-hexyl)piperidine. Other compounds found were pentane and hexane and some unidentified substances, all of which were present only in small amounts.

For comparative purposes we performed hydrogenolysis of N-(1-pentyl)piperidine. The reaction mixture contained the starting piperidine derivative, pentane, 1-pentylamine, di-1-pentylamine, N-(2-pentyl)piperidine and N-(3-pentyl)piperidine. Prolongation of reaction time led to an increase in the amount of piperidine, together with an increase in the amount of products of piperidine hydrogenolysis.

These results show that the cleavage of N-(1-pentyl)- and N-(1-hexyl)piperidine proceeds simultaneously according to both above mentioned equations. The compounds so formed, *i.e.* piperidine and a secondary amine, undergo further reactions, especially disproportionations, to produce primary, secondary and tertiary amines. It seems likely that acid sites of the catalyst play a role in these consecutive reactions.

EXPERIMENTAL

1-*Hexylamine and* 1-*pentylamine* were prepared by reaction of piperidine with hexyl bromide or pentyl bromide. After initial reaction subsided, the reaction mixture was left aside and the next day it was acidified and the unreacted alkyl bromide was extracted with diethyl ether. After alkalization of the solution, both compounds were obtained by usual procedure. Their purity was verified by gas chromatography.

1-*Pentyl*-1-*hexylamine*. To a solution of 14·5 g of caproyl chloride in 65 ml of pentane, 20·65 g of 1-pentylamine were slowly added at —60°C under stirring and external cooling. The reaction mixture was allowed to stand at room temperature for 2 h, then it was diluted with 25 ml of pentane and poured onto ice slurry acidified with hydrochloric acid. The organic layer was separated and washed successively with water and 5% solution of $NaHCO_3$. After drying over sodium sulphate, distillation through a short column yielded 18·27 g (91·5%) of 1-pentylamide of caproic acid; b.p. 112—114°C/66·5 Pa, m.p. 39·0—39·5°C. For $C_{11}H_{23}NO$ (185·3) calculated: 71·30% C, 12·51% H; found: 71·65% C, 12·47% H. To a solution of 57 g of 60% toluene solution of $NaAlH_2$. $(OCH_2CH_2OCH_3)_2$ (0·17 mol) and 50 ml of dry toluene, 10·42 g (0·056 mol) of 1-pentylamide of caproic acid dissolved in 50 ml of toluene were added. The reaction mixture, which evolved hydrogen under temperature increase due to exothermic reaction, was refluxed for 1 h, cooled to room temperature and decomposed by dilute hydrochloric acid. All volatile products were steam-distilled. The reaction mixture was made alkaline by KOH solution and 1-pentyl-1-hexyl-amine was obtained by steam distillation. The amine which was poorly soluble in the distillate was extracted by diethyl ether, the extract was dried over solid KOH and distilled. A total of 7·65 g (80%) of the base were obtained which boiled at 89—90°C/1·3 kPa. Attempted reduction of the amide by $LiAlH_4$ in diethyl ether according to the procedure reported for the reduction of 1-butyl-amide of valeric acid and of 1-pentylamide of isocaproic acid[7] led after 10 h-refluxing to recovering of 58% of the starting amide, after decomposition of the reaction mixture.

Gas chromatography was carried out with the aid of Chrom 3 instrument equipped with a flame-ionisation detector using 2% Methyl Phenyl Silicone Oil +0·2% poly(ethylene glycol) 4000, Chrom 42 instrument equipped with the same detector and a column filled with 11·5% Sil E 312 on Chromosorb W and finally with the aid of T 10 instrument (workshops of the Institute) which was equipped with a flame-ionisation detector and its column was packed with 4% PEG 1 500 + 3% KOH on Chromosorb W. The amount of the ammonia formed could not be therefore determined.

Catalyst was prepared by impregnation of a commercial γ-alumina by ammonium molybdate and cobalt(II) nitrate. The CoO: MoO_3 : Al_2O_3 ratio was 1 : 2 : 30. The catalyst was dried and then calcinated at 550°C for 5 h and sulphided in a stream of $H_2 + H_2S$ (9 : 1) at 450°C until the sulphur content reached 1·4 per cent.

Hydrogenolysis of N-(1-*hexyl*)*piperidine*. The amine (20 g) and 1 g of the catalyst were heated in an autoclave at 300°C for 1 h at the initial hydrogen pressure 6·0 MPa. The maximal pressure was 12·1 MPa. After cooling, the sample was withdrawn (sample A) and the contents were heated for another 7 h (sample B). Samples A and B contained unreacted N-(1-hexyl)piperidine with traces of di-1-pentylamine (96·7 and 85·0%, resp.), N-(1-pentyl)piperidine (1·5 and 5·8%), piperidine contaminated with 1-pentylamine and 1-hexylamine (1·3 and 5·4%), di-1-hexylamine (0·3 and 3·0%) and 1-pentyl-1-hexylamine (0·1 and 0·8%), along with small amounts of pentane and hexane (1 : 10 ratio).

Hydrogenolysis of N-(1-*pentyl*)*piperidine*. The amine (20 g) and 1 g of the catalyst were heated in an autoclave at 300°C for 1 h. The initial hydrogen pressure was 5 MPa. The reaction mixture

contained a small amount of pentane, 97% of the starting compound and further piperidine, N-(2-pentyl)piperidine, N-(3-pentyl)piperidine, 1-pentylamine and di-1-pentylamine in 1 : 1·8 : : 0·9 : 15 : 10 ratio. After heating prolonged to 9 h, the content of the starting amine decreased to 88% and the sample contained in addition to the above compounds also N-(1-butyl)piperidine, N-(1-ethyl)piperidine and decane.

Hydrogenolysis of 1-*pentyl*-1-*hexylamine* in the presence of piperidine. A mixture of 5 g of 1-pentyl-1-hexylamine, 0·5 g of piperidine and 0·25 g of the catalyst was heated under initial hydrogen pressure of 6 MPa at 300°C for 1 h. The reaction mixture contained 63% of 1-pentyl-1-hexylamine, 6·5% piperidine, 8% of N-(1-hexyl)piperidine, 5·5% of N-(1-pentyl)piperidine, 1% of 1-pentylamine, 2·5% of di-1-pentylamine, 4% of 1-hexylamine, 3% of di-1-hexylamine, 1% of a pentane–hexane mixture, 5% of a higher boiling product and 0·5% of a lower boiling substance which were not identified.

REFERENCES

1. McIlvried H. C.: Ind. Eng. Chem., Process Des. Develop. *10*, 125 (1971).
2. Satterfield C. N., Modell M., Mayer J. F.: AIChE J. *21*, 1100 (1975).
3. Sonnemans J., Goudriaan F., Mars P.: Proc. Fifth Int. Congr. Catal., Miami Beach, 1972 (North-Holland Publ., Amsterdam 1973), p. 1085.
4. Sonnemans J., Neyens W. J., Mars P.: J. Catal. *34*, 230 (1974).
5. Sonnemans J., Mars P.: J. Catal. *34*, 215 (1974).
6. Černý M.: This Journal *44*, 85 (1979).
7. Corey E. J., Hertler W. R.: J. Amer. Chem. Soc. *82*, 1657 (1960).

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