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Abstract

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CATALYTIC TRANSFORMATIONS OF N,N-DIALKYLCYCLOHEXYLAMINES

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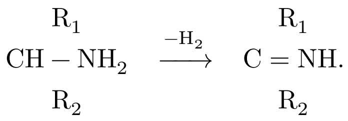
The literature data on the catalytic vapor-phase dehydrogenation of amines are limited to the works of A. A. Balandin and co-workers ([1], [2]), who studied the dehydrogenation of primary aliphatic amines on metallic catalysts. According to these works, upon dehydrogenation amines split off a molecule of hydrogen with formation of a C=N bond:



$$\overset{R_1}{\underset{R_2}{CH}} - NH_2 \xrightarrow{-H_2} \overset{R_1}{\underset{R_2}{C}} = NH.$$

The conversion of amines into ketimines can proceed, as is evident from the scheme, only in the case of primary or secondary amines. It was of considerable interest to study the dehydrogenation of tertiary amines, for which, apparently, the possibility of ketimine formation is excluded. The present communication gives the results of an investigation of the catalytic dehydrogenation of tertiary amines, using N,N-dimethyl- and N,N-diethylcyclohexylamine as examples.

The reaction was carried out at atmospheric pressure, in a flow system, over the temperature range 220-300°. The catalyst—20% $CuAl_2O_3$—was prepared by impregnating Al_2O_3 with a solution of copper nitrate, followed by calcination at 360° and reduction with hydrogen at 250°. In the first part of the work, N,N-dimethylcyclohexylamine was studied, b.p. 158-159°, n_D^{20} 1.4530. Literature data ([3]): b.p. 158-159°, n_D^{20} 1.4528.

As a result of contact, a liquid catalyzate and a gas, consisting of pure hydrogen, were obtained. Acid hydrolysis of the catalyzate led to the isolation of a "ketone fraction," which, according to analysis, consisted of cyclohexanone and 2-methylcyclohexanone. The latter was identified as the 2,4-dinitrophenylhydrazone: orange leaflets (alcohol), m.p. 135°. Literature data ([4]): m.p. 135°.

Found, %:	N 19.19; 19.05
$C_{13}H_{16}N_4O_4$. Calculated, %:	N 19.16

Fig. 1 and Fig. 2: graphs showing dependence of ketone yield on steam dilution and temperature

Figure 1: Fig. 1 and Fig. 2: graphs showing dependence of ketone yield on steam dilution and temperature

In searching for conditions favorable to increasing the yield of ketones, dilution of the starting amine with hydrogen, nitrogen, and water vapor was tested. The best results were observed upon dilution with water vapor: in this case 85-90% of the N,N-dimethylcyclohexylamine taken for conversion was converted into ketones.

For the separate determination of cyclohexanone and 2-methylcyclohexanone present in the mixture, a simplified procedure was used, based on the poor solubility, discovered by us, of the semicarbazone of 2-methylcyclohexanone in 40% alcohol. By this method, in the "ketone fraction" isolated from the experiment, the total ketone content was determined by oximation, and then

in a separate sample the amount of 2-methylcyclohexanone was determined and, finally, the cyclohexanone content was calculated from the difference. In a number of experiments the dependence of the yield of ketones, calculated on the amine passed through, on the temperature and the degree of dilution with steam was investigated. The charge of N,N-dimethylcyclohexylamine on the catalyst in all experiments was constant—100 g/l • hr. The results of these experiments are presented in Figs. 1 and 2.

In several experiments, the mixture of amines remaining in the acidic hydrolysate after distillation of the "ketone fraction" was isolated. Analysis showed that the mixture consisted of unchanged N,N-dimethylcyclohexylamine, dimethylamine, and methylamine.

Fig. 1. Dependence of the yield of ketones on the degree of dilution with steam at 280°:
I—mixture of ketones, *II*—2-methylcyclohexanone

Fig. 2. Dependence of the yield of ketones on temperature. Molar ratio amine : water = 1 : 10.
I—mixture of ketones, *II*—2-methylcyclohexanone

The study of the catalytic transformation was continued with N,N-diethylcyclohexylamine, obtained according to (5), b.p. 193-194°. Literature data (5): b.p. 193°. At 280°, a space velocity of 0.1 hr^{-1}, and a molar ratio amine : water = 1 : 10, a mixture of ketones was obtained containing approximately 30% 2-ethylcyclohexanone and 70% cyclohexanone. The 2,4-dinitrophenylhydrazone of 2-ethylcyclohexanone—bright-red needles (alcohol), m.p. 161°. Literature data (6): m.p. 162°.

Found, %: N 18.28; 18.48

$C_{14}H_{18}N_4O_4$. Calculated, %: N 18.30

Thus, the results of the present investigation show that N,N-dialkylcyclohexylamines, in the presence of steam over a $Cu{-}Al_2O_3$ catalyst, undergo catalytic conversion into a mixture of two ketones—cyclohexanone and 2-alkylcyclohexanone. It may be assumed that the first stage of the transformation is dehydrogenation of the cyclohexane ring with formation of an α, β-unsaturated amine:

$$[\text{cyclohexyl}{-}NR_2] \xrightarrow{-H_2} [\text{cyclohexenyl}{-}NR_2]$$

According to literature data (7, 8), α, β-unsaturated amines, better known as enamines, have a strongly pronounced tendency toward electrophilic substitution reactions at the β-C atom. In addition, enamines are capable of being very readily hydrolyzed by water with the formation of carbonyl-containing compounds (9).

Taking into account the indicated properties of enamines, the catalytic transformation discovered by us receives the following explanation: the enamine (I) formed initially rearranges into the β-alkylenamine (II), which then hydrolyzes with formation of 2-alkylcyclohexanone; the cyclohexanone always present in the mixture is formed upon hydrolysis of enamine (I):

$$\begin{array}{ccccc} \text{N, N-dialkylcyclohexylamine} & \xrightarrow{-H_2} & \text{I} & \longrightarrow & \text{II} \\ & & \text{1-(N, N-dialkylamino)cyclohexene} & & \text{2-alkyl-}_1\text{-(N-alkylamino)} \\ & & \downarrow H_2O & & \downarrow H_2O \\ & & \text{cyclohexanone} + R_2NH & & \text{2-alkylcyclohexanone} \end{array}$$

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Note: Figure translations are in progress. See original paper for figures.