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SYNTHESIS OF LONG CHAIN ALIPHATIC AMINES FROM THE CORRESPONDING ALCOHOLS

A. Baiker*, W. Richarz

Swiss Federal Institute of Technology (ETH)

Department of Industrial and Engineering Chemistry, Zurich, Switzerland

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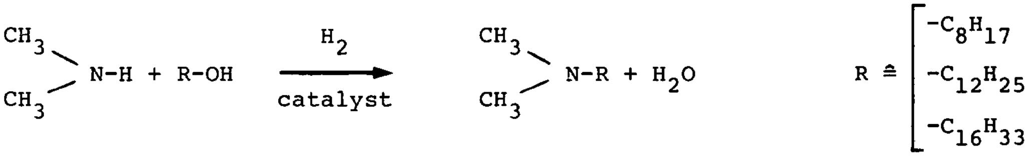
The synthesis of long chain aliphatic amines is of particular interest since they are widely used as corrosion inhibitors, epoxy hardeners, textile additives etc. (1,2). Several ways of synthesis are known, starting from olefines (1,3), fatty acids (1,4) or from the corresponding alcohols (1,5,6). In this work a process is described which gives far better selectivities and yields of tertiary amines than the comparable methods of synthesis starting from the corresponding alcohols.

The investigated amination reactions take place according to the following scheme:

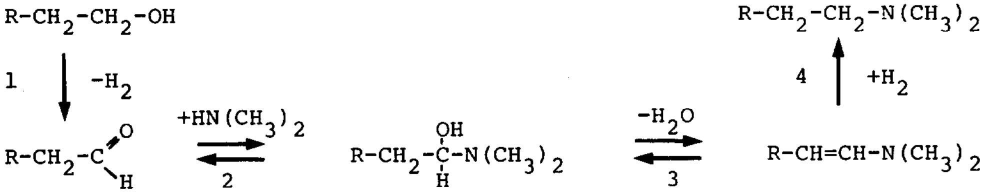


On the basis of preliminary tests of about 30 commercially available catalysts, it has been found that copper-chromium oxide catalysts give in the presence of hydrogen a selectivity of over 96% at practically quantitative conversion. In our experiments the BASF H3-10 catalyst was used which has the following composition (% weight): CuO (25%), Cr_2O_3 (1%), Na_2O (0,1%), SiO_2 (70%), H_2O (about 4%).

The experiments were run at atmospheric pressure in a heated glass tube containing the catalyst which was covered with some inert packing (glass beads). Gas and liquid were added continuously from the top of the reactor. The following table contains the results of runs of three different alcohols. In all cases the catalyst load was 10 grams.

product	$C_8H_{17}N(CH_3)_2$	$C_{12}H_{25}N(CH_3)_2$	$C_{16}H_{33}N(CH_3)_2$
temperature	220°C	230°C	235°C
feeds: ROH	6.0 g/h	6.0 g/h	6.0 g/h
$NH(CH_3)_2$	8.3 g/h	5.6 g/h	4.5 g/h
H_2	6 l/h	6 l/h	6 l/h
conversion	98 %	98 %	97 %
yield of $R-N(CH_3)_2$	97 %	97 %	96 %

On the basis of kinetic and adsorption measurements the following reaction scheme is proposed:



The aldehyde could be isolated as an intermediate. Furthermore, it was shown that the dehydrogenation and hydrogenation (step 1 and step 4) take place essentially on the Cu-centers of the catalyst surface.

References

1. Shinzo Otsuka, Yukagaku (Jap.) 15, 416 (1966).
2. M.I. Yakushkin, Khim Prom. (Russ.) 42, 493 (1966).
3. U.S. patent 3 401 203 (1968).
4. Brit. patent 1 067 762 (1967).
5. U.S. patent 3 223 734 (1961).
6. Neth. patent 6 507 514 (1965).