



SYNTHESIS OF TERTIARY ALIPHATIC AMINES

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Higher tertiary aliphatic amines are widely used in various industries, however, these are not manufactured in China. A substantial amount of C₄ fraction is available from the growing petroleum industry which provides the opportunity for the integration of refining with the petrochemicals plant. C₄ olefins can be used as starting materials for aliphatic amine production via butene oligomerization. In this paper, the industrial scale synthetic methods for production of tertiary aliphatic amines including the amination of olefins are reviewed.

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Introduction

The rapid growth of petroleum industry in China provides favourable conditions for C₄ utilization. C₄ olefins can be transformed into heavy olefins via oligomerization, and then be used as feedstock for the production of a variety of fine chemicals, such as tertiary amine.

Higher aliphatic amines (C₈-C₂₂) are often used as organic intermediates in the production of dye, oil, plastics, cosmetics and textile industry, mining and metal processing, etc. Primary amines are convertible into secondary and tertiary amines or diamines. The secondary and tertiary amines are raw materials to produce quaternary ammonium salts, polyoxyethylene aliphatic amines and tertiary amine oxides. About 98% of the secondary amines are used for preparing dialkylmethylated tertiary amines.¹

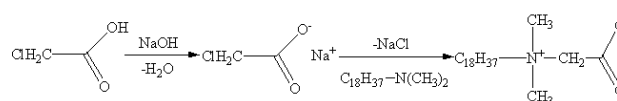
Application of tertiary alkylamines

Tertiary alkylamines, based on the number of long-chain alkyl groups, involve mono-, di- and tri-tertiary alkylamines.² Among them, the trialkylamines are the most widely used derivatives.³ The tertiary alkylamines can be used directly as intermediates during the production of various chemicals,⁴ such as surfactants during the production of citric acid, fuel oils, cosmetics and as starting materials for the production of preservatives, fungicides and metal extracting agents.⁵

The reactions of tertiary amines with alkylating agents such as alkyl halides, alkyl sulfate or benzyl chloride result in quaternary ammonium salt, a group of widely used cationic surfactants. Long chain alkyl dimethylamines can be transformed into long chain alkyl dimethylamine oxides by hydrogen peroxide. These amine oxides are often used as household cleansing products such as shampoos, shower gels, facial cleansers, foaming agents and other type of detergents.

Betaines, important amphoteric surfactants, are prepared by the reaction of dimethyl amine with chloroacetic acid and

sodium hydroxide.⁶ The preparation of octodecyl betaine is showed in Scheme 1.



Scheme 1 Preparation process of octodecyl betaine

Betaines are often used as antistatic electric agents, softeners, detergents and wetting agents in textile industry; shampoos, classical detergents and baby cosmetics in daily chemical industry; fuel additives, metal antirusting agents, disinfectants, fungicides, etc.

Production of tertiary alkylamines

As the raw material for the production of biodegradable detergents, the preparation of tertiary alkylamines has caught much attention. Therefore, several methods have been developed, such as Liu Carter method, reductive-methylation, aliphatic alcohol amination, amination of chloroalkane, alcohol sulfation, bromination of α -olefin, amination of α -olefin epoxide, etc. Among them, the method of aliphatic alcohol amination is more popular.

In 1988, Feng⁷ first reported the way to synthesize aliphatic tertiary amines from alcohol in China. This method was much attractive for its simple operation and little wastage. The key to this process was to develop catalysts with high selectivity and high activity. Li⁸⁻¹³ discovered a catalyst system in which Cu and Ni were used as the main components, and adding the third one such as Zn, Co, Cr, La, Ba, Mg, Mo, Sn etc., to improve the catalytic performance. The catalyst Cu-Ni/Al₂O₃-SiO₂, invented by Kao (a Japanese company) in 1998, gave a conversion of 98 – 99 % for the amination of alcohol.¹⁴ At present, the alcohol is used as the starting material for aliphatic tertiary amines by more than 95% of manufacturers including Kao, P&G and Lonza Lion. In China, more than 30 manufacturers are using this method. However, the strict requirements on the purity of raw materials, alcohol and methylamine, to be higher than 99% leads to a high cost. Therefore, the starting materials do not catch up with the standard in China.¹⁵

Tertiary amine synthesis routes

The route of industrial production for tertiary amine is shown in Figure 1.

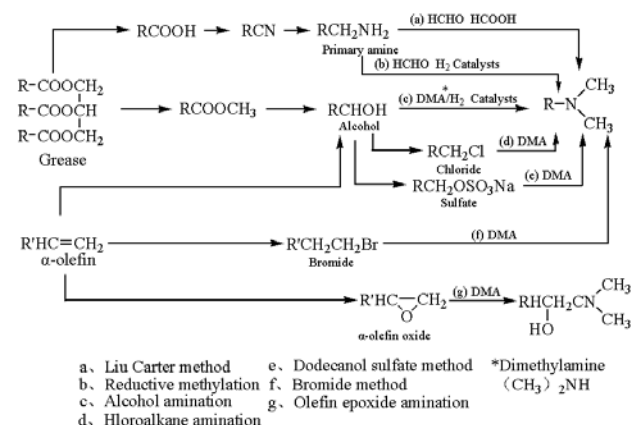
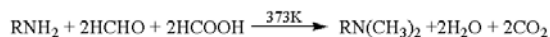


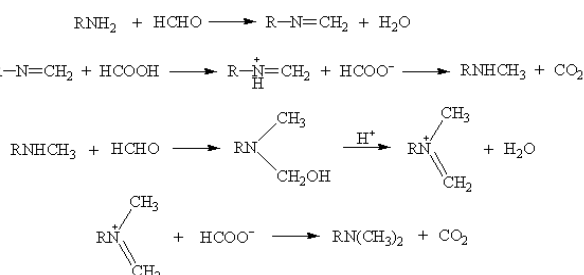
Figure 1. The manufacturing process of the aliphatic tertiary amines

(a) Liu Carter method (methylation of formic acid and formaldehyde)

At 373K, aliphatic tertiary amine can be prepared from primary amine, formaldehyde and formic acid.



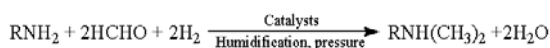
The reaction mechanism for the above reaction is as follows:^{17,18}



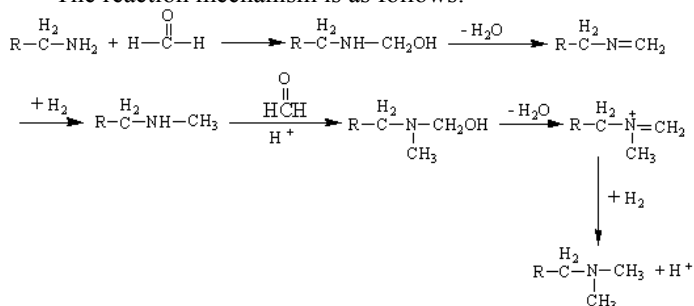
This method has disadvantages such as long process, many side reactions, high consumption of starting materials, treating of the waste gas, and bad quality of products.

(b) Reductive-methylation

The aliphatic tertiary amine can also be prepared by the reaction of primary amine with formaldehyde and hydrogen.

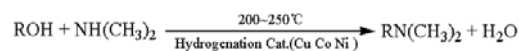


The reaction mechanism is as follows:¹⁹



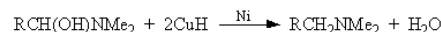
(c) Aliphatic alcohol amination

This method is important for the production of mono-long chain tertiary amine and has been used by Kao for a long time. The primary product has a purity of 95-99 %. d 99 % after distillation.

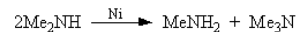


The reaction mechanism is as follows:^{17,18}

Main reaction:



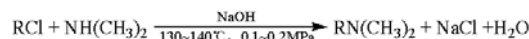
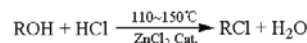
Side reaction:



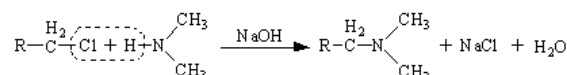
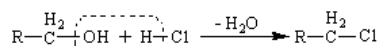
The product can then be used to prepare quaternary ammonium cation, alkyl betaines and amine oxides, sanitizers, algicides, antistatic agents, fabric softener, etc.¹⁶

(d) Amination of chloroalkane

The chloroalkanes can be synthesized from aliphatic alcohols, and then transformed into aliphatic tertiary amines by amination.



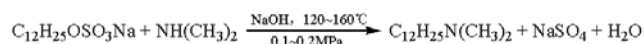
The reaction mechanism is as follows¹⁸:



As an important way to produce alkyl dimethyl amine, this process consists of two reaction steps, giving a total yield of about 80%.

(e) Alcohol sulfation

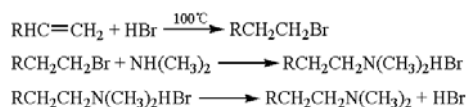
Dodecyl dimethyl amine can be prepared by the reaction from sodium lauryl sulfate and dimethylamine.



The method is being used by Albright & Wilson in England, and by the Third Synthetic Detergent Factory of Shanghai. The purity of product is 95 %.

(f) Bromination of α -olefins

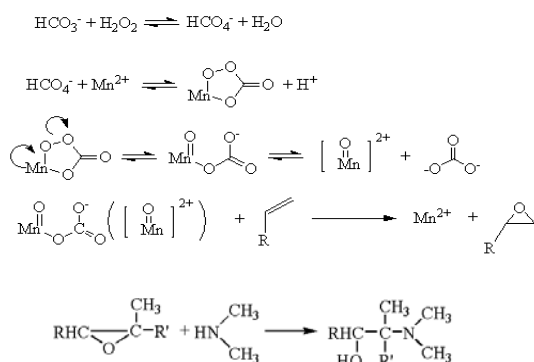
Aliphatic tertiary amines can be obtained through three successive steps: bromination of α -olefins, amination and decomposition of quaternary ammonium salts.



In China, the purity of the final product is *ca.* 98%, and the byproducts are mainly primary and secondary amines. The recycling of hydrogen bromide is still a problem to be solved.²⁰ Moreover, the shortage for α -olefin and the high level of byproducts limit its industrial use.¹⁶

(g) Amination of α -olefin epoxide

α -Olefins can be easily transformed into epoxide compounds by chlorohydrin process. However, it is reported²³ that the chlorohydrin method consumes much energy and chlorine, discharges large amount of wastewater containing calcium chloride, calcium hydroxide and organic chloride. In 1998, Drago²⁴ proposed the BAP (bicarbonate activated peroxide) system, in which the HCO_3^- was converted into HCO_4^- by H_2O_2 . This observation led a new catalyst system for amination of olefins. The reaction mechanism:



It will be a new route to prepare tertiary amine by dimethylamine and epoxide compound.

Summary

As shown in Figure 1, the primary amine and aliphatic alcohols are produced from natural grease, and the halides and epoxides are prepared by α -olefins using routes (f) and (g).

(1) The grease can be converted into primary amines through hydrolysis, cyanidation and hydrogenation process sequentially. Then the aliphatic tertiary amines can be obtained by route “a” or “b”. The whole technical process consists of too many reaction steps and the hydrolysis of grease is carried out at high temperature and high pressure (5.5MPa-6.5MPa).²¹⁻²²

(2) The routes “c”, “d” and “e” are competitive for their mild conditions, good product quality and non-corrosive pollution. However, much higher purities are required for the raw materials (alcohol and methylamine).¹⁵ For example, lauryl alcohol (dodecanol), used in route “c”, needs a purity of more than 99%, and is provided by Mitsubishi Corporation in China.¹¹

(3) The route “f”, involving the recycling of hydrogen bromide is not practical in China. Although the productions of epoxide compounds by chlorohydrination or with peroxyacid as oxidant in route (g) are not practical, yet the amination of α -olefin epoxides prepared with hydrogen peroxide is a meaningful route.

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