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CATALYTIC METHODS OF PREPARING ALIPHATIC AND ALICYCLIC AMINES

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I. INTRODUCTION

The chemistry of amines has long attracted the attention of research workers. In particular there are numerous papers on the chemistry of the aromatic amines, but during the past decade more and more papers on the aliphatic and alicyclic amines and on catalytic methods of synthesising them have appeared. These compounds have been the object not only of theoretical investigations but also of a number of investigations connected with the solution of important scientific and technical problems. Information on the aliphatic and alicyclic amines has not been unified and there are no review papers on this important branch of chemistry in recent literature. The well known review paper of Emerson[1] appeared in 1949 and, of course, does not contain material published later.

Aliphatic amines were first discovered by Würtz in 1849 [2] in distilling isocyanates with potassium hydroxide:

$$R{-}N{=}C{=}O + 2KOH \longrightarrow RNH_2 + K_2CO_3.$$

At present there are a number of general and particular methods of synthesising amines. Catalytic methods are the most widely used. The methods are very diverse both with regard to the starting materials and to the catalysts employed; by changing the reaction conditions the yield of primary, secondary, and tertiary amine can be altered as required. Alcohols, ethers, halogen derivatives, aldehydes, ketones, nitrogen-containing compounds, and unsaturated hydrocarbons are used as starting materials for the synthesis of amines. Catalysts have been proposed with the aid of which some amines may be converted into others. Because of the extensive literature on this problem, we considered it expedient to deal only with problems connected with amines proper and not consider amino-derivatives with other functional groups.

Amines are produced in large tonnages by the basic organic synthesis industry. They are used in the production of plastics, explosives, dyes, artificial fibres, and in a number of other branches of industry. For example, vinylamines are used as inhibitors in the polymerisation of vinyl acetylene [3] and also as accelerators in vulcanisation [4] and in the dyeing of polyacrylic fibres [5]. Primary, secondary and tertiary amines are used as addition compounds with boranes in the reduction of organic compounds [6]. Secondary aliphatic amines are used in the synthesis of enamines, the polymerisation and copolymerisation of which yield auxiliary materials used in the textile industry and in the production of plastics [7]. Some higher primary amines, for example, palmitylamine and stearylamine, give auxiliary materials for the textile industry when condensed with hydroxymethylamides [8]. Primary and secondary aliphatic amines are used for the preparation of aminoacroleins [9]. Aliphatic amines with 2 to 20 carbon atoms in the molecule are used as additives to bind metallic impurities in the distillation of alcohols obtained by the hydroformylation of alkenes and subsequent reduction of the aldehydes formed by hydrogen on a nickel catalyst [10]. In connection with reports that some high-molecular primary alkylamines suppress the development of the tubercule bacillus, 1-aminododecane, 2-aminotridecane, and 3-aminotridecane have been synthesised and show the maximum activity *in vitro* [11]. It has been shown that primary amines containing no more than five carbon atoms in the molecule ignite on mixing rapidly with highly concentrated nitric acid and can be used as fuel for liquid reaction engines; branching of the hydrocarbon chain in the amine molecule reduces the rate of ignition [that is, increases the ignition delay (Ed. of Translation)]; on the other hand, an increase in the number of alkyl groups attached to the amino-group increases it. A solution of triethylamine in 2,6-xylidine was used by the Germans under the name "Tonka 250" as a fuel for rocket engines. A mixture of stereoisomeric 2,7-diaminooctanes is used for the preparation of polyamides from adipic acid. In the polycondensation, polyamides with a molecular weight of ~ 50 000 are formed [12]. The secondary diamines

$$C_2H_5NHCR_2(CH_2)_n\,CR_2NHC_2H_5$$

(where R = CH_3 or C_2H_5 and n = 2–7) have been synthesised for tests of ganglionolytic activity; the greatest activity is found when n = 4 and R = C_2H_5. [13] Aliphatic amines of the type $(CH_3)_2NH$ etc. are used for the synthesis of some ethanolamines with spasmolytic properties. For example,

4-methoxy-ω-chloroacetophenone and dimethylamine yield the effective 4-hydroxy-ω-dimethylaminoacetophenone[14].

Midzhoyan and coworkers[15] carried out investigations in the field of amines and their derivatives with the object of preparing some chloroacetamides and urethanes. Compounds of the general formula

$$p\text{-}ROC_6H_4CH_2CH_2NHCOCH_2Cl$$

where R = CH_3, C_2H_5, C_3H_7, iso-C_3H_7, C_4H_9, iso-C_4H_9, have been synthesised by the following scheme:

$$p\text{-}ROC_6H_4CH_2Cl + NaCN \longrightarrow p\text{-}ROC_6H_4CH_2CN,$$
$$p\text{-}ROC_6H_4CH_2CN + H_2 \longrightarrow p\text{-}ROC_6H_4CH_2CH_2NH_2;$$
$$p\text{-}ROC_6H_4CH_2CH_2NH_2 + ClCH_2COCl \longrightarrow p\text{-}ROC_6H_4CH_2CH_2NHCOCH_2Cl.$$

Changes in the anticonvulsant action of compounds of the type p-$ROC_6H_4CH_2CH_2NHCOCH_2Cl$ have been studied. With R increasing, amines of the type p-$ROC_6H_4CH_2CH_2NH_2$ have also been used for the synthesis of some urethanes of interest because of their cancerolytic activity.

Khorlin and coworkers synthesised tertiary aliphatic amines with ganglionolytic activity. The amines obtained were subjected to pharmacological examination[16].

Kyo Fujie[17] synthesised seven derivatives of 2-(diphenylmethoxy)ethylamine and six derivatives of 3-(diphenylmethoxy)propylamine and tested them for papaverine-like anticonvulsant activity. The tests were carried out on smooth muscle from the rat uterus, the mouse intestine, and tracheal muscles of the guinea-pig.

Bonvicino and coworkers synthesised the hypnotics xanthene- and thioxanthene-$\Delta^{9\gamma}$-propylamines and related compounds[18].

Ryan and coworkers synthesised halogenoethyl-derivatives of acetyleneamines and carried out pharmacological tests on rats[19]. The greatest activity was found in compounds having the t-butyl group on a nitrogen atom and also having a methyl group.

Björn[20], in a search for new anaesthetics and a study of the effect of structure on physiological activity, prepared s-butylaminoacetanilides. It was shown that the introduction of a methyl-group on the α-C-atom in the amine part of the molecule does not always increase the anaesthetic activity, but it always increases the toxicity; it was shown that replacement of the isopropyl by a s-butyl group on the nitrogen, with the remainder of the molecule unchanged, increases both the anaesthetic activity and the toxicity.

In the presence of small quantities of orthoboric acid, polyamides are obtained from diamines (trimethylenediamine, etc.) and high-molecular-weight fatty acids; these are used as antioxidants for plastics[21]. Resin amines are used for the preparation of effective inhibitors of the corrosion of steel and other metals[22]. *N*-Substituted acrylamides, required for polymerisation and copolymerisation, are obtained by the dehydration of *N*-substituted hydracrylamides, which are synthesised by the reaction of β-propiolactone with amines in the presence of water[23]. Some amines, for example methylamine, are used technically for condensation with *l*-acetylphenylmethanol in the presence of a platinum catalyst[24]. Amines are also used for the stabilisation of sorbic acid salts[25]. 1,4,7-Triazaheptane is used with ethylene oxide for the preparation of polyhydroxyethylated polyamino-compounds (1,11-dihydroxy-3,6,9-triazaundecane-*NN'N''*-triacetic acid) which form water-soluble complexes with the metals calcium, barium, strontium, magnesium, iron, cobalt, nickel, copper, zinc, manganese, and aluminium. The iron complex is used in agriculture for supplying iron to citrus plants growing on calcareous soil[26]. Accelerators for the dyeing of acrylonitrile fibres with anionic dyes are obtained by the reaction of acrylonitrile with mono-, di-, and poly-amines[27]. New complexes are synthesised from isocyanates and tertiary amines[28]. Diaminoalkenes are used commercially as additives to fuel to increase the rate of combustion[29]. Methylamines are used in the leather industry, for the preparation of rubber vulcanisation accelerators, and for the production of explosives, bactericides, and pharmaceutical preparations[30]. Cyclohexylamine is used in making emulsifiers, anticorrosion coatings, rubber vulcanisers, etc.[31] The literature cited on the uses of amines is not exhaustive, but it illustrates the great diversity of uses for amines in different branches of the economy.

II. METHODS OF SYNTHESISING ALIPHATIC AMINES

The methods of synthesis of aliphatic amines and the conditions for the preparation of these reactive and labile compounds are very diverse. The methods differ substantially according to the nature of the starting materials and for this reason the methods are arranged here according to the nature of the materials being aminated.

1. Amination of Alcohols

Baum[32] considers that of all the dehydrating catalysts for the preparation of amines from alcohols or ethers the best catalyst is aluminium oxide. He studied the amination of n-propyl, n-butyl, isobutyl, and isopentyl alcohols and n-dibutyl ether at 220–550°. It was found that the optimal temperature lies within the range 200–350° for primary alcohols, 300–530° for secondary, and 400–550° for tertiary alcohols. The ratio of the quantity of ammonia to alcohol has a substantial effect on the relative amounts of amines formed. If primary amines are to predominate, the molar ratio alcohol:ammonia should be 4:1; for the formation of secondary amines from normal alcohols this ratio should be 2:1 or 3:1; and for iso-alcohols it should be 1:1. The contact time has a considerable effect on the amine yield. On the basis of his interpretations of the mechanism of catalytic amination, the author recommends that a small quantity of water should be introduced into the alcohol–ammonia or ether–ammonia system. It was found that this addition increases the yield of primary amines without affecting the total yield of amines. At temperatures up to 400° the aluminium oxide catalyst retains its activity practically indefinitely.

Goschorn[33] synthesised amines by the vapour-phase amination of aliphatic alcohols or ethers at 300–400° with a catalyst of oxides of metals of Groups II, III, or IV of the Periodic System, or silica gel on which oxides of metals of Groups V, VI, VII, or VIII have been deposited. Most frequently he used oxides of chromium, nickel, or cobalt. In a second patent[34], he obtained 24.9% of primary and 29.2% of secondary butylamine by the catalytic amination of butanol at 347° with a 1:4 molar ratio of butanol to ammonia. In a third patent[35], he aminated butanol at 320° in the presence of a catalyst based on ammonium molybdate, which enabled the reaction to be carried out at a lower temperature. The yield was 32.6% of primary and 23.6%

of secondary butylamine. Smith[36] recommends aluminium oxide as a catalyst in the reaction of methanol with ammonia at 450°; formation of trimethylamine may be kept to a minimum by the addition of 1–2 moles of water vapour.

Taylor and Raynolds[37] obtained amines from aliphatic alcohols with 2 to 13 carbon atoms in the molecule. Alcohol vapour together with ammonia and hydrogen was passed over a hydrogenation catalyst at 140–230°; the catalyst was an element of Group VIII of the Periodic System.

Doyvis and coworkers[38] proposed a method of preparing amines from aliphatic primary and secondary alcohols with 2–9 carbon atoms in the molecule or the corresponding aldehydes or ketones: the alcohol vapour with ammonia and hydrogen at 10–25 atm is passed over a copper catalyst at 240–300°.

Fowler[39] synthesised 1,2-diaminopropane from 1-aminopropan-2-ol by heating the latter with ammonia in the liquid phase at 150–250° and a pressure of 28–140 atm in the presence of a hydrogenation catalyst consisting of finely divided nickel or cobalt.

A Swiss patent[40] describes a method of preparing mono-, di-, and tri-alkylamines from primary and secondary aliphatic alcohols in the presence of a copper or aluminium/barium hydroxide catalyst at 240–300° and a pressure of 10–25 atm.

A French patent[41] describes a method of preparing primary amines from aliphatic alcohols in two stages. First alcohol vapour and excess of ammonia are passed over a catalyst of iron oxides at 360–420°. After the excess of ammonia has been removed from the condensate obtained, the latter is passed over a nickel hydrogenation catalyst at 100–130° and a pressure of 100–150 atm.

Popov and Shuikin[42] studied the amination of alcohols and were unable to confirm the views of Baum that aldehydes, ketones, ethers, or unstable compounds of alcohol with the catalyst are formed in this reaction. In their opinion amines are formed by the direct elimination of the elements of water from the molecules of alcohol and ammonia when they collide on the active surface of the catalyst.

Kozlov and Panova obtained aliphatic amines in high yield by the catalytic amination of ethers[43]. The vapour of dibutyl ether or diisobutyl ether was passed over alumina or thoria/alumina in a stream of ammonia under a pressure of 1–9 atm;[43] optimal results were obtained at 370–375° and a pressure of 9 atm; after distillation of the catalysate, mixtures of butylamine with dibutylamine and isobutylamine with diisobutylamine were obtained.

Bel'chev and Shuikin catalytically aminated n-butyl alcohol on a mixed oxide catalyst[44]; in the presence of 85% aluminia and 15% iron(III) oxide, which was the most active catalyst, at 405° and a volume flow of 0.75, amines were obtained in 42.8% yield (17.5% primary, 20.5% secondary, and 4.8% tertiary).

Kozlov and Panova[45] aminated butyl alcohols at 250–400° and a pressure of 1–10 atm in the presence of alumina. n-Butyl alcohol gave 89.9% of amines (62% primary, 29.8% secondary, and 8.2% tertiary); under the same conditions isobutyl alcohol gave 68.8% of amines and t-butyl alcohol gave 25.3%.

In a French patent[46] it is proposed to aminate primary or secondary aliphatic alcohols by gaseous ammonia on reduced metal catalysts (nickel, cobalt, copper, platinum, or palladium) in the presence of a hydrogen acceptor (the aldehyde or ketone corresponding to the alcohol). The yield of amines reaches 85%.

Rice and Kohn developed a method of preparing secondary and tertiary amines[47]; primary or secondary aliphatic amines are alkylated with alcohols in the presence of Raney nickel. Butylamine and anhydrous ethanol gave $C_2H_5N(n\text{-}C_4H_9)_2$ in 54% yield. Dibutylamine and anhydrous ethanol gave $C_2H_5N(n\text{-}C_4H_9)_2$ in 42% yield. Noeske and Kolling obtained amines from aliphatic alcohols through nitriles[48]. At first alcohol vapour and excess of ammonia were passed over an iron catalyst at 300–470°. After the excess of ammonia had been removed, the condensate obtained was hydrogenated on a nickel catalyst at 80–160° and a pressure of 100–150 atm. The yield of primary amines was 75–85%, and the yield of secondary and tertiary amines 5–15%.

Patnak and Rao synthesised methylamines, starting from methanol at 425° in the presence of alumina[49]. The yield was 50% of CH_3NH_2, 25% of $(CH_3)_2NH$, and 25% of $(CH_3)_3N$.

Bashkirov and coworkers[50] developed a method for the reductive amination of aliphatic alcohols or aldehydes at 230° and 100 atm pressure on Fe_3O_4 (V_2O_5). The yield of amines was 95–97%.

Bel'chev and coworkers[51] carried out the vapour-phase amination of primary alcohols (butyl and pentyl) on alumina and mixed catalysts; the highest yield of butylamines (80%) was obtained in the presence of 5% titanium dioxide/alumina.

Kochetkov and coworkers[52] synthesised secondary amines with a branched chain of the general formula:

$$C_2H_5NHCR_2[CH_2]_nCR_2NHC_2H_5,$$

where R = CH_3 or C_2H_5 and n = 2–7. Diols of the type $HOCR_2[CH_2]_nCR_2OH$ were used as starting materials.

Kagan and coworkers[53] studied the amination of higher aliphatic alcohols in the presence of a promoted fused iron catalyst under the pressure of hydrogen. Using the amination of octyl alcohols as an example, they found the effect on this process of pressure, temperature, volume flow, composition of the starting gas, and also the effect of the structure of starting alcohols. In the amination of octan-1-ol when the temperature is raised from 230° to 270° the total degree of conversion is increased from 89.5 to 96.5% but the yield of by-products increases by a factor of 3; at 240–250° and 100 atm pressure the yield of amines passes through a maximum of 86%. In the amination of octan-2-ol the yield of primary amines increases to 92%. Branching of the carbon chain sharply reduces the yield of amines and leads to a reduction in the yield of secondary and tertiary amines in the catalysate. Thus, 2-methylheptan-4-ol is converted into amines with only 71.0% yield; the yield from octan-4-ol is 85.0%, that from 2-ethylhexan-2-ol 75%, and that from octan-1-ol 90%.

Kozlov[54] aminated primary, secondary, and tertiary aliphatic and alicyclic alcohols under pressure in the presence of alumina at 370–380°. Increasing the pressure of the ammonia to 8–10 atm suppresses side-reactions and in some cases increases the yield of amines to 90% of the theoretical, based on alcohol reacting.

2. Amination of Carbonyl Compounds

Carbonyl compounds as possible starting materials for the synthesis of amines difficult to obtain from other compounds have attracted the attention of a number of workers.

Grigorovskii and Margolina[55] studied the reductive amination of butanal in the liquid phase with finely divided nickel as catalyst. The yield of butylamine was 74–80%.

Olin and McKenna[56] studied the vapour-phase amination of aldehydes at 175–180° in the presence of hydrogen on nickel or cobalt. The yield of amines was 87.7–90.9%.

Bami and coworkers[57] carried out the reductive amination of ketones on finely divided nickel (5–10%). The yield of amines was over 80%. 2-Aminobutane, 2-aminopentane, 2-aminoheptane, 2-aminooctane, 3-aminopentane, and 2-aminohexane were obtained.

Alexander and Misegades[58] obtained primary amines by the reductive amination of ketones under pressure. They used platinum as a catalyst and they noted that the addition of ammonium chloride increases the yield of amines.

Popov and Shuikin[59] studied the possibility of aminating acetone under the action of hydrogen and ammonia in the gas phase in the presence of platinised silica gel. They found that acetone at 240° under these conditions gives up to 37.1% of primary amine.

In a later paper, Popov and coworkers[60] studied the effect on the yield of amines in catalytic amination of the nature of the hydrocarbon radicals in different ketones. It was found that aliphatic ketones with the same hydrocarbon groups are more easily aminated than ketones with different groups. Lengthening the carbon chain in one of the groups leads to a reduction in the yield of amines and the greater the difference between the number of carbon atoms in the two groups the greater will be the reduction in yield.

Hentrich and Kaiser[61] proposed a method for the preparation of aliphatic amines from unsaturated ketones and ammonia or a primary amine. The reaction is carried out in the presence of a nickel–manganese–iron catalyst at 120° and 80 atm.

Iffland and Yen Teh-Fu[62] obtained aliphatic amines by the reduction of the corresponding ketoximes on a Raney nickel catalyst at 20° and 4 atm. The yield of amines was 51–85% (2-aminopentane 85%, 2-aminooctane 51%, 2-aminoheptane 45%).

Teter[63] gives directions for preparing an amination catalyst for use in suspensions; it contains 30–70% of cobalt on a kieselguhr carrier with a small amount of alumina.

Skita and coworkers[64] recommend a method for preparing tertiary aliphatic amines by the catalytic reduction of carbonyl compounds in a liquid phase in a solution close to neutral at normal temperature and high pressure. In the presence of $Pt/BaSO_4$ at 20° and 3.4 atm, triethylamine, tributylamine, and other amines were obtained from an aqueous alcoholic solution of ammonium acetate and the corresponding aldehydes.

Reppe and coworkers[65] synthesised secondary and tertiary aliphatic amines (diethylamine, diethylisobutylamine, etc.) by interaction of aldehydes or ketones with ammonia or amines for 24 h in the presence of water at 160° and the introduction of carbon monoxide under a pressure of 120–200 atm in a stainless steel autoclave.

Treszczanowicz and coworkers[66] synthesised ethylamine from acetaldehyde, hydrogen, and ammonia in the presence of a dehydrating catalyst. Comparative studies were done in the presence of two different catalysts: (1) 1–7.9% nickel, 2.1% chromium(III) oxide and 90% pumice, and (2) 4.9% nickel and 51% alumina. The yield of amines was 58.7 and 64.5%.

In a British patent[67] a method of producing aliphatic or cycloaliphatic amines is based on the interaction of aldehydes with ammonia or amines in the presence of nickel or cobalt. The reaction is carried out in the liquid phase with a low-boiling solvent (alcohol, hydrocarbons). Subsequent hydrogenation is carried out at elevated temperature under pressure.

Schade and coworkers[68] have patented a method for the preparation of pure n-butylamine from commercial butyraldehyde containing ketones and ethers as impurities. The formation of dibutylamine depends on the amount of ammonia introduced into the reaction and the presence of ketones in the starting aldehyde; the reaction is carried out in the presence of 50% nickel on alumina.

Schade and Sperling[69] developed a method of converting mono- and tri-ethylamine into diethylamine. The mono- and tri-ethylamine are brought into reaction with one another at 150–180° in the presence of nickel/alumina and, hydrogen and ammonia under a pressure of 2–3 atm. The mixture of mono- and tri-ethylamine is formed as a by-product in the preparation of diethylamine by the reductive amination of acetaldehyde.

Tindall[70] obtained secondary aliphatic amines by hydrogenating a mixture of aliphatic ketones with anhydrous ammonia or primary amines containing from 1 to 8 carbon atoms. The reaction is carried out in the presence of cobalt on calcium or barium sulphate at 160° and a pressure of 70–105 atm. Diisopropylamine is obtained in 73% yield.

Rauch[71] has proposed a method for the preparation of alkylidenealkenylamines from isobutyraldehyde and ammonia at 200° with the use of a manganese–cobalt oxide catalyst on pumice (7.5% manganese and 1.5% cobalt). Isobutylideneisobutylenamine is obtained in 97.4% yield.

For the preparation of diethylamine from acetaldehyde, hydrogen, and ammonia, Treszczanowicz and coworkers[72] used a catalyst of 49% nickel on alumina reduced by hydrogen at 320°. The yield of diethylamine was 54.2%, based on acetaldehyde.

In a further patent, Treszczanowicz and coworkers[73] propose that the preparation of amines from aldehydes, ammonia, and hydrogen[68] should be improved by evaporating at ~40° before it is mixed with the hydrogen; this prevents the formation of resins and significantly lengthens the life of the catalyst.

Günter and Jutta[74] hydrogenated polyenealdoximes on Raney nickel under pressure and obtained the corresponding higher primary n-alkylamines in good yield; decylamine was obtained in 90% yield from decatetraenealdoxime.

Morris and coworkers[75] developed two methods of preparing cycloheptylamine. In the first method, cycloheptanone oxime is hydrogenated in methanol at 60° and 0.75–1 atm in the presence of rhodium on alumina; the yield is 80%. In the second method, cyclopentanone in a mixture with liquid ammonia and alcohol is hydrogenated at 70° and 100 atm; the yield is 61%. Saito Atsudzi[76] obtained hexamethylenediamine in 72% yield from hydroxyadipaldehyde; the aldehyde reacts with ammonia and hydrogen for 6 h with a small amount of alcohol in the presence of Raney nickel at 220–240°.

3. Amination of Halogen Derivatives

The synthesis of amines by the catalytic amination of halogen derivatives seems very attractive and promising in the first place because the haloalkanes are produced on a large scale and form a cheap raw material. Moreover, it should be borne in mind that at present it is possible to obtain haloalkanes of practically any given structure and therefore a great diversity of amines can be obtained from them.

Nekrasova and Shuikin[77] studied the catalytic alkylation of ammonia by halogen derivatives of alkanes and cyclanes in the vapour phase at atmospheric pressure. Chloroalkanes were aminated at 310° in contact with a catalyst based on magnesium oxide. The yield of amines in the catalysate changed from 60 to 78.6% as the length of the chain was increased from C_4 to C_{10}. Chlorocyclopentane, chlorocyclohexane, and bromocyclohexane were aminated at 340°;[78] the effect of the nature of the halogen and its position in the molecule on amination was also studied. The greatest yield of amines was obtained by amination of the chloro-derivative and the least by amination of the iodo-derivatives. The position of the halogen in the haloalkanes has a considerable effect on the yield of amines.

Brown and Lester[79] set out to synthesise primary alkylamines with a long carbon chain and also with different arrangements of the amino-group in the carbon chain. The amines were synthesised in three ways: by Hofmann's reaction, by Leuckart's reaction, and by the reduction of amides in ether in a Soxhlet apparatus. The yield of amines by the first method was 60–78%. The amines were prepared by Leuckart's reaction from the corresponding ketones in 50–63% yield. In the third method the amines were obtained by the reduction of amides with lithium aluminium hydride in ether in a heated Soxhlet apparatus; the yield varied between 50 and 62%.

Schulte and Goe[80] synthesised primary aliphatic amines with a triple bond from 1-haloalkynes and hexamethylenetetramine in chloroform with subsequent decomposition of the quaternary hexaminium salt by alcoholic solution of hydrogen chloride. The effect of chain length and the position of the triple bond was studied. The quaternary hexaminium salt readily forms at ~ 20° in 90% yield from 1-haloalk-2-ynes independently of the chain length. The quaternary hexaminium salt is not formed from 1-haloalk-1-ynes in the cold or with heating. The stability of the quaternary hexaminium salt decreases with increasing chain length.

Tkaczynski and Kotelko[81] obtained ethylenediamine in 45% yield by the reaction of dichloroethane with ammonia; at the same time 1,4,7-triazaheptane (34%) and 1,4,7,10-tetrazadecane (12%) were separated. Tkaczynski obtained 1,2-diaminopropane and other diamines in an analogous manner, starting from dihalo-derivatives[82].

Hennion and Hanzel[83] prepared amines that were difficult to synthesise for steric reasons. Primary and secondary amines were alkylated with t-alkynyl chlorides. *N*-Isopropyl-1,1-dimethylprop-2-ynylamine was obtained from isopropylamine and 3-chloro-3-methylbut-1-yne at 20° after 7 d; the yield was 58%. The alkynamines were reduced to the corresponding allyl and saturated amines. Thus, *N*-isopropyl-1,1-dimethylprop-2-ynylamine in petroleum ether containing 0.01 g 10% palladium on carbon was reduced under pressure over 7 h at 20°, and *N*-isopropyl-1,1-dimethylprop-2-enylamine was obtained in 71% yield.

Nelson and coworkers[84] obtained $ClC(R)(R')CH{=}CHCl$ by the interaction of $HOC(R)(R')C{\equiv}CH$ with HCl; with the appropriate amines this gives $R''NHC(R)(R')CH{=}CHCl$ in 10–35% yield. Dehydrohalogenation of the compound $R''NHC(R)(R')CH{=}CHCl$ leads to $R''NHC(R)(R')C{\equiv}CH$ in 50–70% yield.

4. Addition of Ammonia to Alkenes

The considerable development of the petrochemical industry in the past decade has led to alkenes becoming bulk raw materials in the basic organic synthesis industry. This is the main reason why, in the search for uses for alkenes, the addition of ammonia to alkenes to form amines was investigated.

Teter[85] has proposed nickel or cobalt on a carrier as a catalyst in the amination of unsaturated compounds or their conversion into nitriles. With this catalyst, propene reacts with ammonia at 343–427° and high pressure. He has also patented[86] a method for the preparation of a cobalt catalyst with the addition of magnesium silicate for the amination of unsaturated compounds. The addition of 1% magnesium oxide as a promoter to the cobalt catalyst suppresses side-reactions and prevents the formation of carbon. He has also proposed[87] a method for the preparation of a new catalyst for the conversion of alkenes into amines. For this purpose a reduced nickel or cobalt catalyst is prepared on bentonite clay; it contains 40–50% of metal. Teter also investigated the catalytic amination and cyanation of alkenes in the presence of a cobalt catalyst[88,89].

The use of sodium as a catalyst for the synthesis of amines from alkenes and ammonia is described in a British patent[90]. For example, when isobutylene is heated to 250–265° with liquid ammonia under a pressure of 650–700 atm in the presence of metallic sodium, t-butylamine is obtained.

Tindall[91] has proposed a method of preparing amines by the reduction of nitroalkenes of the type $R{-}CH{=}C(NO_2){-}R'$, where R is alkyl or aryl and R' is alkyl. The reaction is carried out in the presence of Raney nickel catalyst under pressure in an inert organic solvent and in the presence of an organic acid with a dissociation constant between 1.86×10^{-5} and 1.1×10^{-3}.

Thurston[92] prepared amines from alkenes containing a double bond inside or at the end of the carbon chain and an alkyl group on the second hydrogen atom. The alkenes are first brought into reaction with cyanogen chloride or cyanogen bromide in the presence of an acid catalyst in the liquid phase; the reaction mixture is then subjected to hydrolysis and amine separates.

Graf[93] synthesised aliphatic amines by condensing alkenes with hydrogen cyanide in the presence of a strongly acid catalyst and hydrolysing the reaction product. Thus, 3-formylamino-3-methylheptane is obtained by the condensation of 2-ethylhex-1-ene with hydrogen cyanide in the presence of concentrated sulphuric acid and hydrolysis of the reaction product with sodium hydroxide; hydrolysis of the 3-formylamino-3-methylheptane with concentrated sulphuric acid gives 3-amino-3-methylheptane. Octylamines, 4-aminoheptane, a mixture of dodecylamine isomers, 2-aminodecane, etc. are obtained in a similar way.

Howk and coworkers[94] have proposed a method for the catalytic amination of alkenes under the influence of alkali

metals. It has been shown that ammonia, primary amines, and secondary amines are converted into *N*-alkyl derivatives by reaction with ethylene, propene, 2-methylbut-1-ene, but-2-ene, hex-1-ene, butadiene, and cyclohexene in the presence of sodium, potassium, or lithium. The reaction is carried out in a steel autoclave at 200° and 800–1000 atm and the yield reaches 70%.

Urry[95] recommends a method of alkylating primary, secondary, and heterocyclic tertiary amines at the α-carbon atom with the aid of alkenes. The reaction is initiated by alkyl peroxides at 90–130°, or under irradiation at 30–50°. When gaseous alkenes are used the reaction is carried out under pressure.

The alkenylamines are interesting compounds in their chemical possibilities, but there are only a few papers on this type of organic compound.

Engelhardt developed a method of preparing allene and acetylene amines by the interaction of 25% aqueous solutions of methylamine, diethylamine, morpholine, or n-butylamine with vinylacetylene under high pressure at a temperature of ~ 100°.[96]

Hasek and coworkers[97] synthesised allene amines by the following scheme:

$$(CH_3)_2CHCHO + NH_3 \longrightarrow (CH_3)_2CHCH[N{=}CHCH(CH_3)_2]_2 + H_2O$$
$$\downarrow$$
$$(CH_3)_2C{=}CHN{=}CHCH(CH_3)_2 + NH_3.$$

Nelson and coworkers[98] have proposed a method for the preparation of secondary alkynylamines by the interaction of α-chloroalkynes and aliphatic amines in the presence of bronze at a temperature below 40°; the yield is 10–21%, depending on the nature of the hydrocarbon radical of the primary amine.

5. Synthesis of Amines and Diamines by Hydrogenation of Nitriles

a. Synthesis of amines. The synthesis of amines from nitriles is effected under conditions close to those used in the amination of alcohols and haloalkanes, but not quite identical. As a rule, the hydrogenation of nitriles is carried out in the presence of catalysts based on Group VIII elements under increased pressure of 10–60 atm and at temperatures of 150–300°. Since in the reduction of nitriles, especially dinitriles, a complex mixture of products may be formed, it is important to select those conditions under which the reaction will go mainly in the desired direction. It is possible to find the necessary conditions for the synthesis of amines from nitriles by making a rational selection of catalyst, temperature, and pressure and, in a number of cases, by introducing ammonia into the reaction zone. For example, the synthesis of hexamethylenediamine from adipodinitrile is carried out on an industrial scale in many countries.

Pratt and Norris[99] obtained lower secondary and tertiary amines by the action of hydrogen on a mixture of nitrile with aldehyde, ketone, or alcohol at 200–300° in the presence of pure copper, iron, cobalt, or nickel, or with the addition of oxides of thorium, silicon, aluminium, chromium, or cerium. Pumice, silica gel, or bauxite may be used as a carrier. The molar ratio of the nitrile to the other component depends on whether primary or secondary amines are desired. From acetonitrile and acetaldehyde with excess of hydrogen on a nickel catalyst at 200–230° 98% of amines is obtained, consisting of 12% monoethylamine, 24% diethylamine, and 62% triethylamine.

In a patent by Mell[100], a method is proposed for the preparation of primary, secondary, and tertiary amines by the cyanation of alcohols with ammonia at 200° in the presence of nickel on kieselguhr; immediately after this the reaction mixture is passed over a hydrogenating copper or nickel catalyst at 100–180°. A mixture of primary, secondary, and tertiary amines is obtained in close to 100% yield.

A patent of Hoffman recommends the preparation of primary amines from nitriles by the action of liquid ammonia and hydrogen at elevated pressure in the presence of nickel on kieselguhr or Raney nickel[101].

A method for the preparation of primary amines from nitriles of aliphatic acids with ten or more carbon atoms has been patented[102]. These nitriles are converted into the corresponding primary amines by the action of hydrogen and ammonia at 210° and high pressure in the presence of Raney nickel.

A method of preparing high-molecular-weight primary amines from nitriles of higher fatty acids (stearic, etc.) is described in a patent[103]. Hydrogenation is carried out at a pressure up to 20 atm in the presence of nickel and with the addition of a small amount of barium hydroxide solution, caustic alkalis, or a quaternary ammonium base; under these conditions 93.5% of primary octadecylamine is obtained from stearonitrile.

A method of preparing primary aliphatic amines with six or more carbon atoms is described in a patent[104]. The nitriles of the fatty acids of coconut and cottonseed oils are hydrogenated at 130–150° and 15 atm in the presence of ammonia and Raney-nickel catalyst. An aqueous solution of ammonia or sodium hydroxide is introduced into the reaction mixture in quantity sufficient to maintain an alkaline medium during the whole hydrogenation process; the yield of primary amines is 77.4%.

Sakakibara and coworkers[105] catalytically reduced nitriles of higher fatty acids in the presence of bases. Lauronitrile and stearonitrile were hydrogenated on Raney nickel in the presence of liquid ammonia, sodium hydroxide, methylamine, or furfurylamine. The reaction products were separated into primary and secondary amines. In the reduction of nitriles without the addition of bases 19% of secondary amines were obtained with the primary amines; the presence of any of the bases mentioned suppressed the formation of secondary amines.

Renfrew and Warner[106] developed a method for the preparation of aliphatic amines from nitriles containing 8 to 22 carbon atoms, which were hydrogenated at 110–170° and 10.5 atm. A nickel hydrogenation catalyst was used and 0.5 to 10% (based on nitrile) of aliphatic alcohol was introduced together with ammonia.

Komori Saburo and coworkers[107] synthesised saturated and unsaturated aliphatic amines containing 8 to 22 carbon atoms by the reduction of nitriles obtained from natural fats; the reduction is carried out in the presence of nickel on silica gel and liquid ammonia at 90–150° under a hydrogen pressure of 10–200 atm. The presence of ammonia suppresses the formation of secondary amines and increases the yield of primary amines; under these conditions the yield of primary amine is 73.5% and of secondary amine 26.5%.

Suganuma Tokumasa and coworkers[108] obtained a mixture of secondary and tertiary aliphatic amines from aliphatic nitriles containing 8 to 18 carbon atoms in the molecule; the nitriles were reduced at 150–300° at high pressure in the presence of saturated C_1 to C_{18} alcohols and a nickel catalyst. A mixture of secondary and tertiary amines, depending on the quantity of alcohol, is formed according to the following scheme:

$$RCN + R'OH \xrightarrow{H_2} RCH_2NHR';$$
$$RCN + 2R'OH \xrightarrow{H_2} RCH_2NR'_2.$$

Tertiary amines with 20–30% of secondary amines are mainly formed by this method.

Sommers and Aaland[109] synthesised aliphatic amines by reduction of Schiff bases in the presence of lithium tetrahydroaluminate instead of a hydrogenation catalyst.

Kozlov and Panova[110] aminated carboxylic esters in the presence of alumina at 370°. The corresponding nitriles are formed as intermediates in the reaction.

Freifelder[111] synthesised primary amines of the type $R[CH_2]_n.CH_2NH_2$ by the catalytic reduction of the corresponding nitriles on a Raney rhodium–aluminium (Al–5%Rh) catalyst which is used in amounts 10–20% of the weight of nitrile. The reaction is carried out at 20° and 2–3 atm. The high selectivity of the catalyst is worthy of note. The reduction is carried out in the presence of ammonia to avoid the formation of secondary amines.

Yakushkin[112] hydrogenated a C_8–C_{13} fraction of nitriles to the corresponding primary amines in the presence of Raney nickel. The reaction was carried out at 120–200° and a hydrogen pressure of 20–60 atm; it was noted that as the temperature was raised the yield of primary amines diminished. The hydrogenation of n-$C_5H_{11}CN$ showed that the addition of ammonia and absolute alcohol increases the yield of hexylamine.

In a patent Denis[113] describes the synthesis of primary amines by the catalytic hydrogenation at 200° of aliphatic nitriles containing from 6 to 22 carbon atoms. Selective hydrogenation catalysts, Cr_2O_3, ZnO, $ZnO(Cr_2O_3)$ with the addition of CuO are proposed; alumina and aluminosilicate are used as carriers. The yield of amines varies within the range 60–71.2%.

Gould and coworkers[114] studied the hydrogenation of nitriles in the presence of Raney catalysts (nickel, nickel–chromium, cobalt) in acetic anhydride with basic additives. When sodium acetate was added, the activity of the catalyst decreases after three cycles; with sodium hydroxide the catalyst retains its activity for a longer period and the rate of reduction is higher, but the reaction is strongly exothermic. The yield of amines reaches 100%.

b. Synthesis of diamines. In this section other methods are presented apart from the synthesis of diamines from nitriles.

A method of preparing diamines from dinitriles of higher fatty acids by hydrogenation under pressures up to 20 atm in the presence of a nickel catalyst is described in a patent[103]; a small quantity of aqueous barium hydroxide solution, caustic alkalis, or a quaternary ammonium base is added.

Whetstone and Ballard[115] have proposed a method for the preparation of diamines from aliphatic dialdehydes containing 6 to 12 carbon atoms in the molecule, ammonia, hydrogen, and primary or secondary amines in excess of stoichiometric requirements. The reaction is carried out in the presence of a hydrogenation catalyst. Under these conditions diamines were obtained by the condensation of α-hydroxyadipaldehyde at 30–50° and 15–350 atm.

Schryer[116] synthesised 3-methylheptamethylenediamine from 5-methylhex-5-enenitrile. The nitrile was first treated with a mixture of carbon monoxide and hydrogen at 75–200° at a pressure not less than 50 atm in the presence of finely divided cobalt or its naphthenate, oxide, or carbonyl; the 6-cyano-3-methylhexenal obtained under those conditions at 75–250° was treated with a mixture of hydrogen and ammonia to give the diamine.

Roster and Schroeder[117] synthesised diamines by the reaction of the product of ozonization of a mixture of cyclohexene and a lower aliphatic alcohol with amines of the type NHRR', where R and R' are hydrocarbon groups with one to seven atoms of carbon; the reaction product was then hydrogenated in the presence of cobalt or nickel. To prepare the diamines (hexamethylenediamine, etc.), not less than two molecules of secondary amine or ammonia are used per molecule of cyclohexene.

Möller and Schröter[118] obtained tetramethylenediamine by the catalytic hydrogenation of succinodinitrile in an autoclave.

Regby[119] synthesised hexamethylenediamine by the reaction of adipaldehyde in solution with the secondary amine R'RNH and hydrogen at 25–150° in the presence of a hydrogenation catalyst; R and R' are cyclohexyl or alkyl groups containing from 1 to 12 carbon atoms.

Larramona[120] studied the formation of diamines of the type $R''_2NCH_2NR_2$ in the cleavage of α-vinylketones, $CH_2{=}CRCOR'$, by the action of secondary amines. The reaction proceeds through the intermediate formation of the β-aminoketone $R''_2NCH_2CHRCOR'$.

Swerdloff[121] obtained diamines by the catalytic hydrogenation of dinitriles in the presence of anhydrous ammonia and Raney nickel in a stainless steel autoclave.

Schreyer[122] developed a method of preparing di-primary aliphatic diamines. Glycols and aminoglycols containing 6–11 carbon atoms were used as starting materials; these reacted with ammonia at 150–250° and 400–700 atm in the presence of a ruthenium catalyst.

Adam[123] hydrogenated tetramethylenedinitrile in the presence of liquid ammonia and a catalyst containing 20% of cobalt and 0.3% orthophosphoric acid deposited on silicic acid at 85° and a hydrogen pressure of 300 atm. The yield of hexamethylenediamine is 90.9%.

A patent[124] describes the preparation of ethylenediamine from monoethanolamine or ethylene oxide with anhydrous ammonia at 180–210° and 145–150 atm in the presence of a hydrogenation catalyst. The yield of ethylenediamine reaches 80%.

In another patent[125] it is proposed to synthesise ethylenediamine from ethylene oxide or monoethanolamine in the presence of a specific catalyst consisting of finely ground nickel–magnesia. The use of such a catalyst in the proportion of 1–10% of the ethylene oxide or monoethanolamine allows the reaction temperature to be reduced to 150–180°, which reduces the formation of by-products and increases the yield of ethylenediamine.

Wiemann has patented a method of preparing 2,7-diaminooctane from octa-2,7-dione[12]. The reaction is

carried out in an atmosphere of hydrogen in the presence of Raney nickel and 30% ammonium hydroxide. A mixture of stereoisomers of 2,7-diaminooctane is formed.

Jefferson and coworkers[126] developed a detailed formula for the preparation of promoting catalysts based on cobalt oxide for the synthesis of hexamethylenediamine. The catalyst was partially reduced and silica (0.04–1%) and titanium dioxide (0.08–0.18%) were used as promoters.

Indest and Meyer[127] obtained hexamethylenediamine of high purity and in 96 to 99% yield by the continuous catalytic hydrogenation of adipodinitrile. Granulated nickel–aluminium alloy (40–60% nickel) was used as a catalyst. The catalyst retained its activity for 30–60 d, after which it was completely regenerated 7–10 times. The dinitrile was hydrogenated in the presence of a solvent (liquid ammonia, methanol, etc.) at 20–80° and a hydrogen pressure of 100–500 atm. The yield of hexamethylenediamine is 98.7%.

Polkovnikov and coworkers[128] have proposed a method for the preparation of hexamethylenediamine from adipodinitrile by hydrogenating the latter in the presence of cobalt boride at 100° and 130 atm. The yield of hexamethylenediamine is 92.6%.

Nakajima[129] studied the condensation of diethylaminoethanol with various imides; when the condensation product is hydrolysed by heating to 360° *NN*-diethylethylenediamine is formed. The yield is 85%.

Miva Itiro and coworkers[130] obtained diamines in a high degree of purity by the hydrogenation of nitriles in the presence of cobalt or nickel formates at 230° and increased pressure. The yield of hexamethylenediamine is 88.5%.

6. Other Methods of Preparing Amines

Bashkirov and coworkers[131] have developed a new method of preparing aliphatic amines in which a mixture (1 : 2) of carbon monoxide and hydrogen is passed with ammonia over a promoted iron catalyst. The yield of amines is 25% and 82–96% of these are primary amines. These workers have improved this method of synthesising amines from carbon monoxide, hydrogen, and ammonia[132]. As a result of the interaction of these gases in the presence of a fused iron catalyst, aliphatic amines, mainly primary, with one to 20 atoms and more in the carbon chain are formed. From one cubic metre of these gases 120 g of material is obtained containing 54% of alkylamines (33% liquid and 21% gaseous amines). n-Butylamine, n-pentylamine, n-hexylamine, n-heptylamine, and n-octylamine have been identified in the products of the synthesis.

Aygen and Wolfgang[133] have proposed a method of preparing primary, secondary, and tertiary amines by the methylation of ammonia, primary amines, and secondary amines with diazomethane. The reaction is carried out in the presence of halogen, halogenoalkyl, and alkoxy-derivatives of boron at -80° to 0° in an inert organic solvent. The yield of amines reaches 82%.

Dose[134] has developed a method of preparing aliphatic amines by the decarboxylation of α-amino-acids in the presence of aromatic aldehydes, nitrobenzene, xylene, trichlorobenzene, etc. The presence of solvents in the reaction mixture suppresses the formation of by-products. The reaction is carried out according to the following scheme:

$$CH_3—CH_2—CH(NH_2)COOH \rightarrow CO_2 + CH_3(CH_2)_2NH_2.$$

Bashkirov and coworkers[135] studied the synthesis of amines from carbon monoxide, hydrogen, and ammonia on promoted iron catalysts. The best results were obtained by using a mixture of carbon monoxide 12%, hydrogen 68%, and ammonia 20% with a volume rate up to 100 h^{-1} and temperatures up to 200°. The yield of amines reached 50%.

Johnston[136] synthesised amines from amides by reducing them with sodium tetrahydroborate.

Synthesis of alicyclic amines. There is much less information in the literature on the synthesis of alicyclic amines than on the preparation of aliphatic amines. In principle, the methods of synthesis of amines of these two classes of compounds are similar and differ only in the reaction conditions. Because of the limited amount of material it would not be useful to group it in several sections, as was done for the aliphatic amines; we shall confine ourselves to presenting it in chronological order.

Mousseron[138] obtained 3-methylcyclohexylamine in 60% yield (75% *trans* form) from 3-methylcyclohexanone in the presence of platinum(IV) chloride. 2-Methylcyclohexanone gave only 35% of 2-methylcyclohexylamine. The addition of a small quantity of hydrogen hexachloroplatinate(IV) to Harley's catalyst[138] in the amination of 3-methylcyclohexanone reduces the yield of the *trans* form.

Adkins and Billica[139] used a nickel catalyst and hydrogen under a pressure of 15–45 atm at 25–30° for the conversion of cyclohexanone oxime into cyclohexylamine. The yield is 90%.

Popov and Shuikin[140] studied the catalytic amination of cyclohexanol in the presence of hydrogenating and dehydrogenating catalysts. Of these, platinised silica gel was found to be the most active. In the presence of this catalyst at 320° the yield of cyclohexylamine reached 51.3%, calculated on the cyclohexanol consumed in the reaction.

Popov and Shuikin aminated cyclohexanol in the gas phase by the action of hydrogen and ammonia on platinised silica gel[59]. It was found that cyclohexanone at 200° gives up to 89.6% of primary amine.

Kozlov and Akhmetina[141] studied the catalytic amination of cyclohexanol on aluminium oxide in a flowthrough system at 150–380° and an ammonia pressure of 1–20 atm. At a pressure of 5–10 atm the amination predominates and the dehydration of the cyclohexanol almost ceases. It was established that the optimal temperature range is 260–300°; below this the reaction is extremely slow and at a higher temperature the cyclohexylamine decomposes into ammonia and cyclohexene. The yield of cyclohexylamine reaches 70–74%, based on cyclohexanol taken, or 90–95%, based on cyclohexanol consumed in the reaction.

Cairns and Gilbert[142] have proposed a method of preparing polycyclic tertiary amines. Cycloalkanols containing 5–7 carbon atoms and having at least one methylene group in the α-position to the C–O group are used as starting materials.

Popov and Shuikin[143] have synthesised cyclopentylamine by passing a mixture of cyclopentanone with excess of ammonia and hydrogen over nickel on aluminium oxide or pumice. The optimal temperature is 150°; at higher

temperatures resin formation increases and the yield of amines decreases. The best yield of amines on nickel deposited on aluminium oxide was 66.6% (55.6% of cyclopentylamine and 11% of dicyclopentylamine).

Naumov and coworkers[144] studied the reaction for the preparation of cyclohexylamine by hydrogenating aniline on different catalysts in the gas phase at atmospheric pressure. Two reactions were studied:

$$C_6H_5NH_2+3H_2-C_6H_{11}NH_2, \quad (I)$$

$$2C_6H_{11}NH_2 \rightleftarrows NH_3+(C_6H_{11})_2NH. \quad (II)$$

An Ni/Al_2O_3 catalyst promotes the second reaction. A mixed CoO/CaO catalyst at 190–200° is active only in the formation of cyclohexylamine. The ease with which reaction (II) proceeds and its reversibility on a nickel–alumina catalyst makes it possible to convert aniline almost completely into cyclohexylamine and dicyclohexylamine.

Noeske and Kolling[145] have patented a method of preparing alicyclic amines. Saturated alicyclic mono- and di-aldehydes, hydroxyaldehydes, and products of the oxo-synthesis containing alicyclic aldehydes may be used as starting materials. Hydrogenation is carried out in the presence of nickel on magnesium oxide with kieselguhr at 120° and 90 atm. The yield of (tricyclodecylmethyl)-amine from tricyclodecylmethylal is 83%.

Kost[146] studied the possibility of using Raney nickel and cobalt catalysts in the synthesis of amines. It was shown that cobalt catalysts are less effective, but more convenient in practice, because the change of colour of the reaction mass enables the end of the hydroamination to be determined. Methods of preparing mono- and di-cyclohexylamine from cyclohexanol by the Leuckart reaction have been studied and it has been shown that dicyclohexylamine is sometimes contaminated with formylcyclohexylamine formed by hydrolysis.

Naumov and coworkers[147] proposed a synthesis of cyclohexylamine by hydrogenating aniline at 120–170° in contact with cobalt(III) oxide or mixed oxides, hydroxides, or carbonates of magnesium or strontium. The maximal yield of cyclohexylamine is 96–98% with an admixture of 2% of dicyclohexylamine.

Ivanova[148] obtained cyclohexylamine in 97% yield by hydrogenating nitrocyclohexane on a Raney nickel catalyst.

Illick and Robinson[149] have proposed the preparation of cyclohexylamine by hydrogenating aniline in the presence of a rubidium catalyst. The yield of cyclohexylamine is 81.6%.

Zienty obtained substituted amines (2-cyclopentyl-1-methylethylamine, 1-cyclopentyl-2-aminopropane, 2-cyclohexyl- and 2-cycloheptyl-1-methylethylamine) by hydrogenating the corresponding carbonyl derivatives of cyclopentyl-, cyclohexyl-, and cycloheptyl-acetone, etc. in the presence of a nickel catalyst (70% nickel)[150].

Nisimura Keidzo synthesised cyclohexylamine by the hydrogenation of aniline and acetanilide in the presence of Raney nickel–aluminium catalyst; the catalyst was prepared by treating an alloy of nickel–aluminium and a metal of variable valency with a solution of sodium carbonate and barium hydroxide[151]. The hydrogenation was carried out at 200° and 70 atm.

Wheaton obtained cyclohexylamine in 50% yield by the reaction of cyclohexane with ammonia under the action of ionising radiation with energy ⩾ 15 eV.[152]

McKeever and Washburne[154] have proposed a substantial improvement in a method of preparing 1,8-diaminomenthane[153]. As starting material they used limonene, terpin hydrate, dipentene, etc. Reaction with hydrogen cyanide, sulphuric acid, and water was carried out at 50–55° and the 1,8-diaminomenthane was separated; the yield was 57%, calculated on dipentene.

From the great amount of literature material quoted here it is quite clear that for the synthesis of the simplest amines the greatest attention is being devoted to the development of methods based on the catalytic vapour-phase amination of alcohols or alkyl halides. These methods are most promising from the point of view of both production technology and the use of cheap raw materials available in bulk. As far as the catalytic synthesis of more complex amines is concerned, this is often carried out by aminating nitriles or carbonyl compounds in the liquid phase. Metals of Group VIII of the Periodic Table are widely used as catalysts. In recent years papers have begun to appear on the reductive amination of a number of compounds with the aid of aluminium and boron hydrides, fused iron catalysts, and promoted oxides of an acidic and amphoteric character, for example, vanadium pentoxide.

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PROGRESS IN THE STUDY OF THE AGING OF FIBROUS CELLULOSIC MATERIALS

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