

---

# UNIT 19 AMINO COMPOUNDS AND DIAZONIUM SALTS

---

## Structure

- 19.1 Introduction
  - Objectives
- 19.2 Natural Occurrence and Nomenclature of Amines
- 19.3 Structure of Amines
- 19.4 Physical Properties of Amines
- 19.5 Spectral Characteristics of Amines
- 19.6 Preparation of Amines
- 19.7 Reactions of Amines
- 19.8 Reactions of Diazonium Salts
- 19.9 Uses of Amines
- 19.10 Laboratory Detection of Amines
- 19.11 Summary
- 19.12 Terminal Questions
- 19.13 Answers

---

## 19.1 INTRODUCTION

---

Amines represent one of the largest classes of nitrogen containing organic compounds. You are aware that amines are compounds in which one or more alkyl or aryl groups are attached to nitrogen. You have studied in Unit 18 that nitro compounds can be reduced to amines. In this unit, you will study other methods of preparation of amines. Because of the pair of nonbonding electrons on the nitrogen atom, amines are important organic bases. They behave as nucleophiles as you studied in their reactions with carboxylic acid derivatives. They react with nitrous acid which is electrophilic in nature. The reaction of primary aromatic amines and nitrous acid gives diazonium salts which can lead to a large variety of organic compounds. The reactions of diazonium salts will also be dealt with in this unit. Finally, you will study about the uses of amines and the methods employed for their detection in the laboratory.

### Objectives

After studying this unit, you should be able to:

- classify amines as primary, secondary or tertiary,
- give systematic names of amines;
- correlate the physical properties of amines with their structures,
- outline the synthesis of amines using various methods,
- describe the reactions of amines,
- explain the synthetic uses of diazonium salts,
- list some important amines and their uses, and
- give methods of detection of amines in the laboratory.

---

## 19.2 NATURAL OCCURRENCE AND NOMENCLATURE OF AMINES

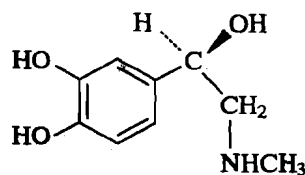
---

Amines are widely distributed in nature. A large class of amines of plant origin is called **alkaloids**. *Strychnine* and *brucine* which you studied in Unit 3 with regard to the resolution of enantiomers are alkaloids. Some of the alkaloids have medicinal while others have poisonous properties. Examples of such alkaloids include *quinine*, which is antimalarial and antimicrobial, *caffeine* and *atropine* which are used as stimulants.

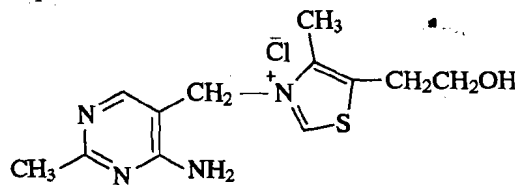
The term **alkaloid** was coined by F.W.A. Sertürner who in 1816, described morphine as basic and *alkali like*.

Alkaloids will also be discussed in Unit 20.

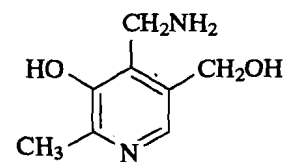
The alkaloids occurring in animals include many essential vitamins and hormones. Some examples are shown below.



adrenaline  
(a hormone secreted  
by adrenal glands)

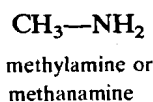


vitamin B<sub>1</sub>  
(thiamine chloride)

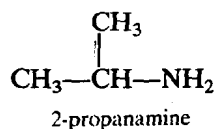


pyridoxamine  
(one of the complex  
B<sub>6</sub> vitamins)

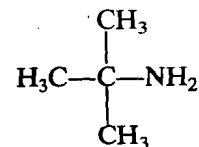
You may recall from Unit 1, Block 1, that amines can be classified as **primary**, **secondary** or **tertiary** depending on the number of alkyl or aryl groups attached to the nitrogen atom. When the substituents attached to the nitrogen are **alkyl** groups, the amine is called an **alkyl amine**. But the amines in which **at least one** of the substituents attached to the nitrogen atom is an **aryl** group, are called **aryl amines**. Examples of primary, secondary and tertiary, alkyl as well as aryl, amines are given below:



a primary alkyl amine

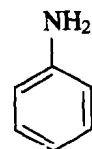


a secondary alkyl amine



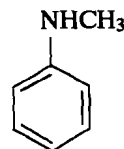
1,1-dimethylethanamine

a tertiary alkyl amine



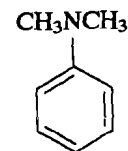
benzenamine  
(aniline)

a primary aryl amine



*N*-methylbenzen-  
amine (*N*-methy-  
laniline)

a secondary aryl amine



*N,N*-dimethyl-  
benzenamine  
(*N,N*-dimethylaniline)

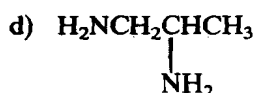
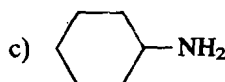
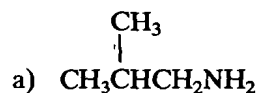
a tertiary aryl amine

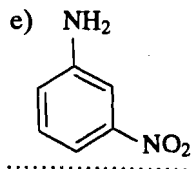
The nomenclature of alkyl and aryl amines was discussed in Block 1, Unit 1, Sec 1.6, whereas the nomenclature of heterocyclic nitrogen compounds was discussed in Block 2, Unit 10, Sec. 10.2.

Why don't you check how much do you remember about the nomenclature of amines by answering the following SAQ.

### SAQ 1

Write systematic names of the following amines:



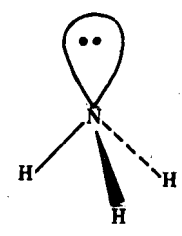


If you don't feel confident that you can correctly name the amines, go back to Block 1, Unit 1, Sec. 1.6 to refresh your knowledge about nomenclature.

### 19.3 STRUCTURE OF AMINES

You may recall from your earlier studies that ammonia has a pyramidal shape. The HNH angle in ammonia,  $107.3^\circ$ , is very close to the angle of a tetrahedron, Hybridisation in ammonia can thus be described as nearly  $sp^3$

The structure of amines is similar to the structure of ammonia. Aliphatic amines have a pyramidal shape or if we regard the lone pair of electrons as a group, an approximately tetrahedral shape. The three vertices of the tetrahedron are occupied by three substituent groups and the fourth is occupied by the lone pair. If the three substituents are different then the nitrogen is *chiral*. This leads to the possibility of existence of enantiomers. The enantiomers of *N*-methylethanamine are shown in Fig. 19.1



ammonia

The nearly tetrahedral structure of methanamine (methylamine)

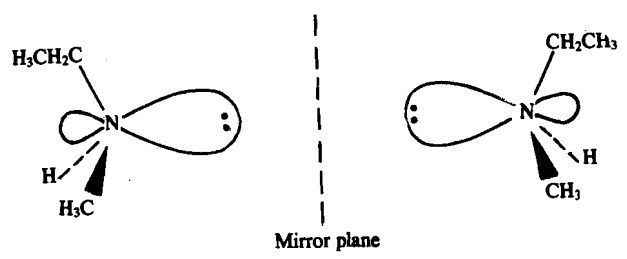
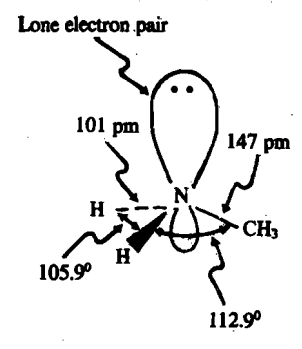


Fig. 19.1 : Enantiomers of *N*-methylethanamine.

But, in the absence of steric factors, amines undergo a *rapid inversion* at nitrogen via a planer transition state to yield their enantiomers, as is shown in Fig. 19.2. So it is not possible to isolate the enantiomers.

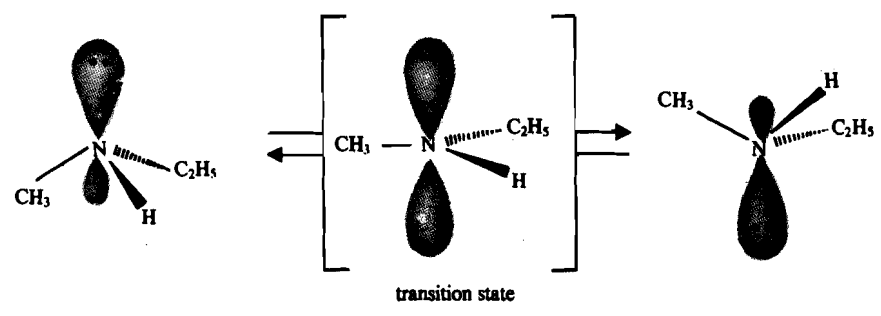
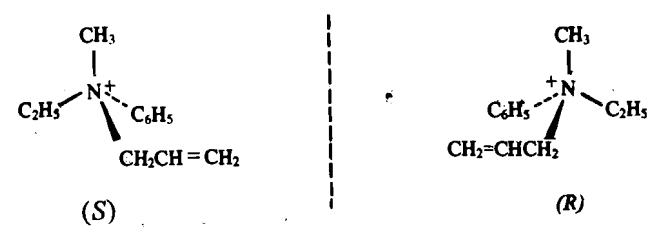
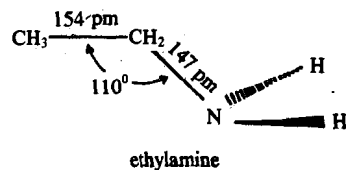
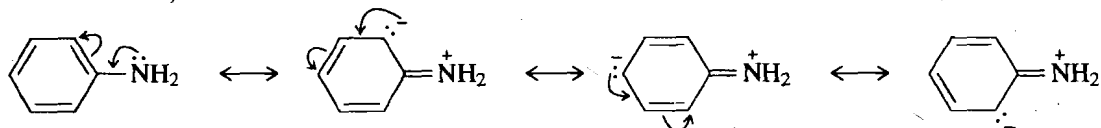


Fig. 19.2 : Inversion at nitrogen interconverts the enantiomers of *N*-methylethanamine.

Since such an inversion is not possible in quaternary ammonium compounds, they can be separated into enantiomers. The enantiomers of such a quaternary ammonium ion are shown below:



Aryl amines have larger HNH and HNC angles indicating that nitrogen in aryl amines is more nearly planar than in alkylamines. In aryl amines, the lone pair of electrons is delocalised with the  $\pi$  electrons of the aromatic ring. The resonance structures, thus, obtained are shown below for benzenamine.



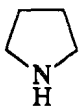
You can see the double bond character of C-N bond in some of these resonance structures. Thus, C—N bond in benzenamine is shorter (140 pm) as compared to that in aliphatic amines (147 pm).

Let us now study the physical properties of amines and try to relate them to the structure of amines.

## 19.4 PHYSICAL PROPERTIES OF AMINES

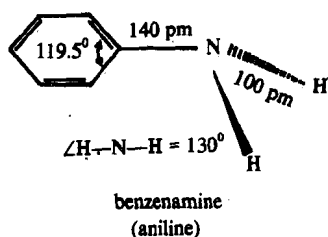
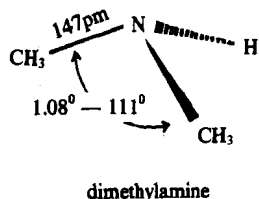
The physical constants of some amines are given in Table 19.1.

Table 19.1 : Physical constants of amines

Amine	Molecular weight	Melting point /K	Boiling point /K
<b>Primary amines</b>			
$\text{CH}_3\text{NH}_2$	31	179	277
$\text{CH}_3\text{CH}_2\text{NH}_2$	45	192	290
$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$	59	190	321
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$	73	224	351
$(\text{CH}_3)_2\text{CHCH}_2\text{NH}_2$	73	188	341
$(\text{CH}_3)_3\text{CNH}_2$	73	206	318
aniline, $\text{C}_6\text{H}_5\text{NH}_2$	93	267	467
<i>o</i> -nitroaniline	138	345	557
<i>m</i> -nitroaniline	138	387	579
<i>p</i> -nitroaniline	138	421	605
<b>Secondary amines</b>			
$(\text{CH}_3)_2\text{NH}$	45	181	280
$(\text{CH}_3\text{CH}_2)_2\text{NH}$	73	223	329
	70	275	336
<i>N</i> -methylaniline	106	216	469
<i>N</i> -ethylaniline	120	210	478
diphenylamine	169	327	575
<b>Tertiary amines</b>			
trimethylamine, $(\text{CH}_3)_3\text{N}$	59	156	276
triethylamine, $(\text{C}_2\text{H}_5)_3\text{N}$	101	159	363
<i>N,N</i> -dimethylaniline	121	276	467
triphenylamine	245	400	638

The physical constants of the amines listed in Table 19.1 show that most amines are liquids. Amines generally have unpleasant fishlike odours.

You can clearly visualise certain trends in the physical constants of amines as listed in Table 19.1 which you studied in Unit 4, Block 1.



Primary and secondary amines can participate in intermolecular hydrogen bonding. The N—H...H hydrogen bonds are weaker than O—H...O hydrogen bonds because nitrogen is less electronegative than oxygen. Thus, the boiling points of primary amines are intermediate between those of alcohols and alkanes of comparable molecular weight. The hydrogen bonding is also a factor governing the water solubility of amines.

### SAQ 2

The melting point and boiling point of 2-nitrobenzamine (*o*-nitroaniline) are lower than its 3-nitro (*meta*-) or 4-nitro (*para*-) isomer. Why?

.....

.....

## 19.5 SPECTRAL CHARACTERISTICS OF AMINES

### UV spectra

The absorptions due to  $n \rightarrow \sigma^*$  transitions of saturated amines occur at short wavelengths ( $\sim 220$  nm) and, therefore, are not of much use for identification purposes.

### IR spectra

The infrared spectra of primary and secondary amines show a characteristic broad band due to N—H stretching absorption in the region between  $3300$  to  $3500$   $\text{cm}^{-1}$ , see Fig. 19.3. Primary amines show two bands in this region whereas secondary amines show only one band. The N—H bending absorption of primary amines is observed near  $1600$   $\text{cm}^{-1}$ .

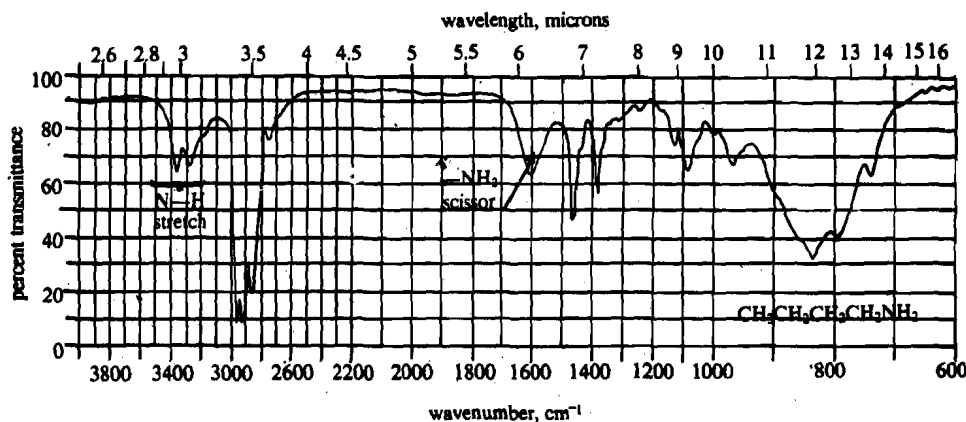
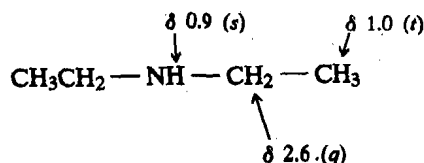


Fig. 19.3 : IR spectrum of butanamine.

### NMR spectra

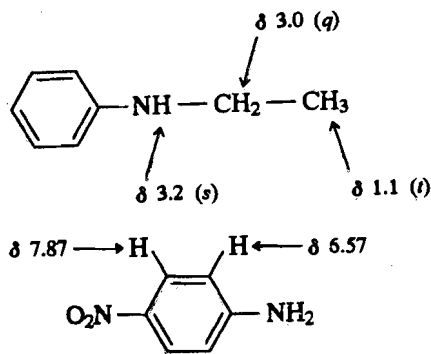
The H—C—N protons of alkylamines show absorption in the range  $\delta$  2.5-3.0. The absorption occurs further downfield in aromatic amines, i.e., near  $\delta$  3. The chemical shift of the N—H proton, like that of the O—H proton in alcohols, depends on the concentration of the amine and on other factors such as solvent and temperature. The N—H proton also undergoes chemical exchange as is observed in case of —OH protons of alcohols.



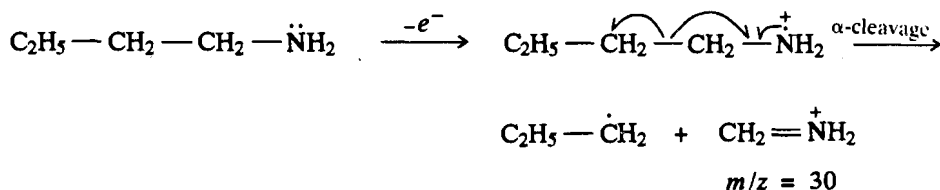
The absorption of protons of aromatic ring *ortho*- and *para*- to the amino nitrogen is shifted to higher field than that of the *meta*-protons indicating the increased electron density at the *ortho*- and *para*-positions.

### Mass spectra

The mass spectra of aliphatic amines show a peak at  $m/z = 30$  due to the following fragmentation from the  $M^+$  ion:



For example,

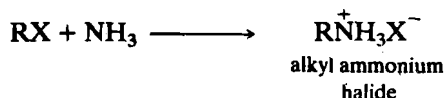


## 19.6 PREPARATION OF AMINES

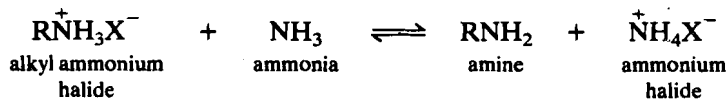
The various methods used for the preparation of amines are discussed below:

### 1) By direct alkylation of ammonia and other amines

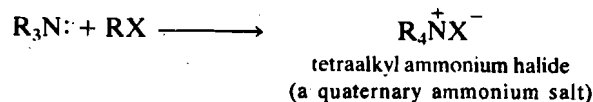
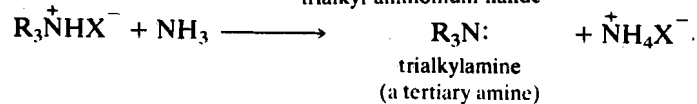
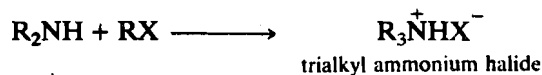
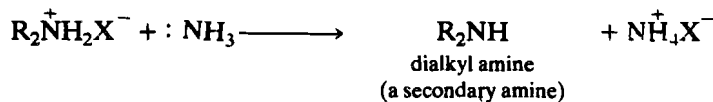
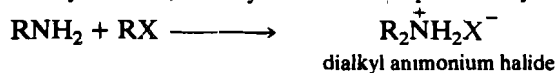
Ammonia and amines react with alkyl halides to yield amines. Let us understand this reaction with the example of ammonia and a primary alkyl halide.



This reaction follows the  $\text{S}_{\text{N}}2$  path. If excess of ammonia is not used then the reaction stops at the stage of alkyl ammonium halide. In the presence of excess ammonia, another molecule of ammonia deprotonates the alkylammonium ion thereby liberating the free amine.

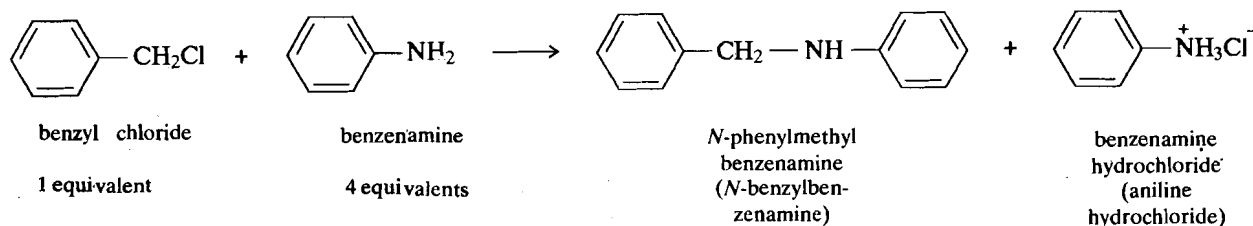
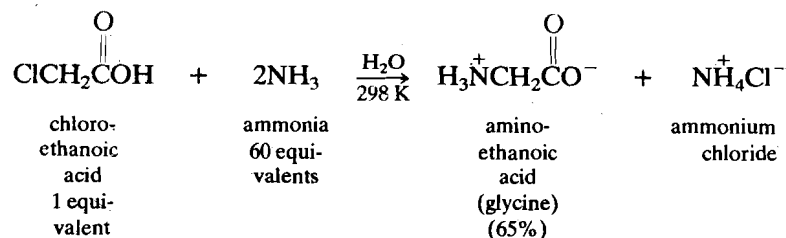


The resulting amine being a nucleophile reacts further with alkyl halide to yield dialkyl amine, trialkyl amine and quaternary ammonium salts as shown below.



A secondary amine is a stronger nucleophile than a primary amine.

Thus, a mixture of products is formed which limits the synthetic value of this reaction for the synthesis of primary amines. The overalkylation may be suppressed by using a large excess of ammonia or amine provided the amine is inexpensive and the desired product can be easily separated from the reaction mixture. Some examples follow:

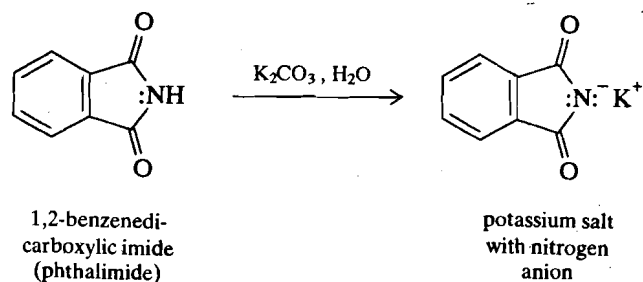


In many cases, even after using a large excess of the amine or ammonia, only moderate yields of desired amine are available. In such cases, indirect methods which give better yields are employed. One such method is the Gabriel synthesis which you will now study.

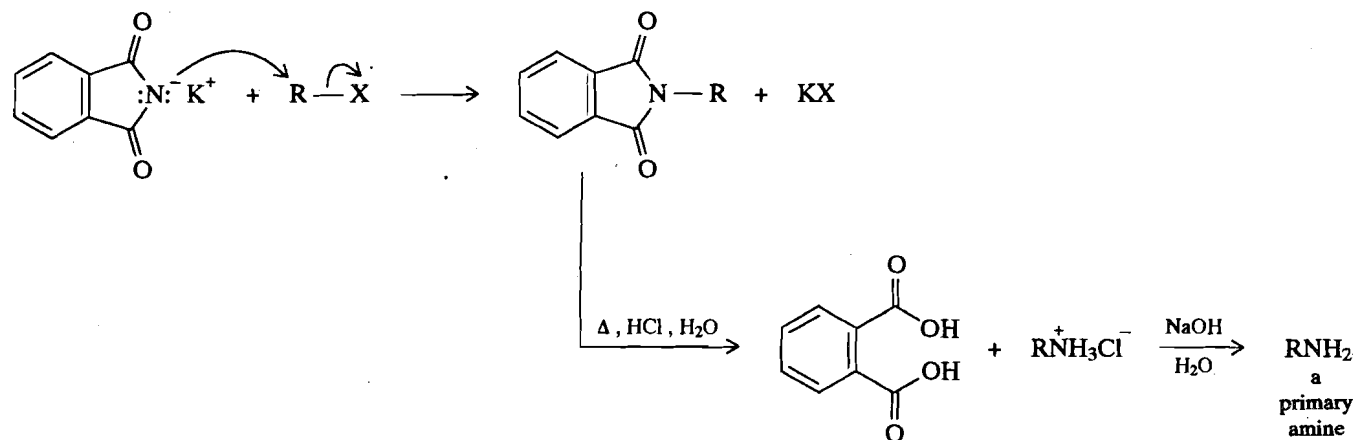
## 2. Indirect alkylation: The Gabriel synthesis

Pure primary amines can be prepared conveniently if the nitrogen atom is protected so that alkylation can take place only once.

Such a protected nitrogen is present in 1,2-benzenedicarboxylic imide. Because the nitrogen atom has two adjacent carbonyl groups, the NH group is acidic enough ( $\text{p}K_a=8.3$ ) to be deprotonated using a mild base to yield a nitrogen anion in a salt.



The nitrogen anion is a good nucleophile and can undergo a wide variety of nucleophilic substitution reactions. It reacts with alkyl halides to yield *N*-alkyl derivative in good yield. *N*-alkyl derivative on acidic hydrolysis yields the ammonium salt from which the free amine can be liberated by treatment with a base. Such a sequence of reactions can be used to prepare amines which are difficult to prepare by simple alkylation of ammonia and is known as Gabriel synthesis.



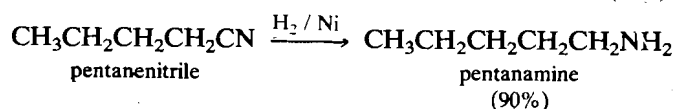
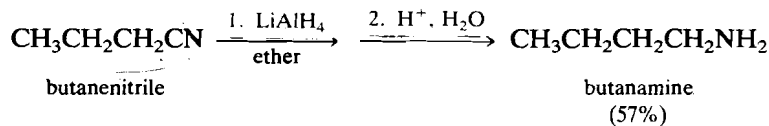
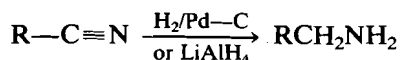
The use of the Gabriel synthesis is limited to primary and unbranched secondary alkyl halides. However, tertiary alkyl halides undergo eliminations under these conditions.

### 3. Reduction of nitro compounds

The reduction of nitro compounds to yield primary amines was discussed in Unit 18, Sec. 18.4.

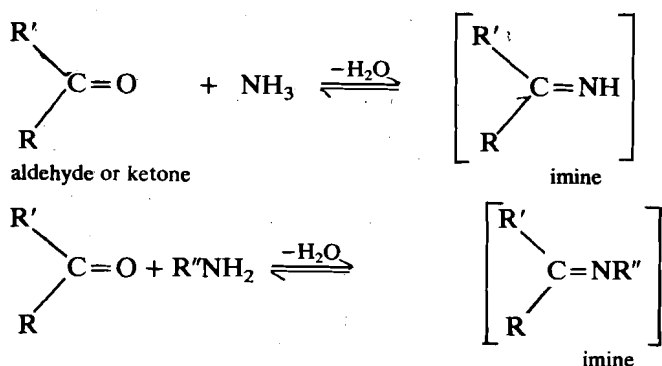
### 4. Reduction of nitriles

Nitriles can be reduced to primary amines by catalytic hydrogenation or by the reaction with  $\text{LiAlH}_4$ .

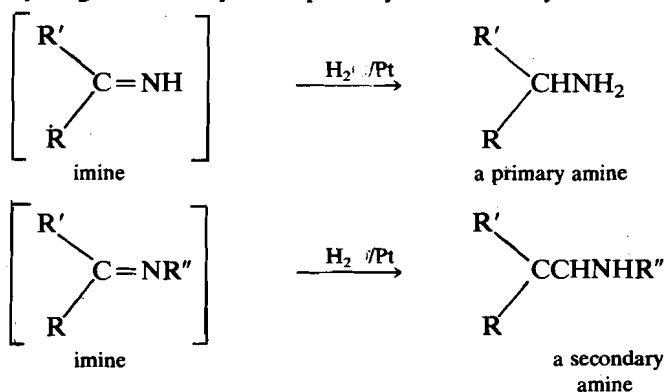


### 5. Reduction of imines

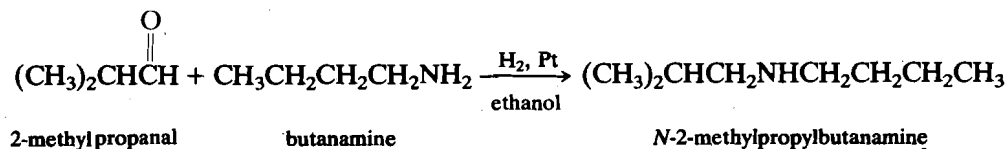
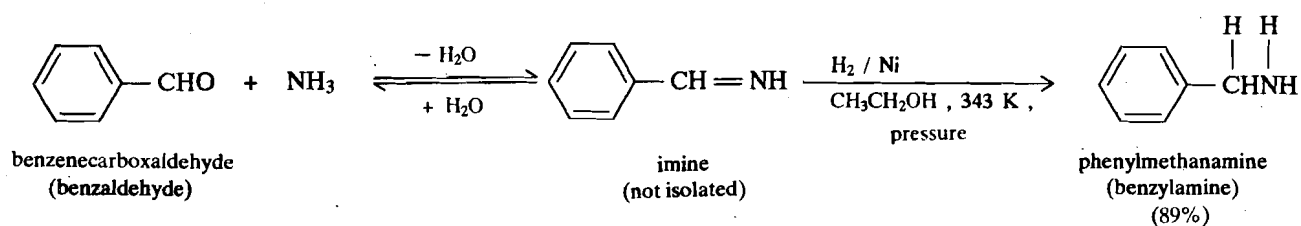
Ammonia and primary amines condense with aldehydes and ketones to yield imines as shown below:



The carbon nitrogen double bond of an imine can be reduced by catalytic hydrogenation to yield a primary or secondary amine.



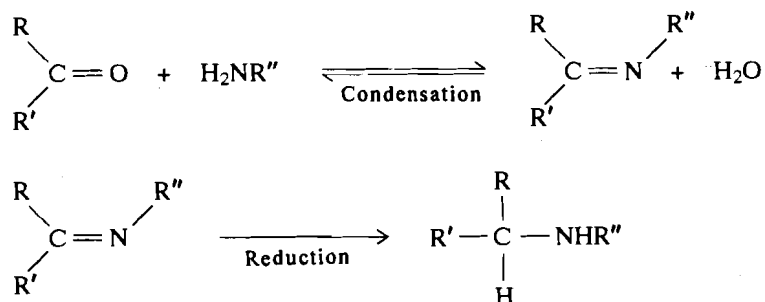
Some examples are given below:





You can see that the carbonyl group is **reduced** in the above reaction and the amine is **alkylated**, hence, the reaction is also known as **reductive alkylation** or **reductive amination**.

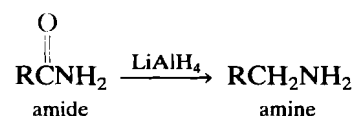
### General Reductive Amination of a Ketone



What makes the reductive amination a useful synthetic procedure is that it can be carried out in a single operation involving the hydrogenation of a solution of the carbonyl compound and ammonia (or amine) in the presence of a catalyst without isolating the intermediate imine.

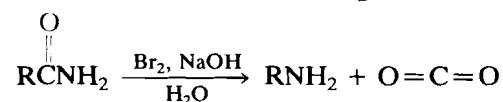
### 6. From amides

You are aware from Unit 17, Sec. 17.8, sub-Sec. 17.8.2 that amides can be reduced to amines, i.e.

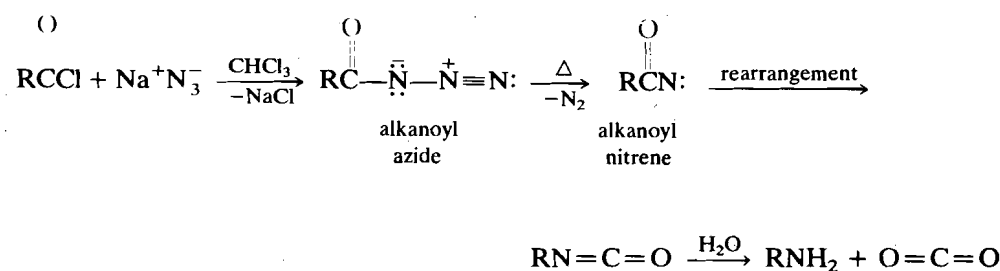


Depending upon the structure of the starting amide, primary, secondary or tertiary amines can be synthesised. Note that the same number of carbon atoms is present in the amine as in the starting amide.

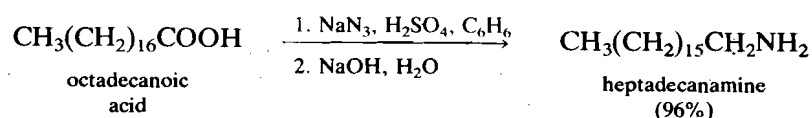
Another method of preparing primary amines from amides is Hofmann rearrangement. The amine obtained contains one carbon atom less than the starting amide. Hofmann rearrangement was discussed in Unit 17, Sec. 17.8. The general reaction of Hofmann rearrangement is shown below :



Similar transformation involving the reaction of an alkanoyl halide with sodium azide,  $\text{NaN}_3$  to yield amines is known as **Curtius rearrangement**. This reaction proceeds via the following steps.

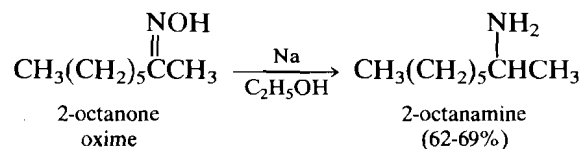


The same sequence of reactions is observed when the starting material is a carboxylic acid. A carboxylic acid when treated with sodium azide in acid catalyst yields an alkanoyl azide which finally yields the amine. This reaction is known as **Schmidt rearrangement**. An example of Schmidt rearrangement is shown below:



## 7. Reduction of oximes

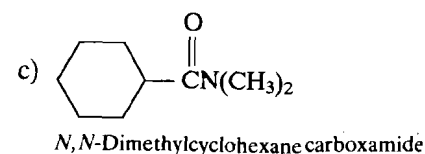
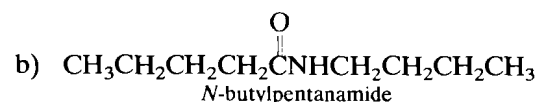
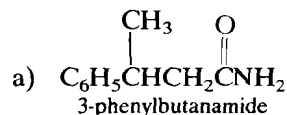
It was pointed out in Block 3, Unit 14, Sec. 14.4 that aldehydes and ketones react with azanol (hydroxylamine) to yield **oximes**. Oximes so obtained can be reduced with  $\text{LiAlH}_4$  or sodium in alcohol to yield primary amines.



Using the knowledge gained so far, answer the following SAQ.

## SAQ 3

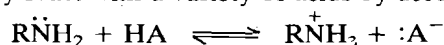
Write the products of reduction of the following amides with  $\text{LiAlH}_4$ .



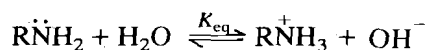
## 19.7 REACTIONS OF AMINES

## 1. As bases

Amines behave as Lewis bases because of the nonbonding electron pair on nitrogen. They react with a variety of acids by accepting a proton.



The aqueous solutions of amines are basic in nature due to the following equilibrium.



where  $K_{\text{eq}}$  is the equilibrium constant.

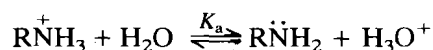
You may recall from Block 1, Unit 5, Sec. 5.3, Eq. 5.6 that  $K_{\text{eq}}$  is related to the basicity constant,  $K_{\text{b}}$ , by the following expression.

$$K_{\text{b}} = K_{\text{eq}}[\text{H}_2\text{O}] = \frac{[\text{R}\overset{+}{\text{N}}\text{H}_3][\text{OH}^-]}{[\text{R}\ddot{\text{N}}\text{H}_2]}$$

Also,

$$\text{p}K_{\text{b}} = -\log K_{\text{b}}$$

It was also pointed out in Unit 5, Block 1 that it is convenient to refer to the base strength also in terms of the dissociation constant,  $K_{\text{a}}$ , of the corresponding ammonium ion, i.e.,



where 
$$K_{\text{a}} = \frac{[\text{R}\ddot{\text{N}}\text{H}_2][\text{H}_3\text{O}^+]}{[\text{R}\overset{+}{\text{N}}\text{H}_3]}$$



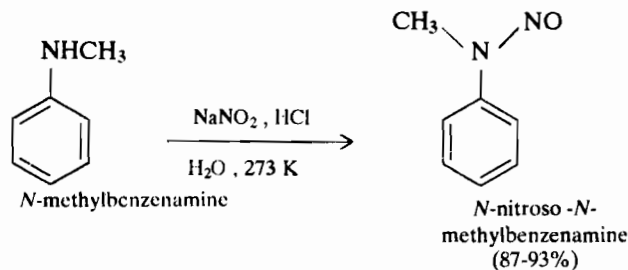
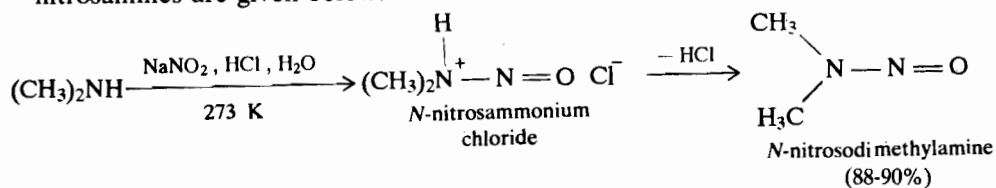




**Nitrosation of secondary amines**

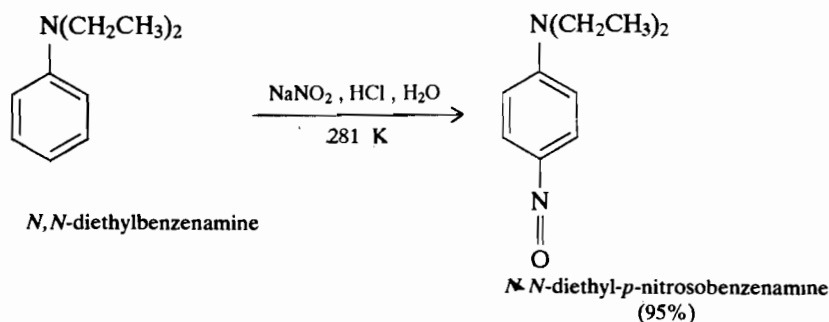
Aliphatic and aromatic secondary amines react with nitrous acid to yield *N*-nitroso compounds, also known as **nitrosamines**. Nitrosamines usually separate from the reaction mixture as yellow oily liquids. Some examples of the formation of nitrosamines are given below:

Nitrosamines are very powerful **carcinogens**. Sodium nitrite, used as a preservative in meats and also the nitrites produced by the reduction of nitrate fertilisers, react with natural amines in the presence of the acid found in stomach to yield nitrosamines. Dimethylamine and methylethylamine are found in tobacco smoke also.

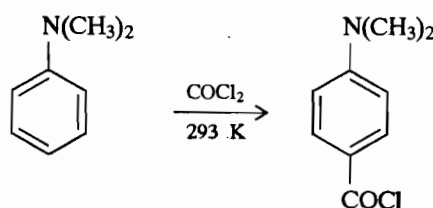
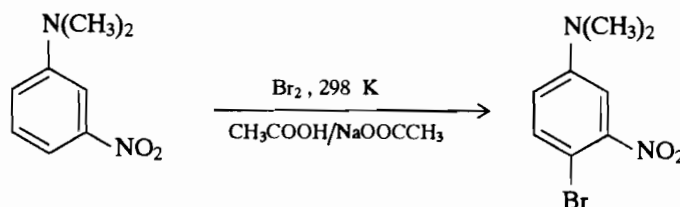
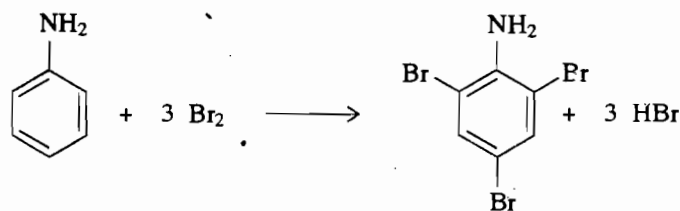
**Nitrosation of tertiary amines**

Tertiary aliphatic amines react with nitrous acid without the evolution of nitrogen to yield complex mixtures.

Tertiary aromatic amines react with nitrous acid to give *C*-nitroso aromatic compounds. Nitrosation takes place almost exclusively at the *para* position of the aromatic ring:

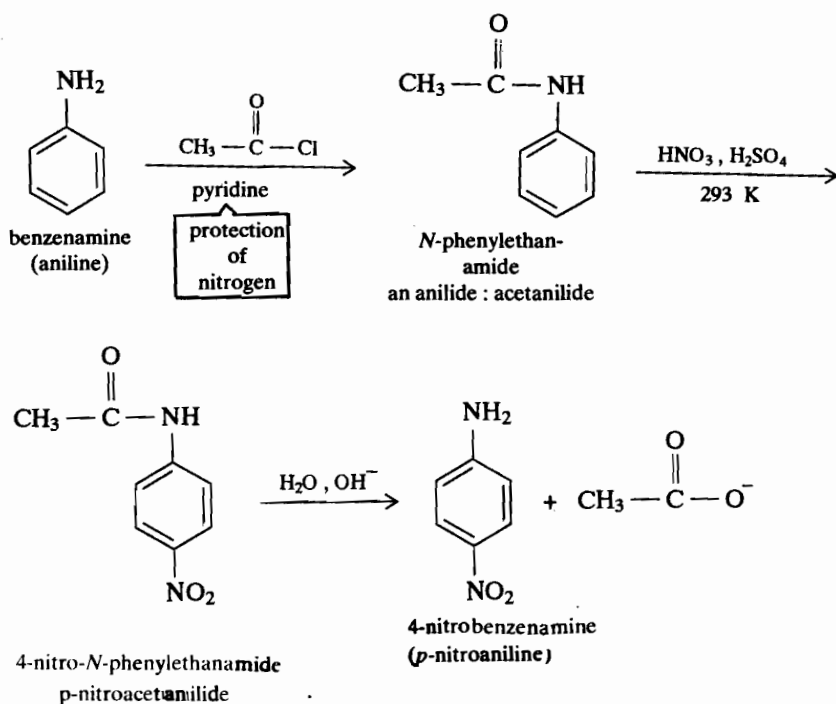
**4. Electrophilic aromatic substitution**

The amino group activates the aromatic ring towards substitution by electrophilic reagents and the reactions require mild conditions. The amino group is an *ortho*-, *para*-directing group, as is illustrated by the following examples:



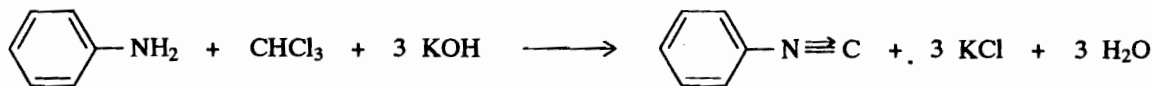
Since amino group is susceptible to attack by a wide variety of reagents such as oxidising agents, alkylating reagents and carbonyl compounds, it must be suitably protected.

The reactivity of the amino group is reduced when it is converted into an amide as is shown below:



### 5. Isocyanide (carbylamine) reaction

Both aliphatic and aromatic primary amines react with chloroform in the presence of potassium hydroxide to produce an isocyanide that has a very nauseating odour. This reaction is so sensitive that it can be used as a test to detect the presence of very small amounts of primary amines as impurities in secondary and tertiary amines.



**Caution :** You should destroy the isocyanide by heating the reaction mixture with an acid before throwing the products into the laboratory sink.

### SAQ 4

When 4-aminobenzenol reacts with one molar equivalent of ethanoic anhydride, a compound having molecular formula,  $\text{C}_8\text{H}_9\text{NO}_2$  is formed which is soluble in alkali. Write its structure.

.....

.....

.....

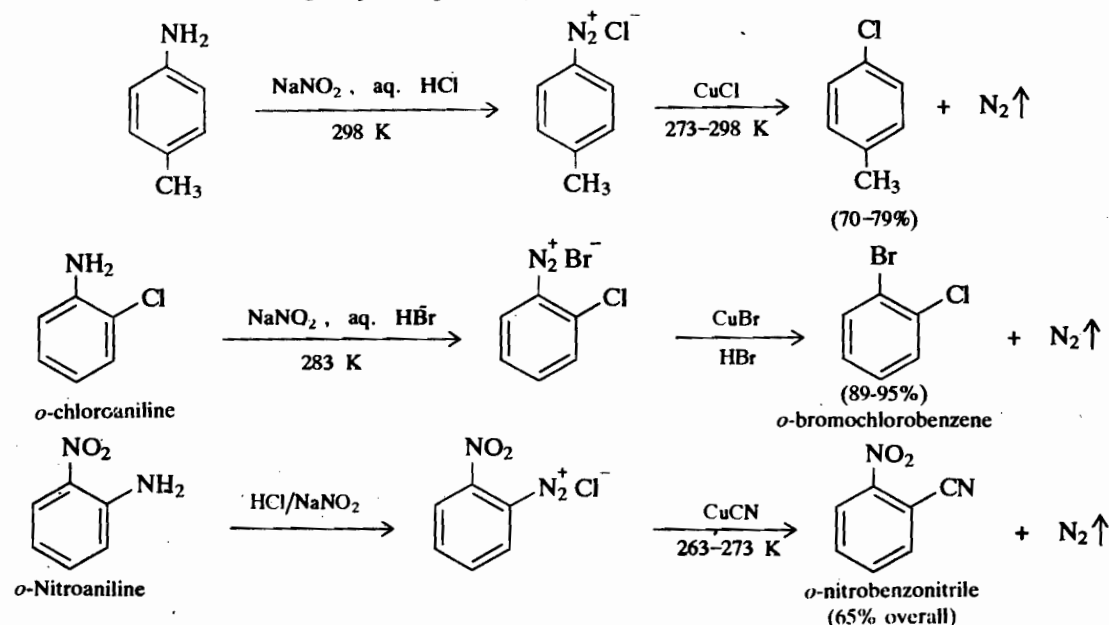
## 19.8 REACTIONS OF DIAZONIUM SALTS

You have studied the formation of diazonium salts in the last section. It has been pointed out there that arenediazonium salts are stable at temperatures below 278 K and can be used in the synthesis of aromatic compounds. You will now study various reactions undergone by arenediazonium salts.

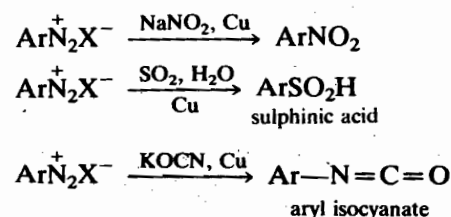
### 1. The Sandmeyer Reaction

The reactions of diazonium salts involving cuprous salts are called Sandmeyer reactions.

Arenediazonium salts react with cuprous chloride, cuprous bromide and cuprous cyanide to give products in which the diazonium group has been replaced by  $-Cl$ ,  $-Br$  and  $-CN$  groups, respectively.

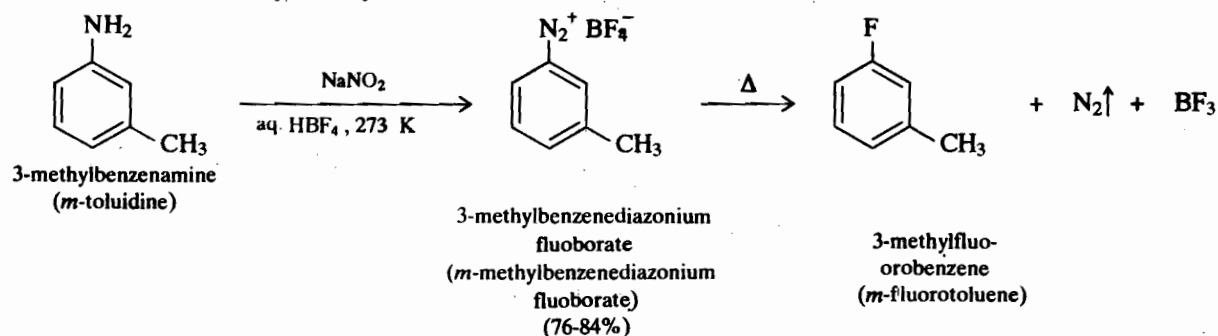


Reactions similar to the Sandmeyer reactions may be accomplished by the use of copper powder as a catalyst for decomposing the diazonium salt. This method is particularly useful in cases where the corresponding cuprous salt cannot be prepared. This variation is called the **Gattermann reaction**.



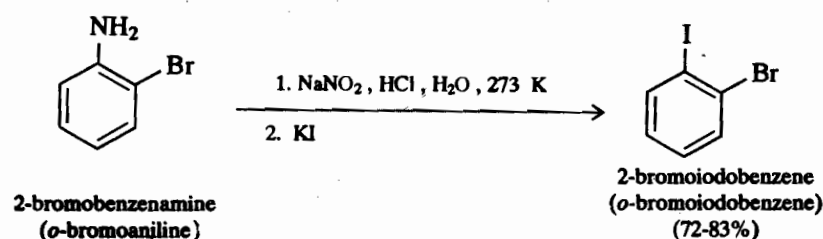
## 2. Formation of aryl fluorides

The diazotisation of an amine with sodium nitrite and fluoboric acid,  $\text{HBF}_4$ , yields fluoborate diazonium salt as a precipitate which is isolated and decomposed thermally to yield aryl fluorides. This reaction is also known as **Schiemann reaction**.



## 3. With potassium iodide

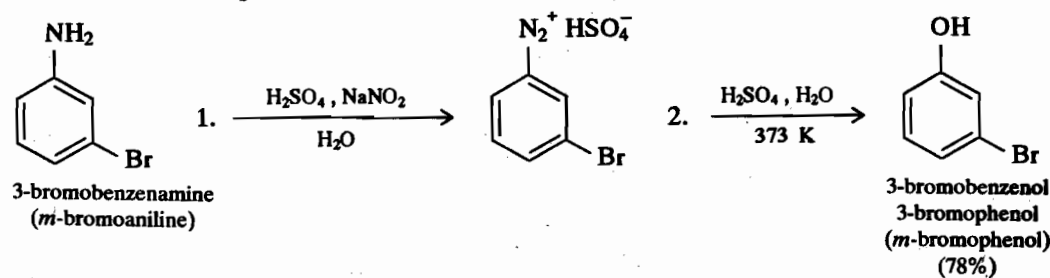
Diazonium salts react with potassium iodide to yield aryl iodides. The diazonium salt is prepared in the usual way and a solution of potassium iodide is then added and the reaction mixture is heated to yield the aryl iodide.





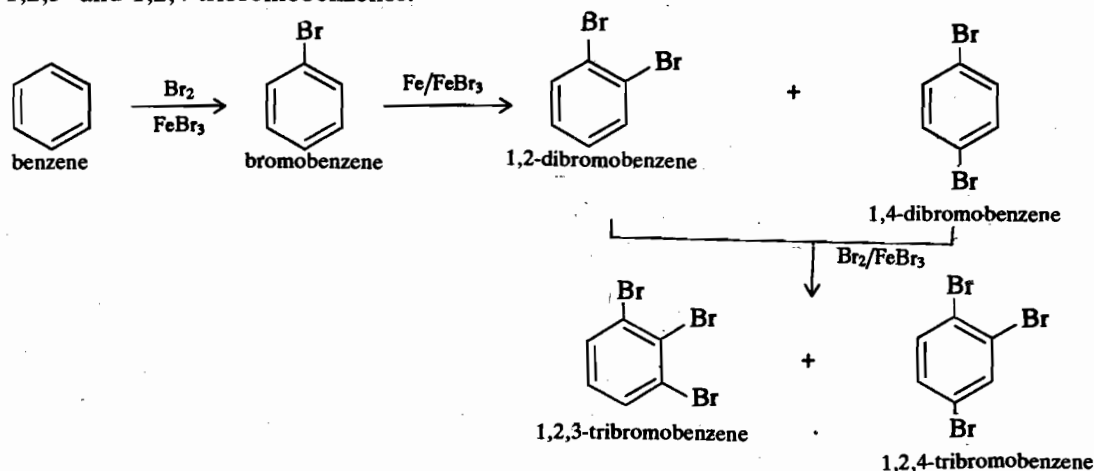
#### 4. With water

The most general method for the preparation of phenols involves the heating of the diazonium salt in aqueous acid.



#### 5. Replacement of diazonium group by hydrogen

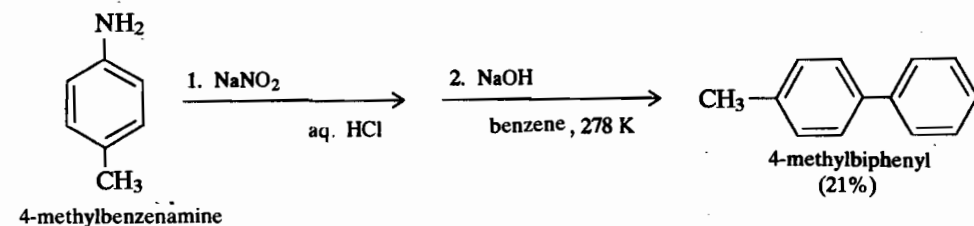
When a diazonium salt is treated with hypophosphorous acid,  $\text{H}_3\text{PO}_2$ , the diazonium group is replaced by hydrogen. Reactions of this type are called **reductive deaminations**. This reaction is useful when we introduce an amino group into an aromatic ring to influence the orientation of a subsequent reaction. Later the amino group can be removed by converting it into the diazonium salt and then treating the diazonium salt with  $\text{H}_3\text{PO}_2$ . For example, direct bromination of benzene leads to 1,2,3- and 1,2,4-tribromobenzenes.



Thus, 1,3,5-tribromobenzene which cannot be prepared by direct bromination of benzene can be obtained by the reaction of the diazonium salt of tribromoaniline with  $\text{H}_3\text{PO}_2$ .

#### 6. Arylation

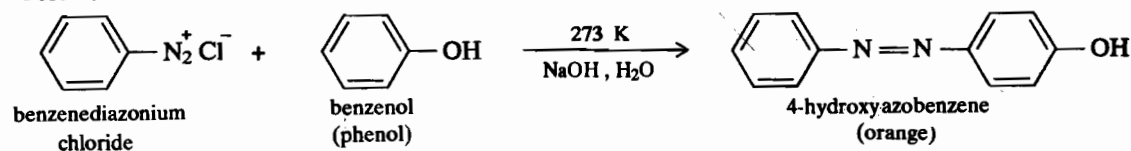
Basic solutions of diazonium salts react with aromatic compounds in cold to yield biaryl compounds in which the diazonium group has been replaced by an aromatic ring. This is illustrated by the following example.

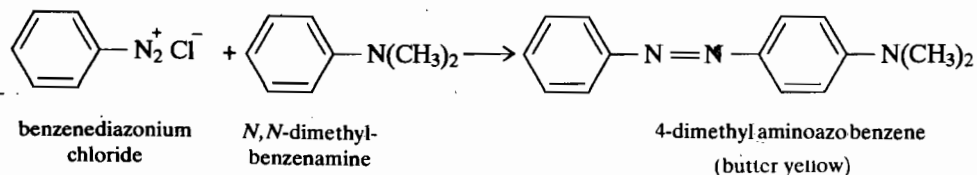


This reaction is called the **Gomberg-Bachmann reaction**.

#### 7. Coupling Reactions

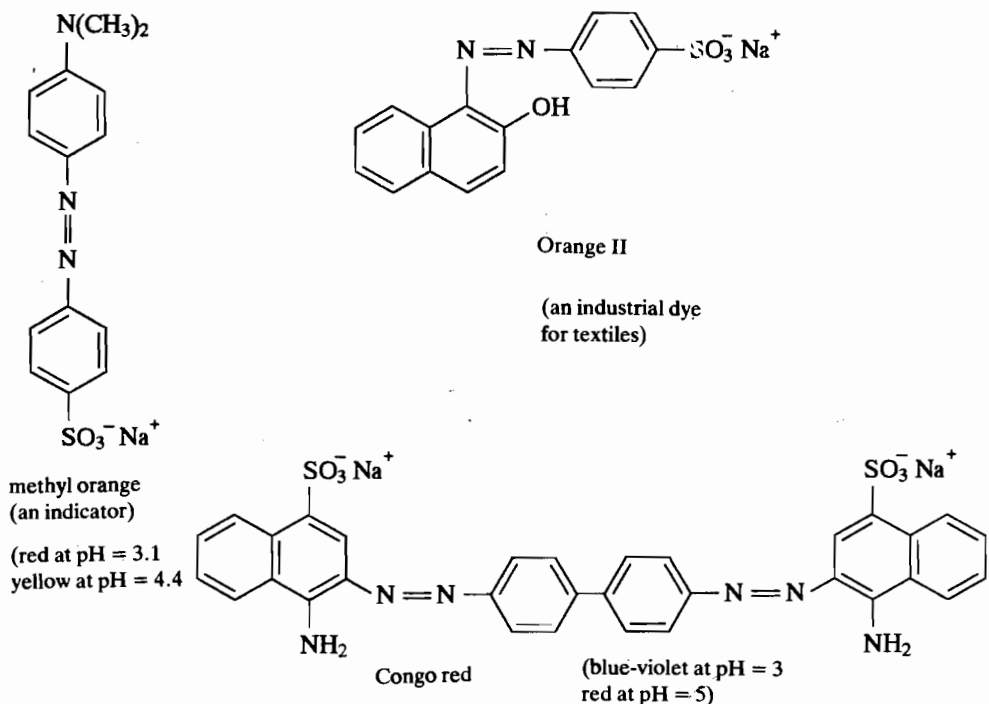
Arenediazonium salts are weak electrophiles and attack aromatic ring of highly activated compounds such as amines and phenols to yield azo compounds. This electrophilic aromatic substitution reaction is called **diazo coupling** and is shown below:





The azo compounds thus obtained are highly coloured and many of them are used as colouring agents and are called **azo dyes**. Butter yellow was once used as a food colouring agent. Azo dyes are also used as indicators and for textile dyeing. Some examples are given below:

Coupling takes place preferably at the *para* position, if it is free. If it is not, then, the coupling takes place at the *ortho* position.



After studying the reactions of diazonium salts, answer the following SAQ.

### SAQ 5

Write the starting materials required for the preparation of azo compounds methyl orange and congo red.

.....

.....

Before closing our discussion on amines, let us study the uses of amines and their detection in the laboratory.

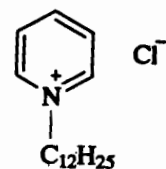
## 19.9 USES OF AMINES

Amines have diverse uses. You have already studied most of them in the discussion about amines in this unit. Let us now restate them.

- 1) Several amines are physiologically active and are used as drugs.
- 2) Some naturally occurring amines, particularly alkaloids are used as resolving agents for optically active compounds. You have studied them in Unit 3, Block 1 also.
- 3) It was also pointed out that quaternary ammonium salts also act as **phase transfer catalysts**. Quaternary ammonium salts are soluble in both water and organic solvents and thus act as mediators for reactions between species dissolved in immiscible liquids. Quaternary ammonium salts having long chain alkyl groups such as hexadecyl trimethylammonium chloride,  $[C_{16}H_{33}N(CH_3)_3]^+ Cl^-$ , have detergent properties. They are known as cationic surfactants or invert soaps

because the surface activity is found in a positive ion rather than in a negative ion as is the case with ordinary soaps. Most surface-active quaternary ammonium salts, such as dodecyl pyridinium chloride are potent germicides.

- 4) Diazonium salts available from amines can be used to synthesise a variety of aromatic compounds and azo dyes.



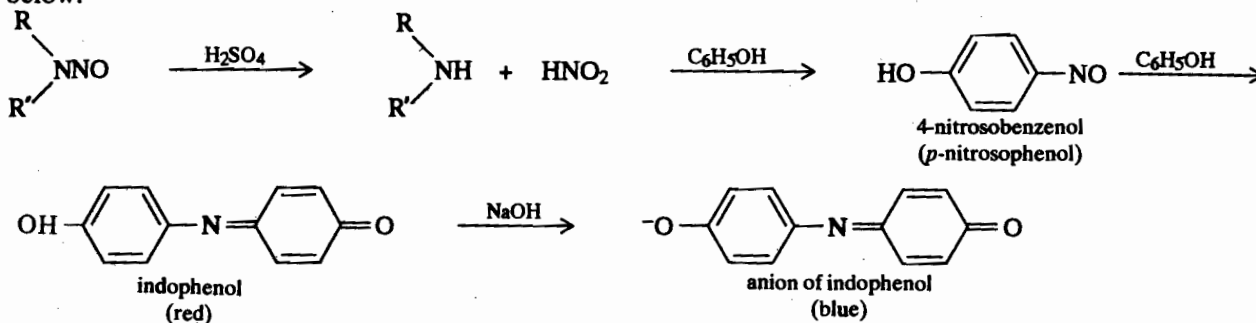
dodecyl  
pyridinium chloride

## 19.10 LABORATORY DETECTION OF AMINES

Amines are characterised by their basic nature. They dissolve in dilute aqueous acids. The elemental analysis of amines shows the presence of nitrogen.

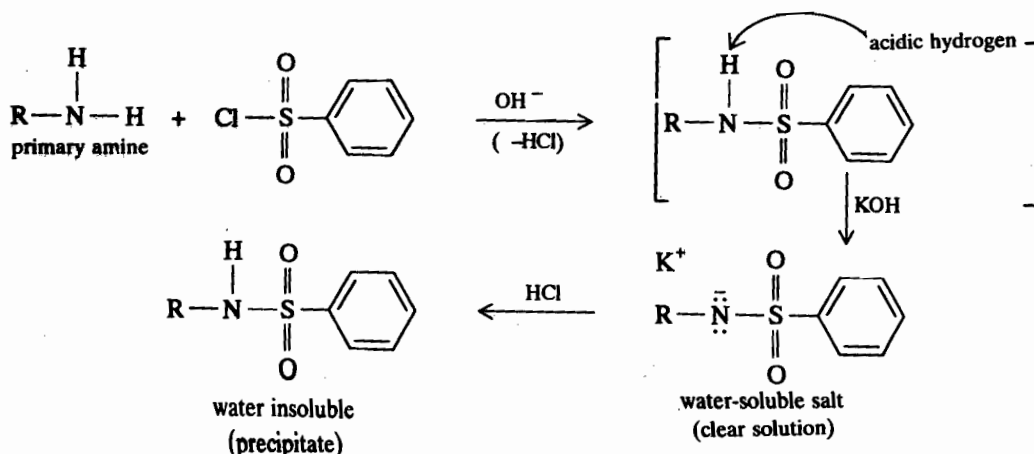
Amines can be characterised by their reaction with nitrous acid. The amine is dissolved in dilute HCl and an ice-cold solution of sodium nitrite is added to it. If a clear solution is obtained with the evolution of nitrogen, the amine is a **primary aliphatic** or **primary alkylaryl amine**. If no nitrogen is evolved, then a cold solution of 2-naphthol in sodium hydroxide solution is added to a portion of the above reaction mixture. If a coloured azo dye is formed, then the amine is a **primary aromatic amine**.

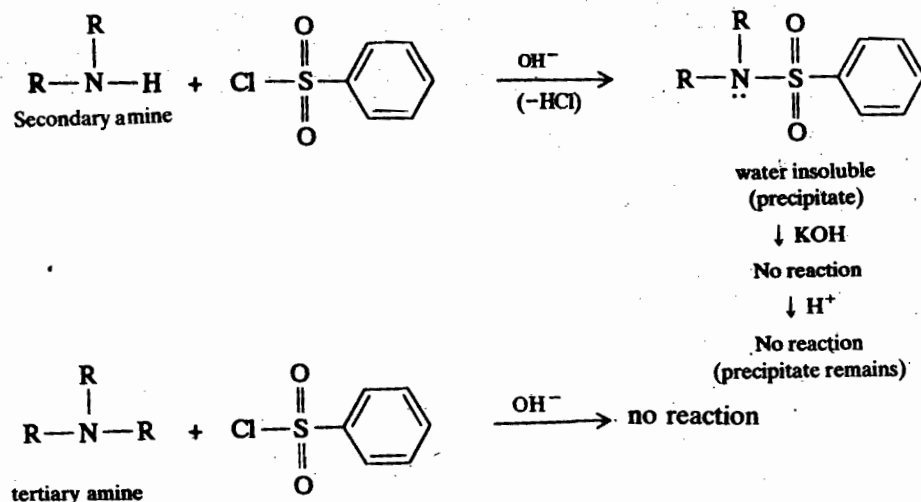
If a yellow oily substance separates out when cold sodium nitrite solution is added to the acidic solution of the amine, then the amine is a **secondary amine**. The formation of the oily nitrosamine is confirmed by the **Liebermann nitroso reaction**. The yellow oily substance is warmed with phenol and concentrated sulphuric acid. Sulphuric acid liberates nitrous acid from nitrosamine which reacts with phenol to yield *p*-nitrosophenol. The *p*-nitrosophenol reacts with another molecule of phenol to yield red coloured indophenol. In alkaline solution indophenol yields its anion which is blue in colour. The sequence of reactions which occur can be represented as shown below:



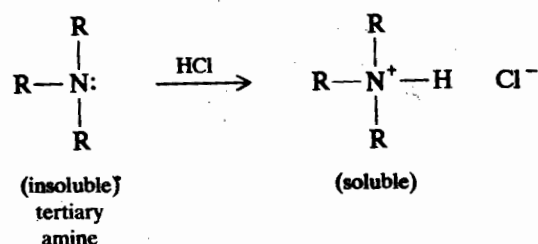
If a dark orange-red solution is obtained on treatment of the amine with nitrous acid and the colour changes to green on adding the alkali, then the amine is a **tertiary aromatic amine**.

An efficient method to distinguish whether an amine is **primary**, **secondary** or **tertiary** is the **Hinsberg test**. This involves the reaction between an amine and benzenesulphonyl chloride in the presence of aqueous potassium hydroxide. Primary and secondary amines form substituted sulphonamides but tertiary amines do not. The sulphonamide from the primary amine may be further distinguished by the fact that it is soluble in potassium hydroxide, whereas the derivative from the secondary amine, having no acidic hydrogen, is insoluble in potassium hydroxide and, therefore, precipitates out. The reactions involved with each type of amine are shown below:





But amine will dissolve on acidification.



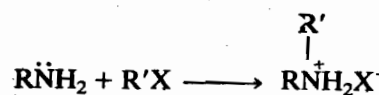
Let us now summarise what we have learnt in this unit.

## 19.11 SUMMARY

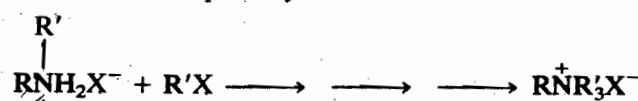
In this unit, you have studied that

- amines are nitrogen-containing organic bases.
- amines can be classified as primary, secondary and tertiary according to the degree of the substitution at the nitrogen atom.
- amines have tetrahedral structure in which the nitrogen is  $sp^3$  hybridised. One of the  $sp^3$  hybrid orbitals is occupied by the unshared pair of electrons.
- trends in the physical properties of amines such as melting and boiling point can be explained on the basis of various factors you studied in Unit 4, Block 1.
- primary and secondary amines can be differentiated with the help of the infrared spectra.
- amines can be prepared by the following methods:

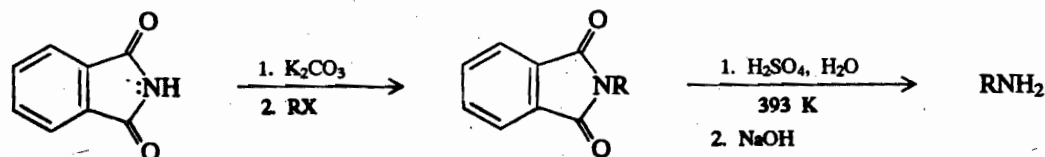
### i) By alkylation



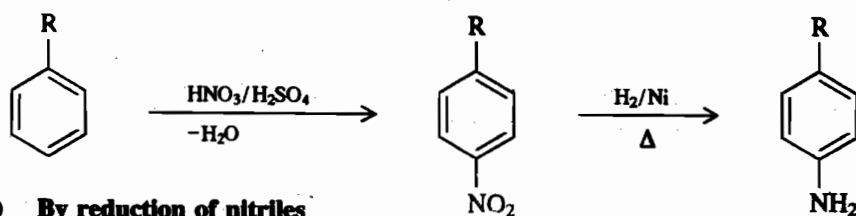
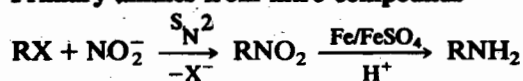
drawback: multiple alkylation.



### ii) Gabriel synthesis of primary amines



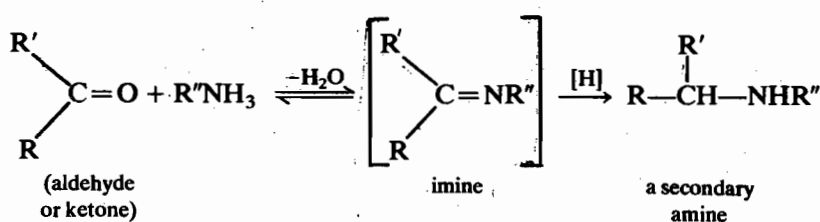
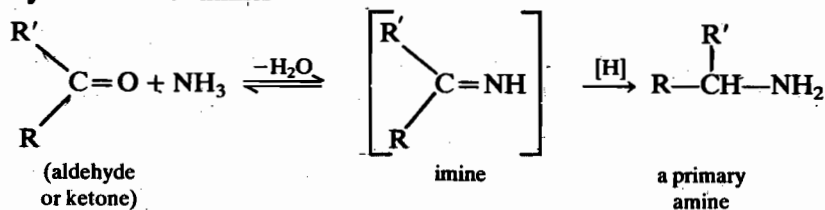
iii) **Primary amines from nitro compounds**



iv) **By reduction of nitriles**

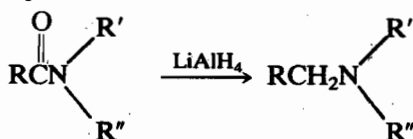


v) **By reduction of imines**

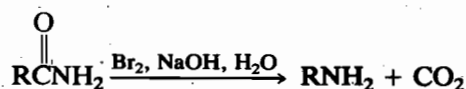


vi) **From amides**

a) **By reduction**

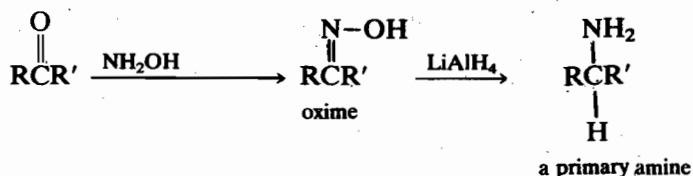


b) **By Hofmann rearrangement**



Similar transformations starting with alkanoyl halides (Curtius rearrangement) and carboxylic acids (Schmidt rearrangement) using sodium azide also yield amines.

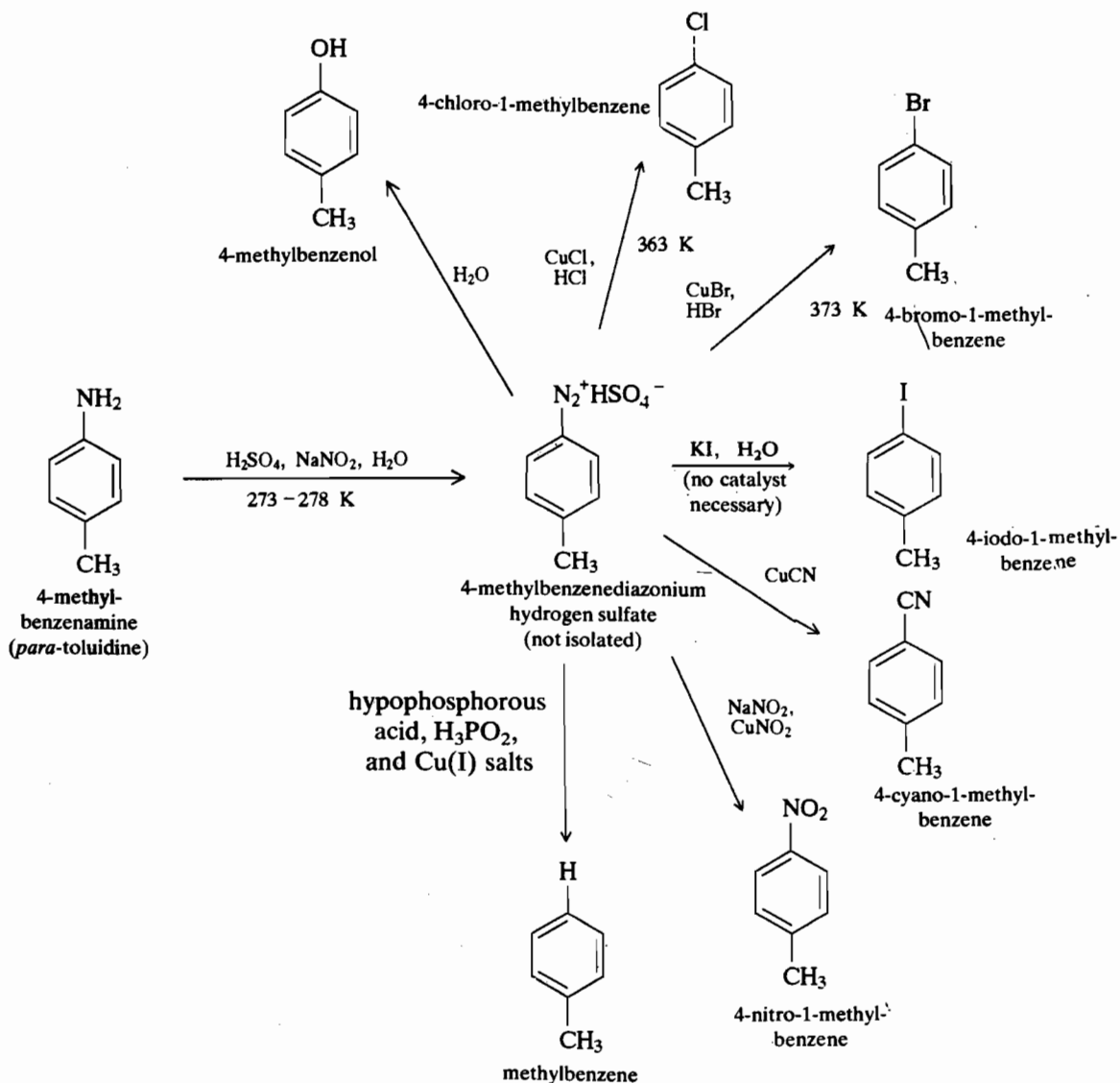
vii) **From Oximes**



• **Amines undergo the following reactions:**

- they behave as bases in aqueous solutions and form salts with acids.
- they undergo alkylation with alkyl halides and alkanoylation with carboxylic acids and their derivatives.
- tertiary aliphatic amines can be oxidised to amine oxides which undergo Cope elimination on heating to yield an alkene and *N,N*-dialkylhydroxylamine.
- Oxidation of aromatic amines leads to a variety of oxidation products depending upon the oxidising agent and reaction conditions.
- **Amines undergo nitrosation reaction** with nitrous acid which gives various products depending upon whether the amine is primary, secondary or tertiary and is aliphatic or aromatic.

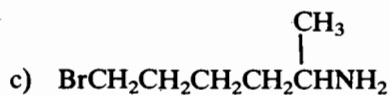
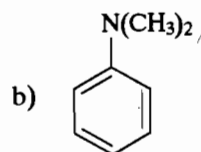
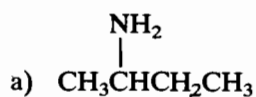
- amino group activates the aromatic ring towards electrophilic substitution reactions.
- Some of the reactions of diazonium salts can be summarised as follows:



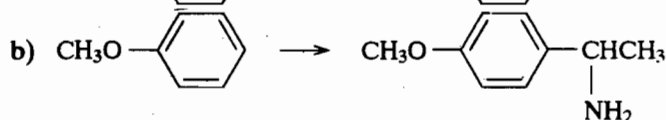
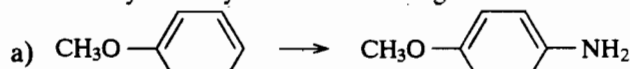
- Amines have various uses.
- Amines can be characterised in the laboratory by their reaction with nitrous acid and Hinsberg test.

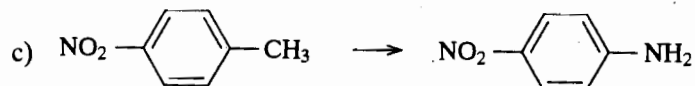
## 19.12 TERMINAL QUESTIONS

1) Name the following amines:

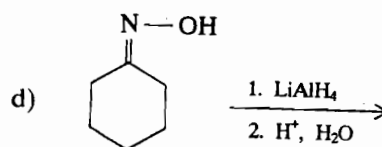
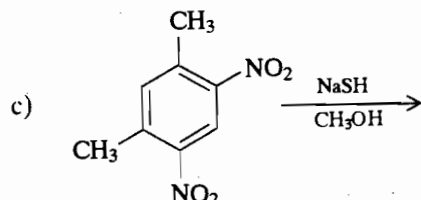
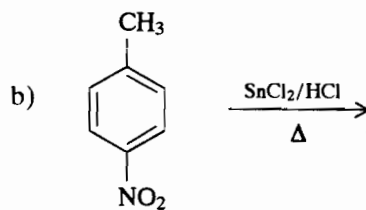
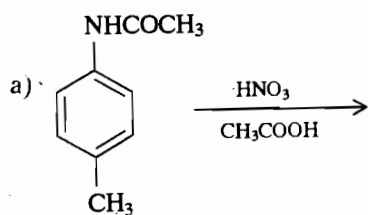


2) How will you carry out the following transformations?

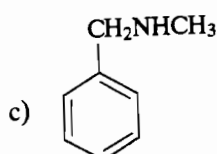
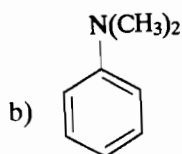
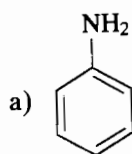




3) Complete the following reactions:



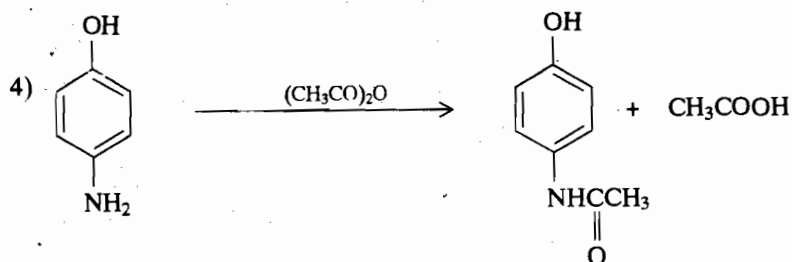
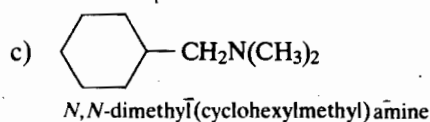
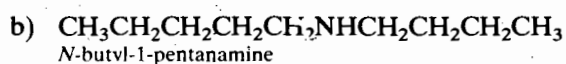
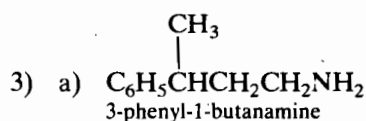
4) Write the products of nitrosation of the following compounds.



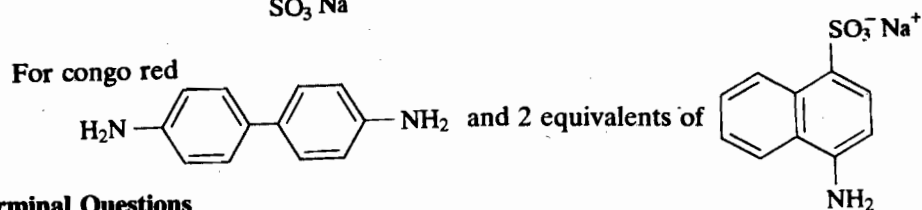
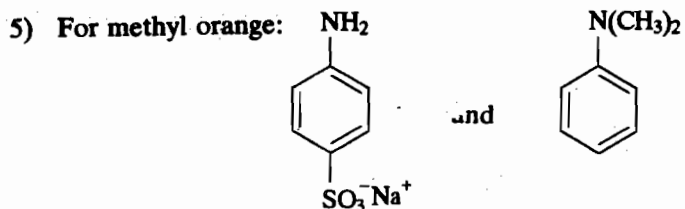
## 19.13 ANSWERS

### Self Assessment Questions

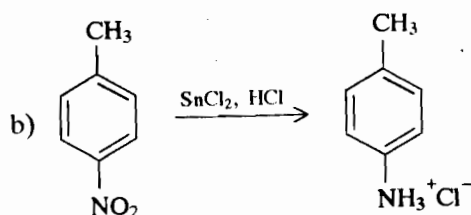
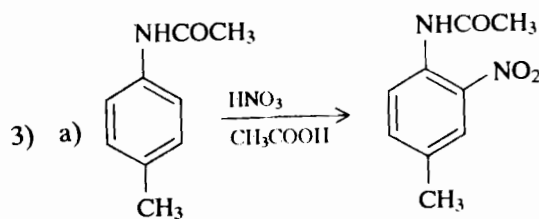
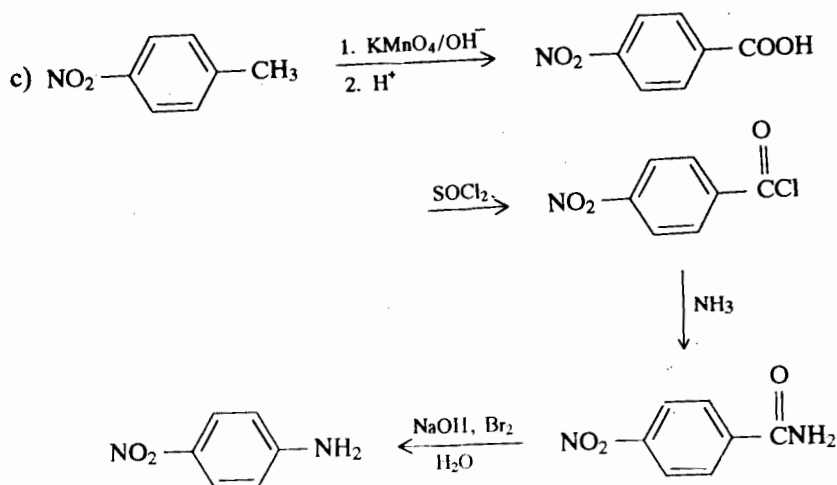
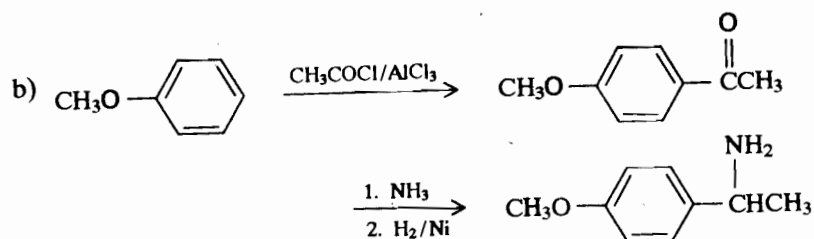
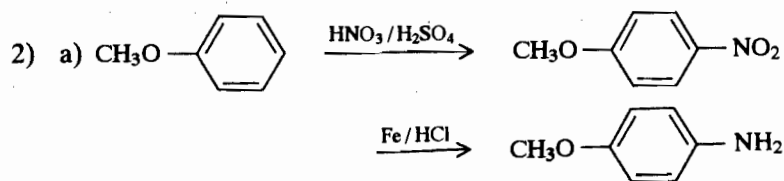
- 2-methylpropanamine
  - N,N*-diethylethanamine or triethylamine
  - cyclohexylamine
  - 1,2-propanediamine
  - 3-nitrobenzenamine or 3-nitroaniline
- o*-Nitroaniline can undergo **intramolecular** hydrogen bonding whereas its **meta**- and **para**- isomers show **intermolecular** hydrogen bonding. This leads to lower melting and boiling points for *o*-nitroaniline.



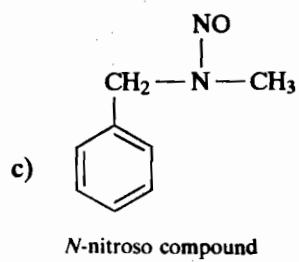
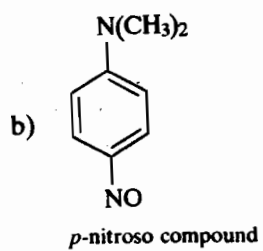
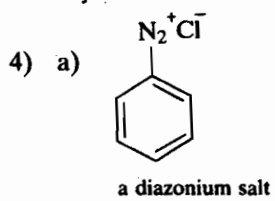
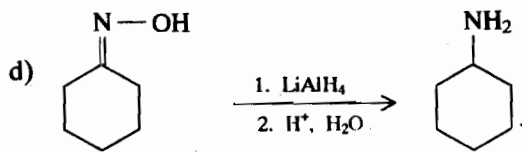
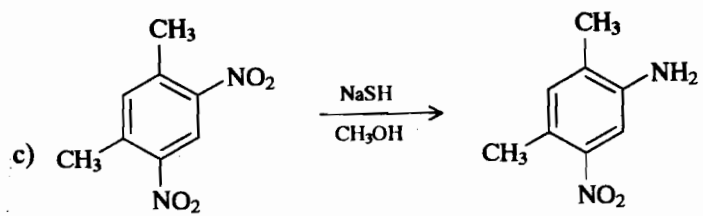
mol. formula -  $C_8H_9NO_2$


**Terminal Questions**

- 1) a) 2-butanamine
- b) *N,N*-dimethylbenzenamine
- c) 6-bromo-2-hexanamine







# UNIT 20 NATURAL PRODUCTS

## Structure

- 20.1 Introduction
  - Objectives
- 20.2 Carbohydrates
  - Classification and Structure of Carbohydrates
- 20.3 Peptides and Proteins
  - Structure of Peptides and Proteins
- 20.4 Nucleic Acids
  - Structure of Nucleic Acids
  - Nucleic Acids and the Genetic Code
- 20.5 Oils and Fats
  - Analysis of Oils and Fats
- 20.6 Terpenes
- 20.7 Steroids
- 20.8 Alkaloids
- 20.9 Antibiotics
- 20.10 Summary
- 20.11 Terminal Questions
- 20.12 Answers

## 20.1 INTRODUCTION

So far we have devoted much of our study of organic chemistry to describe the chemistry involved in the preparation and reactions of compounds containing different functional groups and correlating their behaviour with their structures. There is a unique and vast category of organic compounds produced by living organisms to which you have not yet been exposed. Such compounds are called **natural products**. There are many different classes of natural products. Natural products such as **carbohydrates, proteins, nucleic acids and fats** occur in almost all organisms and play an important and primary role in metabolic processes. These natural products are called **primary metabolites**. Another class of natural products, known as **secondary metabolites**, includes **terpenes, steroids and alkaloids**. The distribution of secondary metabolites is much more species-dependent. These compounds have been used as drugs, flavours, poisons, dyes and so on. This unit will be devoted to the basic concepts and general chemistry associated with the natural products.

### Objectives

After studying this unit, you should be able to:

- classify a carbohydrate as monosaccharide, oligosaccharide (disaccharide, trisaccharide and so on) or a polysaccharide,
- write the structures of various carbohydrates,
- write the structures of nucleic acids and discuss the role of DNA in protein synthesis,
- explain the primary, secondary, tertiary and quaternary structure of peptides and proteins,
- list the acids present in oils and fats,
- define acid value, saponification value and iodine value.
- give some examples of terpenes belonging to each category of this class of compounds.