S6 CHEMISTRY

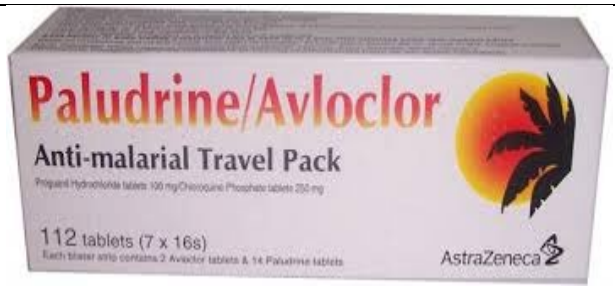
AMINES

My goals
By the end of this unit I will be able to;

- Define amines and homologous series.
- Name amines using IUPAC rules.
- Write and name the isomers of amines.
- Classify amines as primary, secondary or tertiary.
- Explain the physical properties and uses of amines.
- Describe the preparation methods for amines.
- Describe the inductive effect on acidity of carboxylic acids.
- Explain the reactions of amines including appropriate mechanisms.
- Distinguish amines from other organic compounds using appropriate chemical methods.
- State the uses of amines.

Introduction, structure, general formula and classification

❖ Another important class of organic compounds are the **amines**.
❖ Amines and their derivatives are all around us.
❖ Look at these pictures below:

<table>
<tr>
<td> 
The peculiar smell of fish is due amines (trimethylamine) in their oils</td>
<td> 

Paludrine (an anti–malarial drug) is a drug obtained from amines.</td>
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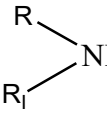
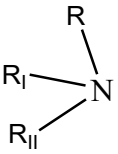
<tr>
<td> 
Detergents called cationic surfactants contain quaternary ammonium salts which help to removes stains.</td>
<td> 
Derivatives of amines are used as anti-oxidants in rubber to prolong the life of rubber articles.</td>
</tr>
<tr>
<td colspan="2">Figure 9.1: Common substances containing amines and their derivatives</td>
</tr>
</table>

- ❖ Amines in combined states are found in proteins. In fact, decomposition of amino acids and proteins release amines (*see Advanced Level Biology Books for details*).
- ❖ The question is what are amines?
- ❖ Amines are organic compounds considered to be derivatives of ammonia (NH_3) formed by replacement of the hydrogen atoms of ammonia with alkyl or aryl groups.
- ❖ They be classified as primary (1^o), secondary (2^o) or tertiary (3^o) amines depending on the number of alkyl/aryl groups directly bonded to the nitrogen atom.
- ❖ For example:
  - If there is only one alkyl/aryl group i.e. RNH_2 for example, CH_3NH_2 and $CH_3CH_2NH_2$, they are referred to as 1^o amines.
  - If only two alkyl/aryl groups are on the nitrogen atom i.e.



; we get 2^o amines. Some examples of secondary amines are: $(CH_3)_2NH$, $CH_3CH_2NHCH_3$ and $CH_3CH_2NHCH_2CH_3$

  - While if there three alkyl/aryl groups on the nitrogen atom i.e.

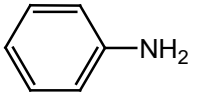


; we get 3^o amines. Some examples of tertiary amines are: $(CH_3)_3N$ and $(CH_3)_2NCH_2CH_3$

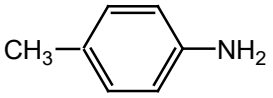
- ❖ Amines have the general formula $C_nH_{2n+1}NH_2$, where n=1,2,3,4,…and have **amino group** $-NH_2$ as the functional group.
- ❖ Simple amines are named by specifying the alkyl/aryl groups attached to the nitrogen atom followed by the ending '**amine**'.
  More complex ones are named as derivatives of the longest carbon chain and italic capital, N inserted before each name of the substituent.
- ❖ Examples:

(a) Primary amines

CH_3NH_2; methylamine CH_3NHCH_3

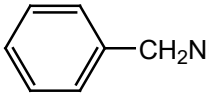


; phenylamine(aniline); simplest aromatic amine



; 4-methylphenylamine

$(CH_3)_2CHNH_2$; 1–methylethylamine

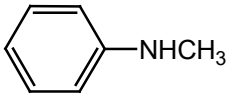


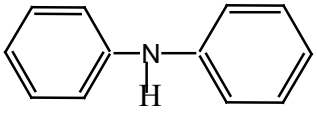
; benzylamine or (phenylmethyl)amine

(b) Secondary amines

$(CH_3)_2NH$ or CH_3NHCH_3; dimethylamine

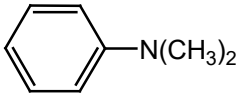
$CH_3CH_2NHCH_3$; ethlylmethylamine

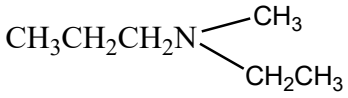

; N-methylphenylamine


; diphenylamine

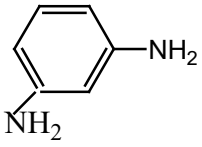
(c) Tertiary amines

$(CH_3)_3N$; trimethylamine $(CH_3CH_2)_3N$; triethylamine


; N,N-dimethylphenylamine


; N-ethyl-N-methylpropylamine

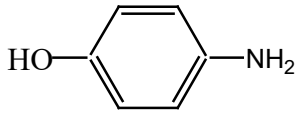
❖ Compounds containing two amine groups are known as **diamines**.

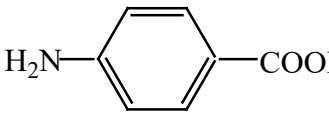

; benzene-1,3-diamine

$H_2N(CH_2)_6NH_2$; hexane-1,6-diamine

❖ Some amines are named as amino-substituted compounds:

$H_2NCH_2CH_2OH$; 2–aminoethanol $H_2NCH_2CO_2H$; 2–aminoethanoic acid


; 4-aminophenol


; 4-aminobenzoic acid

Natural occurrence of amines

We have already some natural sources amines. Amines also occur in other drugs and medicines such as **morphine**, a preferred pain killer to aspirin and in strychnine, a powerful poison. They are found in most dyes used for fabrics and clothes, and in bases of DNA (*see Advanced Level Biology Text Books for details*).

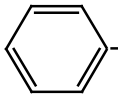
Salts of amines

❖ Due to the presence of a lone pair of electrons on the nitrogen atom, amines are basic (i.e. act as bases/are proton acceptors) and thus form salts with acids.

❖ The salts are named in a similar way like ammonium salts i.e. replacing the suffix amine by ammonium followed the name of the anion.

An example a salt is tetramethylammonium chloride with the formula, $(CH_3)_4N^+Cl^-$
Compare that salt with ammonium chloride, $NH_4^+Cl^-$.

Some other examples are:
$CH_3NH_3^+Cl^-$; methylammonium chloride
$CH_3CH_2NH_3^+NO_3^-$; methylammonium nitrate
$(CH_3)_2NH_2^+HSO_4^-$; dimethyl ammonium hydrogen sulphate

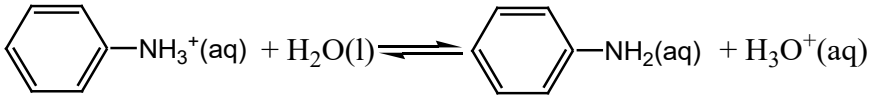


; phenylammonium chloride or anilinium chloride

Question:
Write the formulae and names of the salts $(CH_3)_2NC_2H_5$ can form when reacted with nitric, hydrochloric and sulphuric acids.

- The salts, just like ammonium salts are ionic and readily undergo cationic hydrolysis in aqueous solution to form acidic solutions.

For example:
Recall: NH_4Cl in water hydrolyses as follows:
$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$
Thus, Phenylammonium chloride or anilinium chloride hydrolysis as follows:



Questions:
1. Write equation to show how dimethylammonium nitrate hydrolyses in water.
2. An aqueous solution of methylammonium chloride gives effervescence with magnesium ribbon. Explain this observation.
3. Write the formulae and names of the salts $(CH_3)_2NC_2H_5$ can form when reacted with nitric, hydrochloric and sulphuric acids.

Isomerism in amines

- For example;
  - C_2H_7N has $CH_3CH_2NH_2$ and CH_3NHCH_3
  - C_3H_9N has $CH_3CH_2CH_2NH_2$, $(CH_3)_2CHNH_2$ and $CH_3NHCH_2CH_3$

  In the previous units we have looked at how to write the isomers of some organic compounds.

Question:
A compound Z has the formula $C_4H_{11}N$. Write down the possible isomers of Z. In each case give the IUPAC name and classify the isomer as primary, secondary or tertiary amine.

Physical properties

- Amines just like alcohols and carboxylic acids show interesting properties because their molecules which possess highly polar N–H bond. Can you recall some of the unique physical properties as a result of the presence of the highly polar N–H bond?
- Amines are either gases (simple ones), volatile liquids (higher homologues) and solids (very high RMM amines) at room temperature and pressure with a distinctive 'fishy' smell/odour.

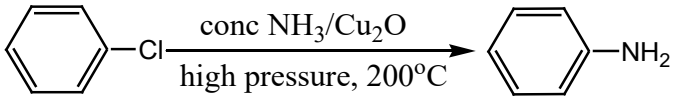
- ❖ Primary and secondary amines possess a highly polar nitrogen—hydrogen bond. This due to the nitrogen atom being highly electronegative. Thus, molecules of primary and secondary amines associate via strong hydrogen bonds. This makes them less volatile (have higher b.pts/m.pts) than non-polar/less polar organic compounds of comparable molecular mass.
- ❖ In tertiary amines, due to lack of a highly polar N-H bond, their molecules associate via weak van der Waals forces of attraction. Thus, their boiling/melting points are similar to those of hydrocarbons of comparable molecular mass.
- ❖ Primary and secondary amines are more volatile (have lower m.pts/b.pts) than alcohols and carboxylic acids of comparable molecular mass. This is because the nitrogen atom in amines is less electronegative than oxygen atom in alcohols and carboxylic acids. The $O-H$ bond is thus, more polar than $N-H$ bond. This makes molecules of amines to associate via weaker hydrogen bonds than those in alcohols and carboxylic acids.
- ❖ All the three classes of amines are capable of forming hydrogen bonds with water molecules. As result, all simple amines (low molecular mass amines) are fairly soluble in water.
- ❖ Amines are also soluble in many of the usual non-polar organic solvents.

Phenylamine (aniline) is a highly toxic liquid and is easily absorbed through the skin.

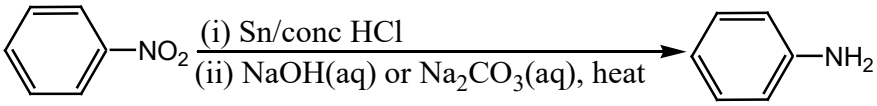
Preparation of amines

(a) Phenylamine

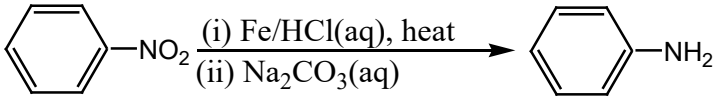
(i) From chlorobenzene



(ii) Reduction of nitrobenzene



Alternatively iron filings which is cheaper is employed in place of expensive tin on an industrial scale.



Uses of phenylamine are:

- Manufacture of drugs, dyes etc.
- Preparation of anti-oxidants and accelerators for vulcanising rubber.
- Starting material for synthesis of many other organic compounds.

Note: Aliphatic nitro compounds can be reduced to amines as follows:

$CH_3CH_2-NO_2 \xrightarrow{H_2/\text{Raney nickel}} CH_3CH_2-NH_2 + H_2O$

(b) Other amines

(i) Hofmann degradation reaction

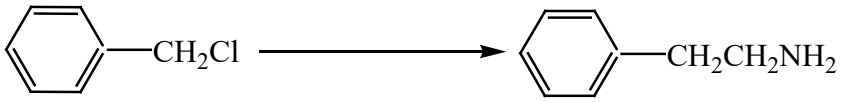
$$RCO_2H \text{ (carboxylic acid)} \xrightarrow[\text{heat}]{(NH_4)_2CO_3(s)} RCONH_2 \text{ (amide)} \xrightarrow[\text{warm}]{Br_2/OH^-(aq)} RNH_2$$

This reaction is of practical importance in organic chemistry for carbon chain reduction.

(ii) Reduction of nitriles (RCN) and amides using Na/ethanol or $LiAlH_4$/dry ether.

$$CH_3CN \xrightarrow[\text{or Na/ethanol}]{LiAlH_4/\text{dry ether}} CH_3CH_2NH_2$$

Question:
Write equation to show how the following conversion can be effected:



(iii) From alkyl halides

$$R{-}X \xrightarrow[\text{heat, high pressure}]{\text{excess conc } NH_3/\text{ethanol}} R{-}NH_2$$

- A mixture of all classes of amines is formed because at each stage, each product acts as substrate and reacts with the alkyl halide present to yield an amine of a higher class. In fact, amines more reactive than ammonia itself.
- The mixture of products can be separated by addition of an alkali to liberate the free amines followed by fractional distillation.
- This method does not give a specific amine and hence not suitable for a particular amine.
- The method also works well for only primary amines.
- 2–bromopropane is the only secondary alkyl halide that forms an amine by this method; the other secondary and tertiary alkyl halides yield alkenes on heating with ammonia due to elimination of HX.
- For example: $(CH_3)_3CBr + \text{conc } NH_3 \xrightarrow{heat,\ high\ pressure} (CH_3)_2C{=}CH_2 + NH_4Br$

(iv) From alcohols

$$R{-}OH \xrightarrow[\text{high pressure, } 400^oC]{NH_3(g)/Al_2O_3} R{-}NH_2 + H_2O$$

A mixture of amines is also formed. Silica gel can be used in place of alumina.

Questions:
Write equation(s) to show how
(a) ethyne can be converted into aniline.
(b) ethylamine can be obtained from a named alcohol.

Basicity of amines

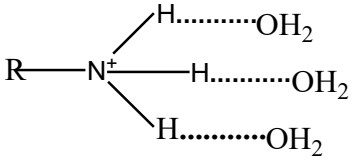
❖ Just like ammonia, amines are weak bases which partially dissolve in water as below:

$$RNH_2(aq) + H_2O(l) \rightleftharpoons RNH_3^+(aq) + OH^-(aq)$$

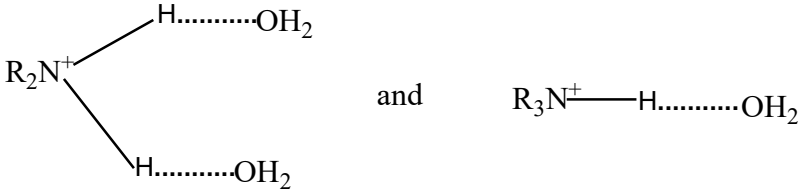
Compare with: $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

- The presence of hydroxide ions in the aqueous solution makes the solution basic.
- In the presence of an acid, amines use their lone pair of electrons on the nitrogen atom to accept a proton to form salts. This reaction makes amines act as bases (just like ammonia) although stronger than water and weaker than alkalis.
- The basic strength of amines in water depends on **three** factors:
  I. The availability/presence of lone pair of electrons on nitrogen atom to react with a proton.
  II. The ease with which the protonated amine can undergo solvation with water molecules and so become stabilised (i.e. the stability of the positive ion/cation formed upon ionisation).
  III. The solubility of amine in water.
- Aliphatic amines are stronger bases than ammonia. This is because the alkyl groups are electron releasing (i.e. have positive inductive effect). They tend to increase the electron density on the nitrogen atom to which they are bonded thus making the lone pair of electrons on the nitrogen atom more available for reaction with protons. The more the alkyl groups the more basic the compound is.
- In ammonia, the hydrogen atoms have no positive inductive. Thus, the lone pair of electrons on the nitrogen atom is less readily available for a reaction with a proton.
- Basing on factor I, the expected basic strength decreases in the order:
  3^o amine > 2^o amine > 1^o amine > NH_3.
- Basing on factor II, the ease of solvation of protonated amines decreases in the order:
  NH_3 > 1^o amine > 2^o amine > 3^o amine
- Solvation in a protonated amine is facilitated by hydrogen bonding between the hydrogen atoms attached to the nitrogen atom of the protonated amine and the oxygen atom of the water molecules.
- For example:

Protonated 1^o amine, $R - N^+H_3$, is solvated as follows:



Solvation of protonated 2^o amine ($R_2N^+H_2$) and 1^o amine (R_3N^+H) is as follows respectively:



- Thus, a protonated 1^o amine is more solvated followed by a protonated 2^o amine and then 3^o amine.
- The more solvated the protonated amine is, the more stable the positive ion formed and the more basic the amine will be.

Note:
Protonated ammonia, $NH_4{}^+$ is more solvated than any of the protonated amines.

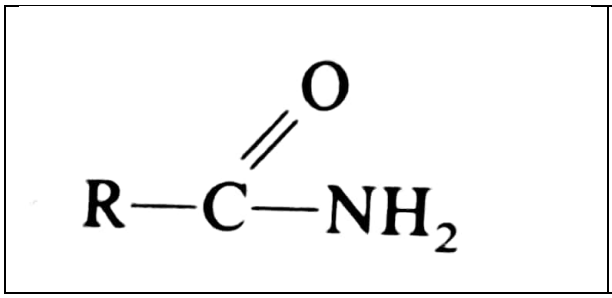
- A combination of the above factors gives basic strength of amines decreasing in the order: 2^{o} amine > 1^{o} amine > 3^{o} amine > NH_3.
- The basic strength in tertiary amines is further reduced by the steric hindrance of the three alkyl groups. They make the proton not to easily access the lone pair of electrons on the nitrogen atom for the reaction to occur.
- Tertiary amines are less soluble in water and furthermore the protonated tertiary amine is less solvated and this makes the cation less stable once formed.
- We can also use the value K_b to tell the strength of a base, where K_b is the base dissociation constant. The higher the K_b value, the stronger the base.

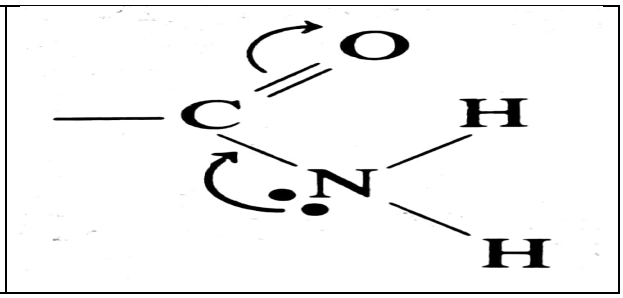
Compound	**K_b (mol dm^{-3}) at 25^{o}C**	**pK_b**
Ammonia	1.8×10^{-5}	4.74
Ethylamine	5.4×10^{-4}	3.28
Dimethylamine	$5.9\ 10^{-4}$	3.23
Trimethylamine	6.3×10^{-5}	4.20

Table 9.5: K_b values of some amines

Questions:
Dimethylamine readily reacts with acid but ethylamine does not. Explain.

- In contrast to aliphatic amines which are stronger bases than ammonia, aromatic amines are even much weaker than bases than ammonia.
  This is because the lone pair of electrons on the nitrogen atom interacts with the delocalised pi electrons in the benzene ring. This reduces the availability of the lone pair of electrons on the nitrogen atom for the reaction with a proton.
- Amides are less basic because of the strong electron withdrawing effect of the carbonyl group. This makes the lone pair of electrons on the nitrogen atom less available for a reaction with a proton.





Reactions of amines

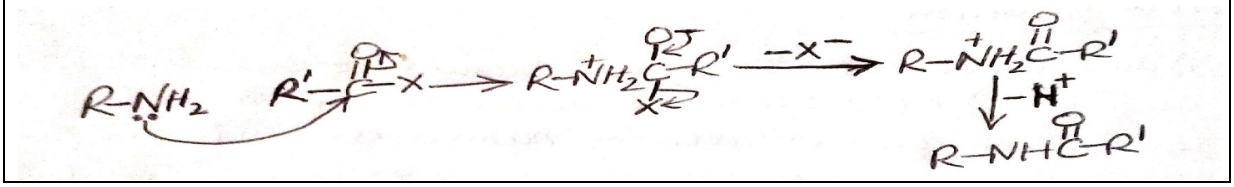
1. Acylation: Amide formation

- Only primary and secondary amines are acylated due to the replaceable hydrogen atoms on the nitrogen atom. Tertiary amines lack replaceable hydrogens atoms on the nitrogen atom and thus cannot form amides.
- Acylation is done by use of an acid(acyl) halides.
- For example:

$$R-NH_2 + \underbrace{R^ICOX}_{acyl\ halide} \longrightarrow \underbrace{RNHCOR^I}_{amide} + HX$$

$$R_2NH + \underbrace{R^ICOX}_{acyl\ halide} \longrightarrow \underbrace{R_2NCOR^I}_{amide} + HX$$

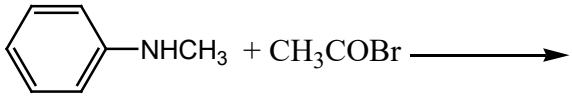
General mechanism:



Questions

Complete and outline a mechanism for the following reactions:

(i) $CH_3C(=O)Cl + CH_3CH_2NH_2 \longrightarrow$

(ii)  $+ CH_3COBr \longrightarrow$

- The amides formed are solids whose melting points can be determined accurately and used to identify the parent amine.

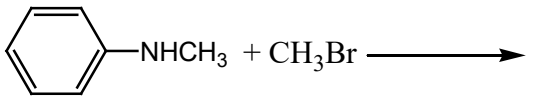
2. Alkylation

- Just like ammonia, all classes of amines react with alkyl halides.
- A mixture of products is formed.
- The reaction involves successive replacement of the hydrogen atoms attached to the nitrogen atom of the amine by an alkyl group.
- The general reaction equation involving a primary amine is:
  $R-NH_2 + R^ICH_2X \longrightarrow \underbrace{RNHCH_2R^I}_{amine} + HX$
- The mechanism is similar to the that in acylation.
- For example:
  (i) $CH_3NH_2 + CH_3CH_2Cl \rightarrow CH_3NHCH_2CH_3 + HCl$
  (ii) $(CH_3)_3N + CH_3Br \xrightarrow{heat} (CH_3)_4N^+Br^-$ Tetramethylammonium bromide
- In tertiary amines heat is required to overcome the steric effect of the three alkyl groups.

Question

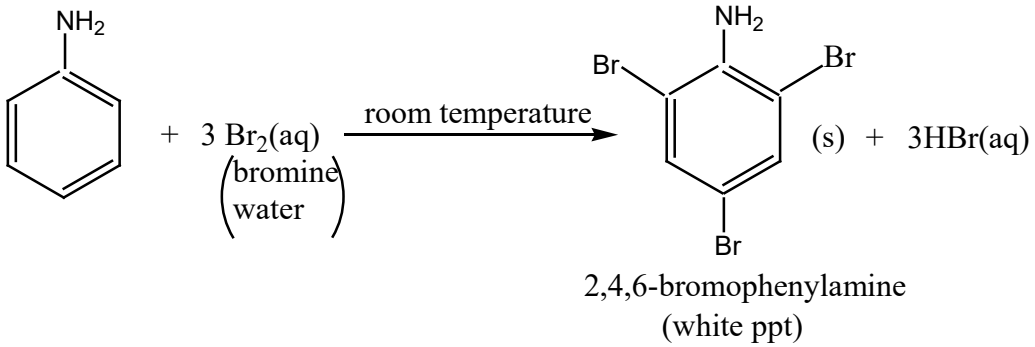
Complete and outline a mechanism for the following reactions:

(i) $CH_3CH_2Cl + CH_3CH_2NH_2 \longrightarrow$

(ii)  $+ CH_3Br \longrightarrow$

3. Ring substitution in aromatic amines

- ❖ Aromatic amines are more reactive than benzene itself.
- ❖ Substitution occurs at the ortho- and para- positions in the ring.
- ❖ For example:



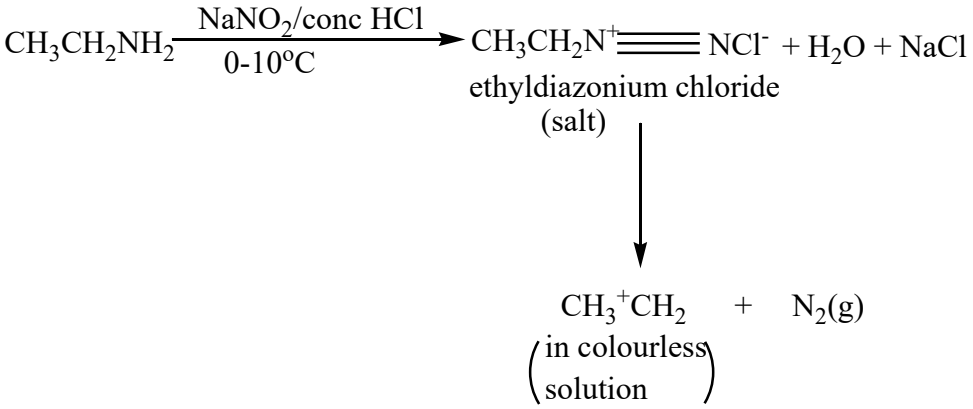
2,4,6-bromophenylamine
(white ppt)

- ❖ A similar reaction occurs with chlorine water.
- ❖ The reaction of primary aromatic amines with bromine water is used to differentiate primary aromatic amines from aliphatic amines.

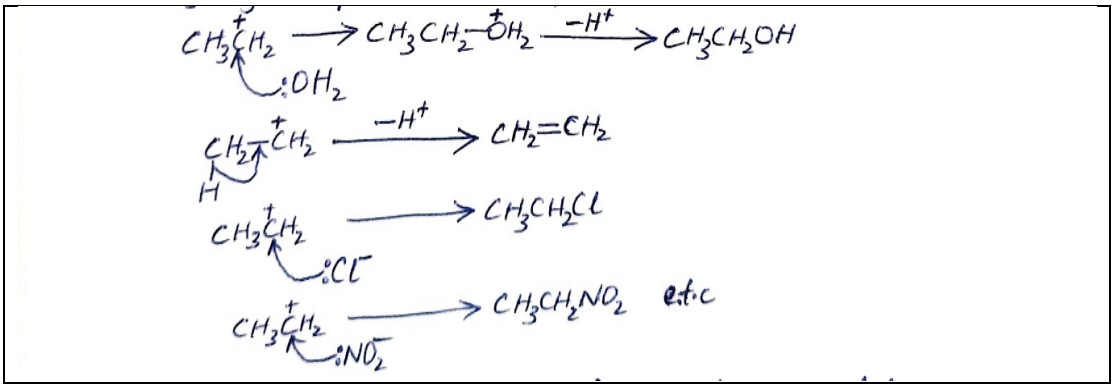
Question:
Explain why aminobenzene (phenylamine) reacts with bromine water at room temperature while benzene does not.

4. Reaction with nitrous (nitric(III)) acid, HNO_2

- ❖ Nitrous acid is very unstable and therefore it is formed in situ (during the reaction) by the action of concentrated (or dilute) hydrochloric or sulphuric acid on aqueous solution of sodium nitrite at $0 - 10^{o}C$.
- ❖ The reaction products depend on the following factors:
  (i) The class/type of amine used.
  (ii) The reaction conditions.
- ❖ For example:
  (a) Aliphatic primary amines evolve a colourless gas, nitrogen with formation of a colourless solution at temperature <10°C.
  For example:



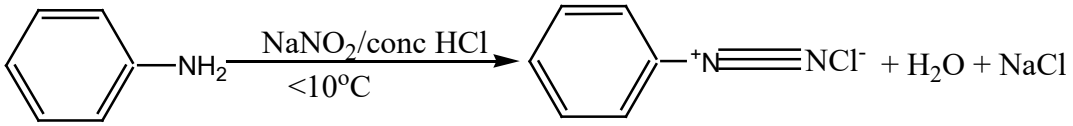
- The colourless solution contains a mixture of products like alkene, alcohol, ether, nitroalkane and haloalkane.
- This is because the carbocation (carbonium ion) formed is unstable and reacts to give a variety of organic products as shown below:



- The amount of nitrogen evolved can be used to determine the amount of amine in solution.

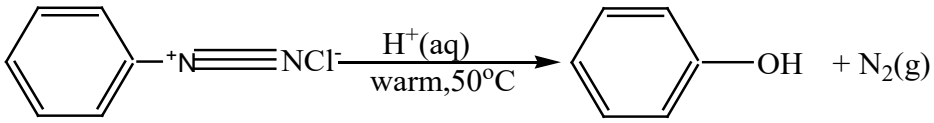
Question: Write a reaction scheme involving methylamine with nitrous acid. Identify all the possible products of the reaction.

(b) Aromatic primary amines form a colourless solution containing a more stable diazonium ion at $0 - 10^oC$.



benzenediazonium chloride
(colourless solution)

When the colourless solution is **warmed** with **excess dilute sulphuric acid**, nitrogen is evolved and **phenol** is left in solution.

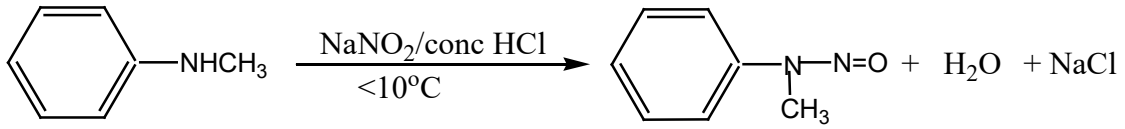


(c) Secondary amines, both aliphatic and aromatic, react with nitrous acid to form N-nitrosoamines which are seen as **yellow oils**. No nitrogen is evolved. The yellow oils are highly carcinogenic.

- The general reaction equation is:
  $R_2NH + HNO_2 \longrightarrow R_2N{-}N{=}O + H_2O$
  N–nitroso–N,N–dialkylamine
  (yellow oil)
- For example:
  $(CH_3)_2NH + HNO_2 \longrightarrow \underbrace{(CH_3)_2N-N=O}_{N-nitroso-N,N-dimethylamine} + H_2O$

  Alternatively, we may write:

$$(CH_3)_2NH + NaNO_2 + HCl \xrightarrow{<10^oC} \underbrace{(CH_3)_2N-N=O}_{N-nitroso-N,N-dimethylamine} + H_2O + NaCl$$



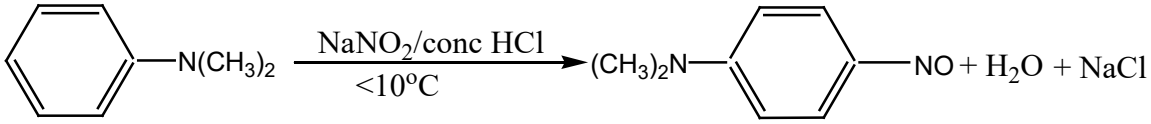
N-nitroso-N-methylphenylamine
(yellow oil)

Question:
Give the name and formula of the product formed when ethylmethylamine is reacted with nitrous acid at temperature < 10°C.

(d) Aliphatic tertiary amines react with nitrous acid to a colourless solution containing the salts.

$$R_3NH + NaNO_2 + HCl \xrightarrow{<10^oC} \underbrace{R_3N^+HNO_2^-}_{salt\ (colourless)} + H_2O + NaCl$$

Tertiary aromatic amines undergo nitrosation in the 4-positin in the ring.



4-nitroso derivative
(colourless solution)

The reaction of amines with ice-cooled mixture of sodium nitrite and concentrated hydrochloric acid is use distinguish between the classes of amines.

5. Reaction with transition ions

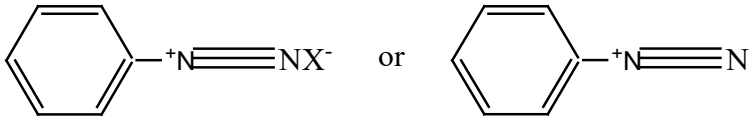
- We have already seen that amines just like ammonia possess a lone pair of electrons on the nitrogen atom and thus can act as electron donors.
- Amines therefore, can react with transition metal ions to form complexes which are mainly deep blue.
- They use the lone pair of electrons on their nitrogen atom to form a dative bond with the central metal ion.
- For example; butylamine reacts with copper(II) ions to form tetrabutylaminecopper(II) ion.
  $Cu^{2+}(aq) + 4C_4H_9NH_2(aq) \rightarrow [Cu(C_4H_9NH_2)_4]^{2+}(aq)$
  Compare with: $Cu^{2+}(aq) + 4NH_3(aq) \rightarrow [Cu(NH_3)_4]^{2+}(aq)$
  Amines are thus called **ligands**.
- This reaction is given by most amines and thus can be used to identify amines in solution.

Uses of other amines

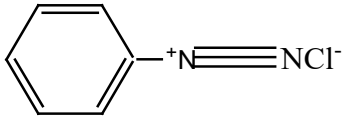
Amines are used in the manufacture of plastics like nylon 66. `Dimethylamine is used for the manufacture of solvents such as dimethlymethanamide.

BENZENEDIAZONIUM SALTS

- General formula:

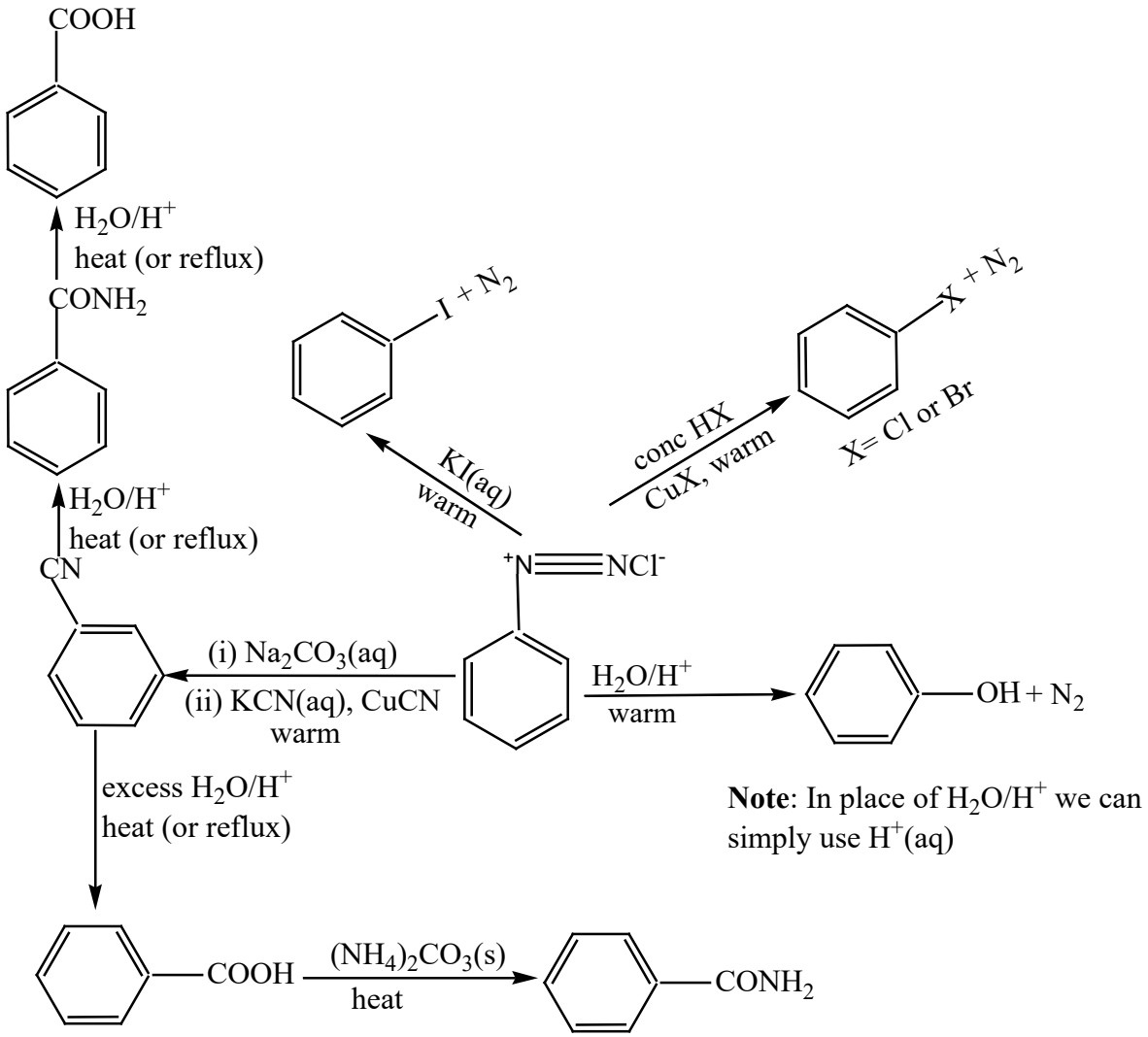


- Most important:



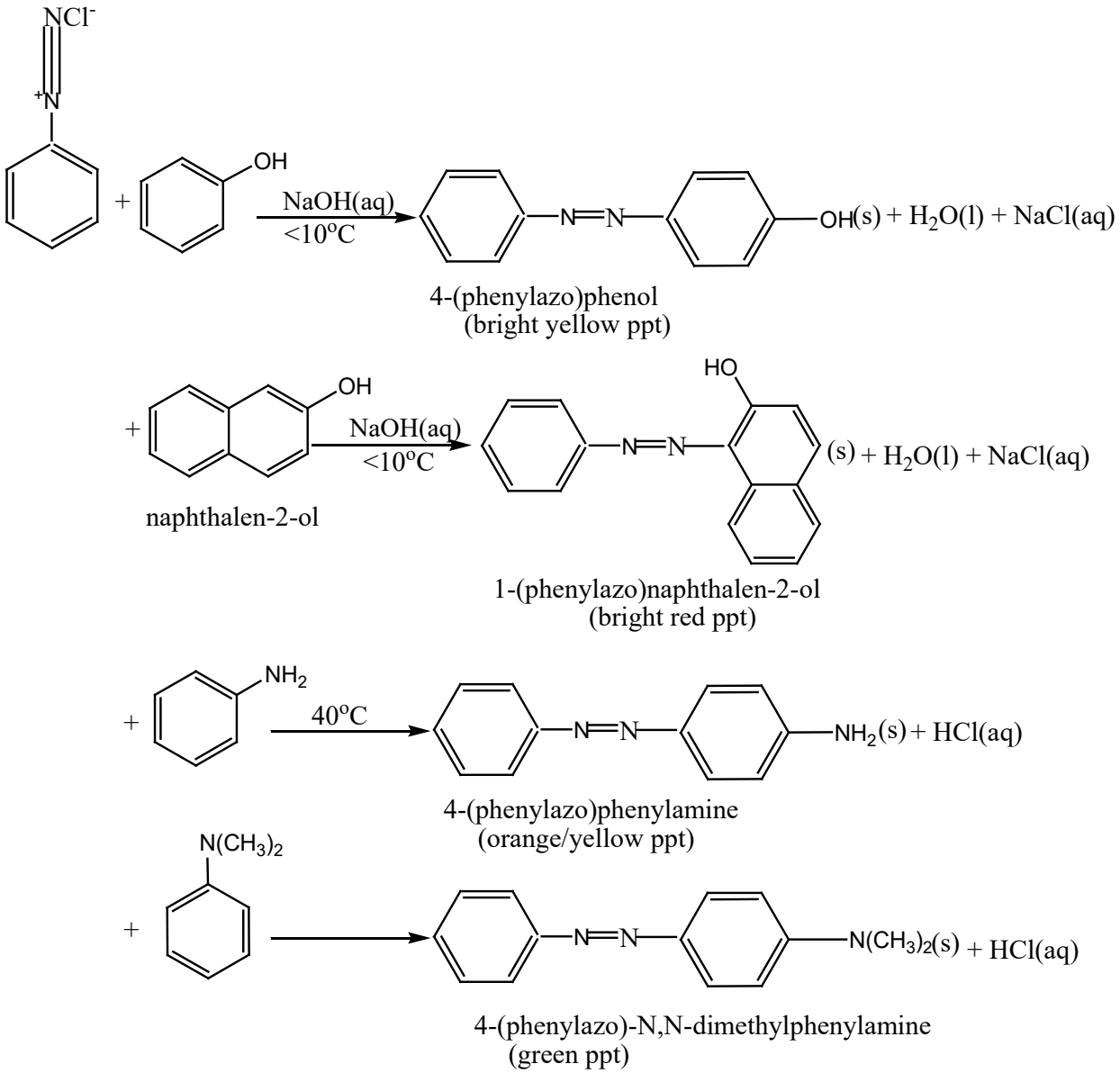
(benzenediazonium chloride)

- The salts undergo **two** types of reactions:
  (a) Nucleophilic substitution reactions; the diazonium group is replaced with evolution of nitrogen gas.
  A new functional group is introduced into the ring.
  For example:



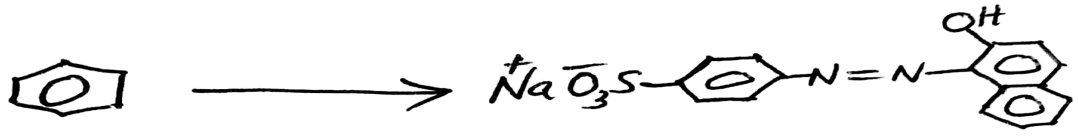
Note: In place of H_2O/H^+ we can simply use H^+(aq)

(b) Coupling reactions; diazonium group is retained.
The reactions are used in the preparation of azo-dyes since the products are highly coloured.
For example:



The reaction of the salt with naphthalen-2-ol in an alkaline medium is used to confirm the presence of primary aromatic amines.
In the test, the amine is first treated with a mixture of ice-cold sodium nitrite and concentrated hydrochloric acid. The resultant mixture is poured into an ice-cold alkaline solution of naphthalen-2-ol. Formation of a bright red precipitate confirms presence of primary aromatic amine.

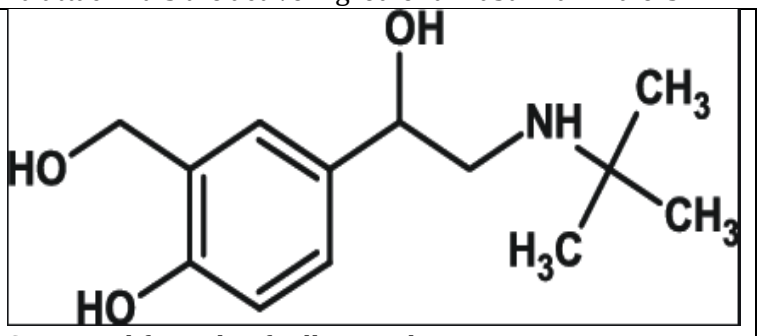
Question
Write equation to show how the following conversion can be effected:



Revision questions

1. One of the uses of amines in making drugs. One of such drugs is **salbutamol**. Salbutamol is a very effective treatment for asthma attack. It is the active ingredient in asthma inhalers.

An asthma patient on asthma inhaler



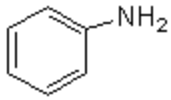
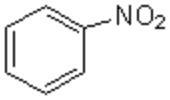
Structural formula of salbutamol

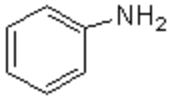
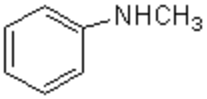
   (a) Identify the functional group(s) in the drug whose formula is given above.
   (b) State whether the amine group is primary, secondary of tertiary. Describe briefly how you would confirm the class of the amine to which the drug belongs.
   (c) The drug reacts with the following compounds; dilute hydrochloric acid, dilute sodium hydroxide sodium hydroxide, methanoic acid and ethanoyl chloride. For each of the compound, write equation to show how the reaction occurs.

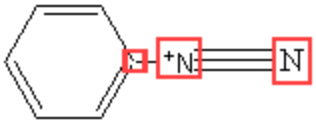
2. A compound X containing carbon, hydrogen and nitrogen has a general formula, $C_nH_{2n+1}NH_2$, was reacted with nitrous acid. 0.1 g of X reacted with nitrous acid and 37.97 cm^3 of nitrogen was evolved at s.t.p (molar gas volume at s.t.p = 22.4 dm^3).
   (i) Calculate the molar mass of X.
   (ii) Determine the molecular formula of X.
   (iii) Write all the possible structures of X.
   (iv) Write equation to show how X can be prepared from 2–chloropropane.
3. Discuss the reactions of amines with nitrous acid. Your descriptions such include suitable examples and reaction equations.
4. Name a reagent that gives a similar observation with methylamine and dimethylamine. State the observations and write equation for the reaction between the named reagent and each of the compounds
5. Name a reagent that can be used to distinguish between the following pair of compounds/ions. In each case, state what would be observed if each member of the pair is treated with the named reagent.

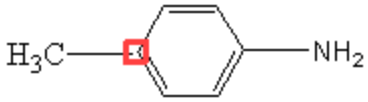
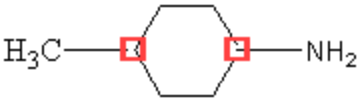
(a) $CH_3CH_2CH_2NH_2$ and $CH_3CH_2NHCH_3$

(b) $(CH_3)_3N$ and $CH_3CH_2CH_2NH_2$ or $CH_3CH_2NHCH_3$

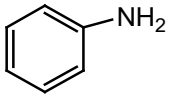
(c)  and 

(d)  and 

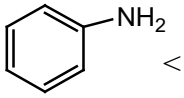
(e)  and 

(f)  and 

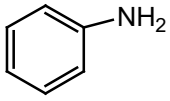
6. Explain the following observations.
   (a) The basicity of amines is in the order:

   $(CH_3CH_2)_2NH > (CH_3)_3N >$ 

   (b) Ethylmethylamine is a stronger base than trimethylamine.
   (c) The boiling points of tertiary amines are lower than those of primary amines of the same molecular mass.
   (d) Dimethylamine is a stronger base than aminobenzene.
   (e) The basic strength of some selected compounds are in the order:

    $< NH_3 <$ $(CH_3)_2NH$

7. The structural formulae of some amines X, Y and Z are given below:

   $CH_3CH_2NH_2$ **Q** $(CH_3CH_2)_2NH$ **X** $(CH_3)_3N$ **Y**  **Z**

   (a) Describe the reactions of the amines with nitric(III) acid (nitrous acid). (Your answer should include observations and equations).
   (b) The basicity of the amines is in the order: **X > Y> Z**. Explain.
   (c) Write equations to show how
      (i) **Z** can be obtained from ethanol.
      (ii) **Q** can be obtained from propan-2-ol.
      (Your answer should include reagents and conditions for the reactions).
   (d) **Z** can be converted into an azo-dye. Outline the steps that can be followed to prepare an azo-dye starting with **Z**. (Your answer should include observations and eqautions).

8. A compound R, relative molecular mass 93, burns with a sooty flame and contains 77.42% carbon, 7.53% hydrogen and the rest being nitrogen.
   (a) Determine the empirical formula R.
   (b) R is soluble in hydrochloric acid. Write the structural formula of R.
   (c) R was reacted with nitrous acid and to the product was added naphthalen-2-ol (2-naphthol).
      (i) State what was observed.
      (ii) Write equation for the reaction that took place.
   (d) R can be prepared from nitrobenzene. Write equation to show how nitrobenzene can be prepared from benzene.

END