CHAPTER 11.0: AMINES

TOPIC	SUBTOPIC	LEARNING OUTCOMES	MAPPING COGNITIVE DOMAINS			
			C1	C2	C3	C4
Amine	11.1 Introduction	a) Draw structures and classify primary, secondary and tertiary amines	√	√		
	11.2 Nomenclature	a) Draw structures and name aliphatic and aromatic amines (parent chain ≤C_{10}) according to the IUPAC nomenclature		√		
		b) Give common names with parent chain ≤C_5	√			
		c) Apply IUPAC rules to name primary, secondary and tertiary amines		√		
	11.3 Physical properties of Amines	a) Explain the physical properties: i. Boiling point of - Primary, secondary and tertiary amines - Amine with alkane, haloalkanes, alcohol, carbonyl compound and carboxylic acid ii. Solubility of primary, secondary and tertiary amines			√	√
		b) Explain the basicity in terms of i. Inductive effect ii. Resonance effect			√	
		c) Compare the basicity of ammonia, aliphatic amines and aromatic amines in terms of: i. Inductive effect ii. Resonance effect				√
	11.4 Preparation of Amines	a) Explain the preparation: i) Aromatic amines by reduction of nitro compounds using Zn/H^+ or $SnCl_2/H^+$ or Fe/H^+ ii) Primary aliphatic amines by reduction of nitriles using $LiAlH_4$ followed by H_3O^+ or $NaBH_4$ in methanol or H_2/catalyst iii) Primary, secondary and tertiary amines by reduction of amides using $LiAlH_4$ followed by H_2O iv) Primary alkyl and aryl amines by Hoffmann's degradation of primary amides			√	
		b) Outline the synthesis of primary, secondary, tertiary aromatic amines				√
	11.5 Chemical properties of Amines	a) Explain the reaction to distinguish classes of amine by using: i. Hinsberg's test ii. Nitrous acid test				√
		b) Distinguish classes of amines by using: i. Hinsberg's test ii. Nitrous acid test			√	
		c) Explain the identification test of aniline using bromine water		√		
		d) Explain the formation of dye by the coupling reaction of benzenediazonium chloride and phenol			√	
		e) Outline the synthesis of compounds related to reactions of amines				√

SUBTOPIC	LEARNING OUTCOMES	MAPPING COGNITIVE DOMAINS			
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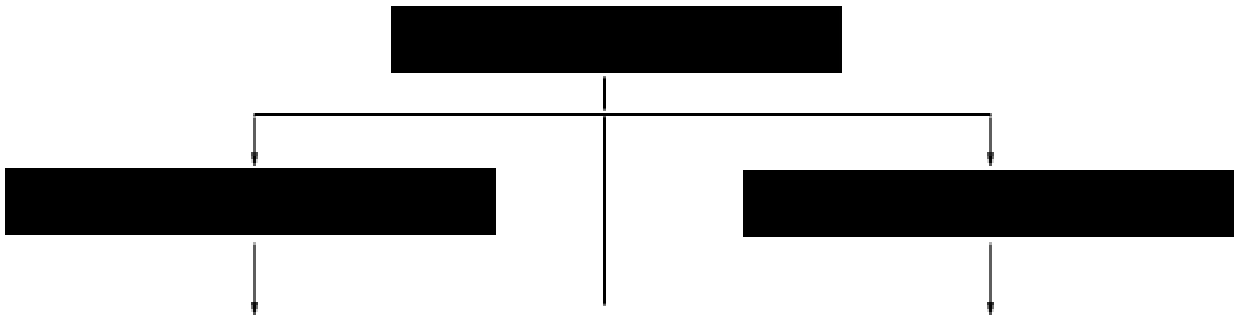
INTRODUCTION

- **Functional group of amines is amino (–NH_2)**
- **Amines** are **derivatives of ammonia, NH_3** by **replacing H atom with alkyl or aryl group.**
- Amines – **basic** and can react as **nucleophile**

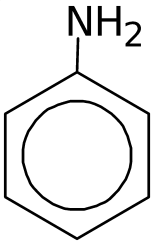


- Aliphatic amines have the amino group directly bonded to the alkyl group.

$R—NH_2$

R = alkyl group

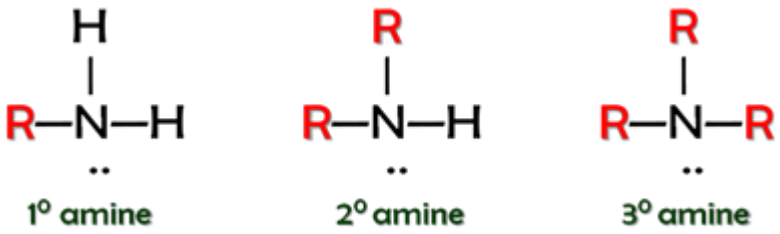
- Aromatic amines have the amino group directly bonded to the benzene ring.



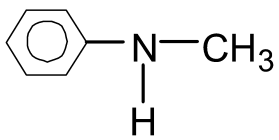
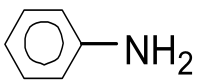
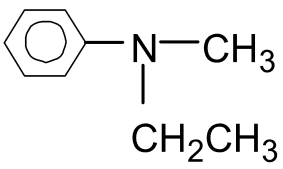
	R = benzene ring

CLASSIFICATION OF AMINES

- Amines are classified as primary, secondary, or tertiary depending on how many alkyl groups attached to the nitrogen atom.



Classify the following amines:

i. $CH_3CH_2CH_2NH_2$	ii. $CH_3CH_2—N(CH_3)—H$	iii. $CH_3CH_2—N(CH_3)—CH_3$
iv. 	v. 	vi. 

NOMENCLATURE OF AMINES

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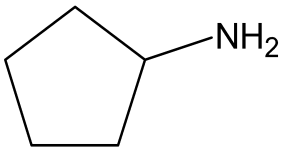
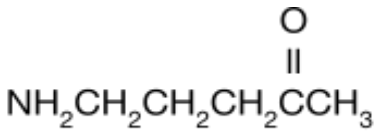
- **Common name : alkylamine**
- **IUPAC name : alkanamine**

Structure	Common Name	IUPAC Name
CH_3NH_2		
$CH_3CH_2NH_2$		
$CH_3CH_2CH_2NH_2$		
$CH_3CH(NH_2)CH_3$		
$NH_2CH_2CH_2NH_2$		

- When multiple functional group are present and the amine group ($-NH_2$) **does not take priority**, it is named as **'amino'** substituents.

Example:

1. 

2. CH_3CHNH_2COOH

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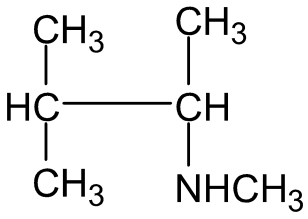
- Same two alkyl group, **R = R' (symmetrical)**
  Common name : **dialkylamine**

- Different alkyl group, **R ≠ R' (unsymmetrical)**
  Common name : **alkylalkyl'amine**

- **IUPAC nomenclature** :
  - longer chain R, gives the parent name
  - the other group as a substituents
  - **N–alkylalkanamine**

Structure	Common Name	IUPAC Name
CH_3NHCH_3		
$CH_3NHCH_2CH_3$		

$CH_3CH_2NHCH_2CH_3$		
$CH_3CH_2CH(NHCH_3)CH_2CH_3$		
		

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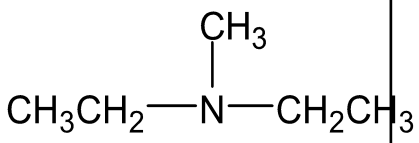
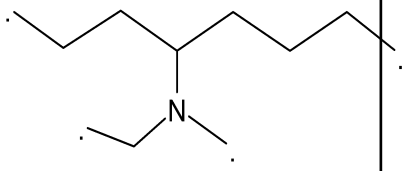
- Three identical alkyl group, **(R = R' = R'')**
  Common name : **trialkylamine**

- If three alkyl group not identical, **(R ≠ R' ≠ R'')**
  Common name : **alkylalkyl'alkyl''amine**

- IUPAC name :
  - longer chain R, gives the parent name
  - **N-alkyl'-N-alkyl''alkanamine**

Structure	Common Name	IUPAC Name

$(CH_3)_3N$		
$(CH_3)_2NCH_2CH_3$		
		
		

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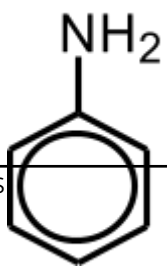
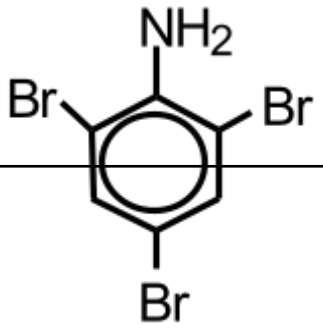
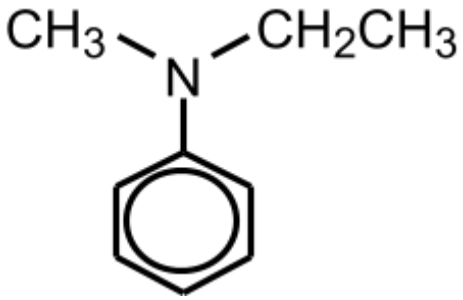
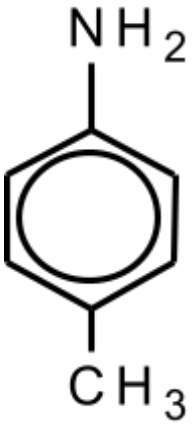
- Aromatic amines are named as derivatives of **aniline**

Example:





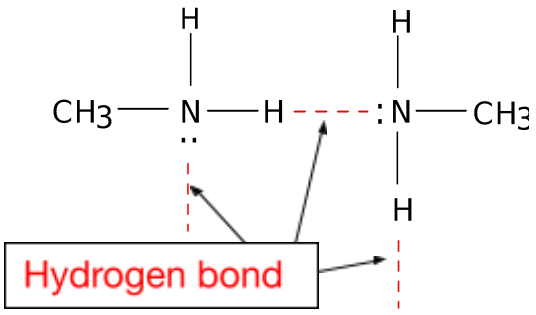
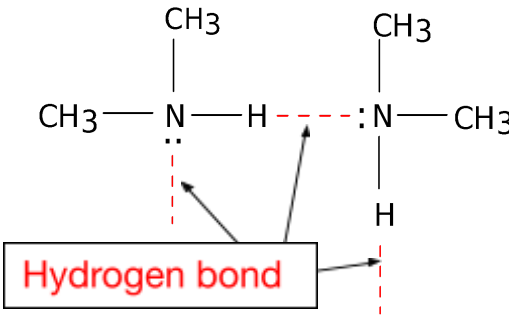
SUBTOPIC	LEARNING OUTCOMES	MAPPING COGNITIVE DOMAINS			
		C1	C2	C3	C4
11.3 Physical properties of Amines	a) Explain the physical properties: i. Boiling point of - Primary, secondary and tertiary amines			√	√

	- Amine with alkane, haloalkanes, alcohol, carbonyl compound and carboxylic acid ii. Solubility of primary, secondary and tertiary amines				

PHYSICAL PROPERTIES OF AMINES

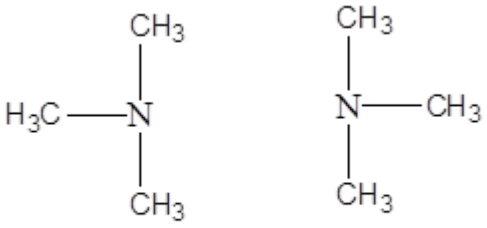
Boiling Point of Amines

- **1° amine > 2° amine > 3° amine**
- Both **primary and secondary** can form **intermolecular hydrogen bonds**.

Intermolecular forces between **primary amine** molecules	Intermolecular forces between **secondary amine** molecules
	

- **1° amine** has **2 hydrogen** atom attach directly to **N** atom, **2° amine** has **1 hydrogen atom** attach directly to **N** atom.
- **1° amine** able to form more **hydrogen bonding** between molecules compare to **2° amine.**
- **Heat energy needed** to **overcome** the hydrogen bonding in **1° amine** is **higher than 2° amine.**
- Thus, **boiling point 1° amine > 2° amine.**

Intermolecular forces between **tertiary amine** molecules:



no hydrogen bond

No intermolecular H bond for 3° amine

- Only Van Der Waals attraction forces between molecules.

Boiling point of Amines: Comparison Boiling Point

Alkane < haloalkane, carbonyl < amines < alcohol < carboxylic acid

Boiling point increases

- **Amines** has **higher boiling point** than **alkanes, haloalkanes/carbonyl** compounds of similar M_r:

Type of intermolecular forces:

Amines → intermolecular hydrogen bond
Alkanes → non polar molecule (London dispersion forces)
Haloalkanes/Carbonyl → polar molecule (dipole-dipole forces)

Strength of IMF:

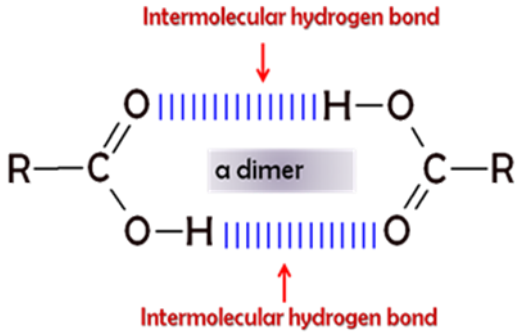
Hydrogen bond > dipole-dipole forces > London dispersion forces

- **Amines** has **lower boiling point** than **alcohol** of similar M_r because:

Hydrogen bond in amine is **weaker than** the **hydrogen bond in alcohol.**
(**Nitrogen** is **less electronegative** than the **Oxygen**)

- **Carboxylic acid has highest boiling point** because:

It can form stable hydrogen bonded dimers



Exercise:

Arrange the following compounds in ascending order of boiling point and explain.

1−butanol, 1−butanamine, propanoic acid, 1−fluoropropane

Answer:

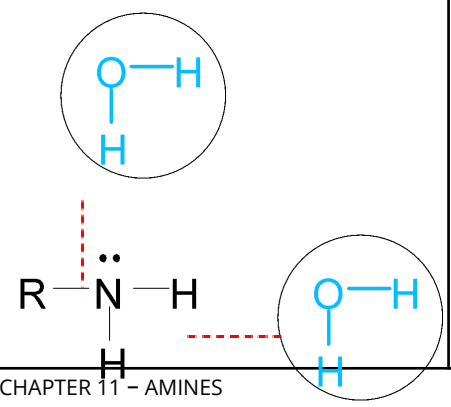
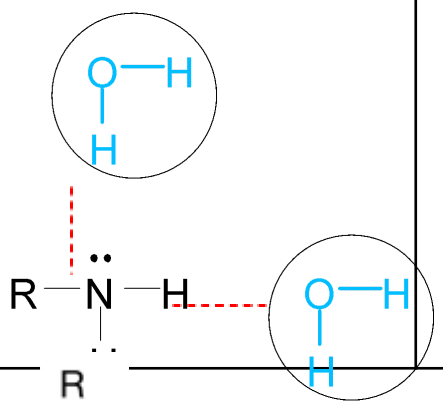
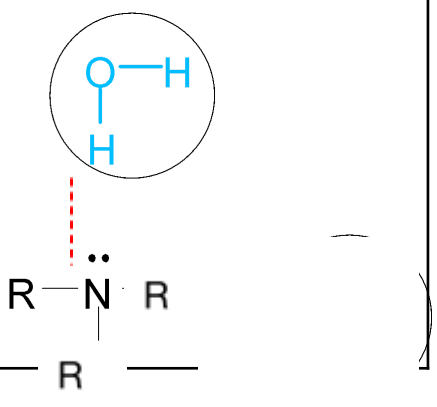
- ..... has no existence of hydrogen bonding between the molecules but only ..... forces.
  Hence, the boiling point of ..... is the lowest among all.

- The electronegativity of O is ..... than N. Hence, the hydrogen bonding for ..... is stronger than .....

- ..... has the highest boiling point because it can form more .....

Solubility in Water

- **All amines** including **tertiary amines**, are **capable of forming hydrogen bonds with water molecules**.
- Amines having **≤ 5C** are **soluble in water**.
- Amines having **> 5C** are **insoluble in water** because the **alkyl portion** (**hydrophobic area**) is **too large** to dissolve in the water.

Primary Amine	Secondary Amine	Tertiary Amine
		

3° amines , 2° amines , 1° amines

Solubility increases

- **1° and 2° amines are more soluble than 3° amines** because they form **more hydrogen bond** with **water molecules**.
- **Solubility decreases** with **increasing of molecular weight** because **hydrophobic area increases**.
- **Aromatic amines less soluble in water** compare to **aliphatic amines** of comparable molecular weight because of **huge aromatic ring (bulky hydrophobic alkyl @ aryl group)**

Exercise:

Compare the solubility of trimethylamine and methylamine in water. Explain

Answer:

Explanation:

- Methylamine is ..... amine which is ..... soluble in water because it can form ..... hydrogen bond with water molecule compared to trimethylamine which is ..... amine.

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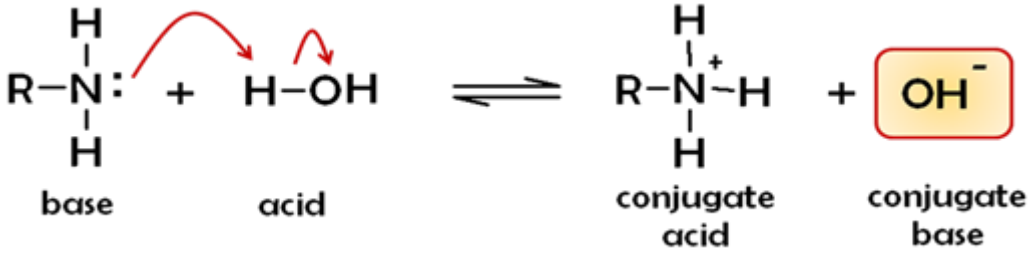
	c) Compare the basicity of ammonia, aliphatic amines and aromatic amines in terms of: i. Inductive effect ii. Resonance effect				√

Basicity of Amines

- Basicity is the tendency of a species to donate electron
- Amines act as **base** because of the presence of **lone pair on the nitrogen** atom which can be **donated to proton, H^+**



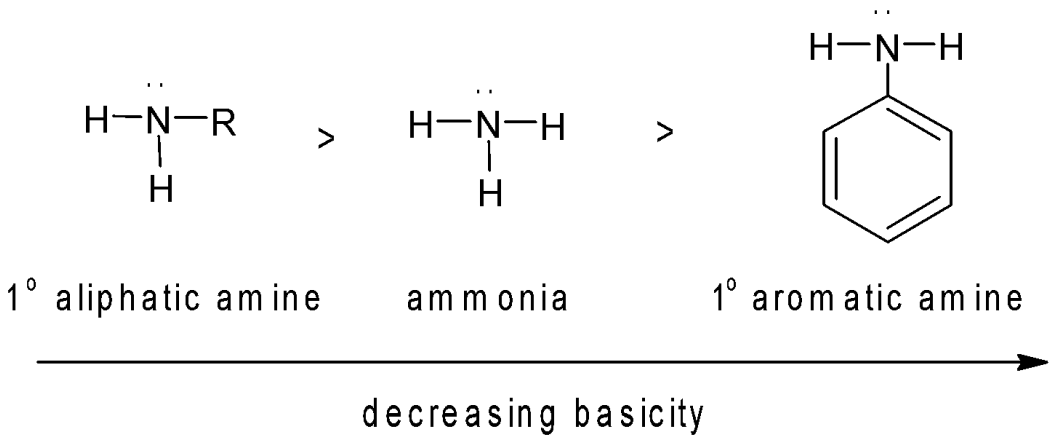
- **Strength of base** depends on the **ability of lone pair on the nitrogen atom to donated to H^+** and the **stability of the conjugate acid.**
- There are **two factors** that **influence the strength of a base**:

(i) Inductive effect – **Electron Donating Group (EDG)**
- **Basicity increase** with the presence of **EDG**

– **Electron Withdrawing Group (EWG)**
- **Basicity decrease** with the presence of **EWG**

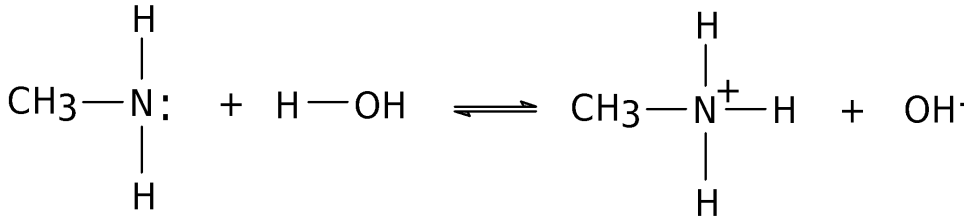
(ii) **Resonance effect** – Compounds are **less basic** if it has a **resonance structure.**

BASICITY OF AMINES

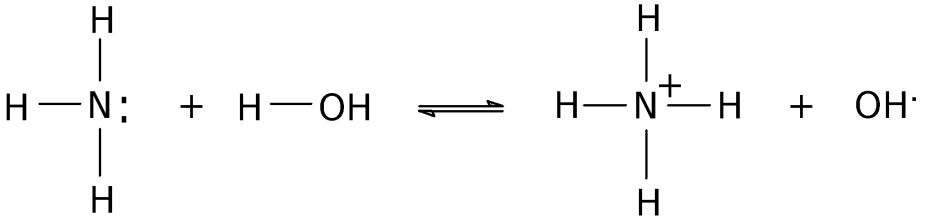


Comparison 1° aliphatic amine & ammonia: INDUCTIVE EFFECT

- **Methylamine** is a **stronger base** than **ammonia** because…..



- The **methyl group** is an **EDG**
- It **increase the electron density at nitrogen atom**
- **Easier for nitrogen to donate electron** and **pick up proton (H^+)**.
- The **methylammonium ion** is **stabilize by EDG**
- **Thus, basicity increases.**

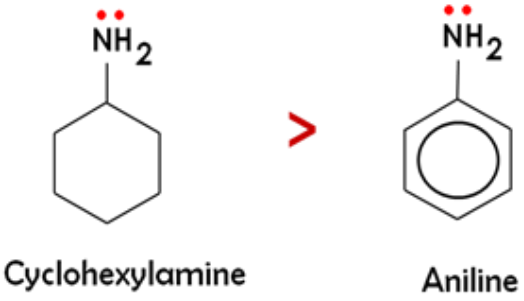


ammonia	ammonium ion

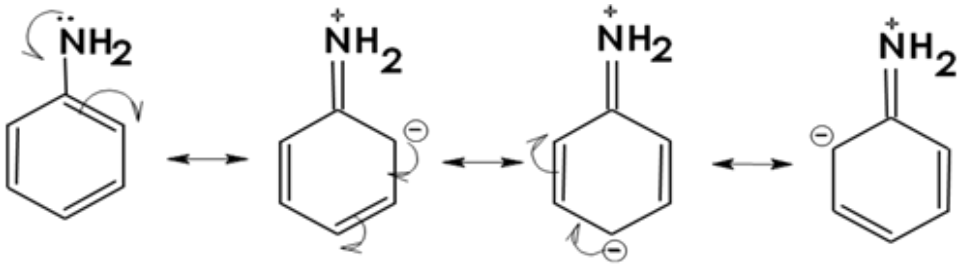
Comparison 1° aromatic amines: RESONANCE EFFECT

- **Aromatic amines (aniline)** are **weaker bases** than the corresponding **aliphatic** and **cyclic amines.**

Compare:

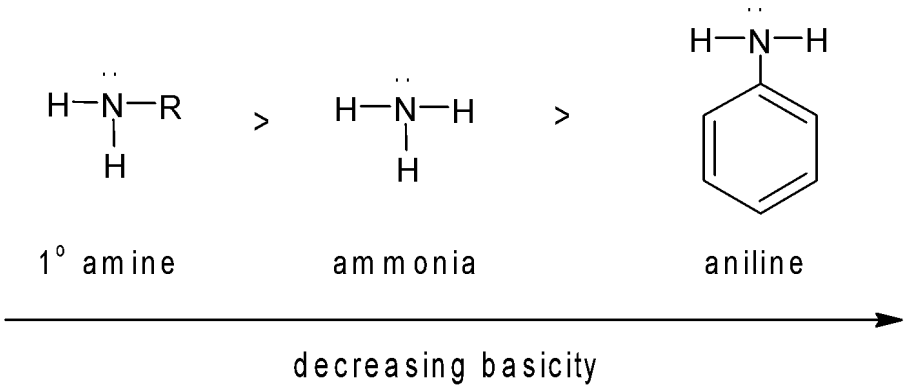


- **Aniline** is **less basic** than **cyclohexylamine** because **resonance effect** in **aromatic amine**:
  - The **lone pair electrons** of **nitrogen atom** are **delocalised** into benzene ring.
  - **Electron density at nitrogen atom decreases**.
  - Ability of nitrogen to **donate electron decreases**.



So we can conclude.....

- The basicity of **1^0 amine, ammonia and aniline** based on **inductive** and **resonance effect** as follows ...



SUBTOPIC	LEARNING OUTCOMES	MAPPING COGNITIVE DOMAINS			
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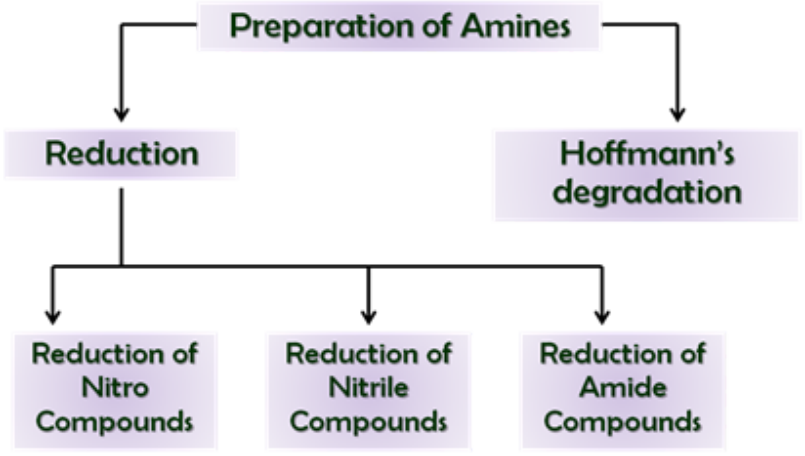
11.4 Preparation of Amines	a) Explain the preparation: i. Aromatic amines by reduction of nitro compounds using Zn/H^+ or $SnCl_2/H^+$ or Fe/H^+ ii. Primary aliphatic amines by reduction of nitriles using $LiAlH_4$ followed by H_3O^+ or $NaBH_4$ in methanol or H_2/catalyst iii. Primary, secondary and tertiary amines by reduction of amides using $LiAlH_4$ followed by H_2O iv. Primary alkyl and aryl amines by Hoffmann's degradation of primary amides			√	
	b) Outline the synthesis of primary, secondary, tertiary aromatic amines				√

PREPARATION OF AMINES



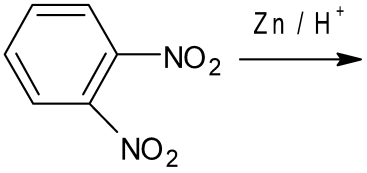
- **Reduction of nitro** compounds is especially useful to prepare **aromatic amines**

$$Ar{-}NO_2 \xrightarrow{[H]} Ar{-}NH_2$$

- The common reducing reagents used: **Zn/H^+ or $SnCl_2/H^+$ or Fe/H**

Example:

1.



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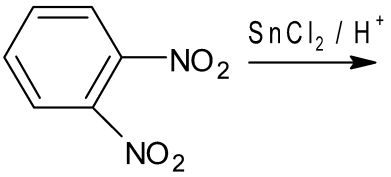

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- Nitrile compounds are reduced to **1° aliphatic amines**

$$R{-}C{\equiv}N \xrightarrow{[H]} R{-}\ CH_2NH_2$$

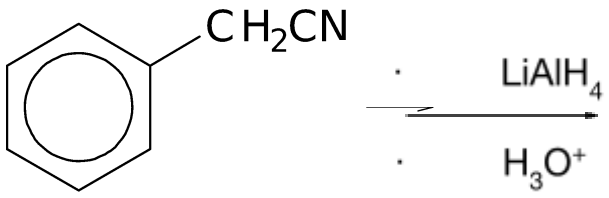
- The common reducing reagents used:
  - H_2 and Pt or Pd or Ni
  - $LiAlH_4$ followed by hydrolysis

Example:

1.

$$CH_3CH_2C{\equiv}N \xrightarrow{H_2,\ Ni}$$

2.



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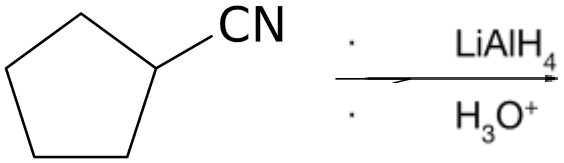

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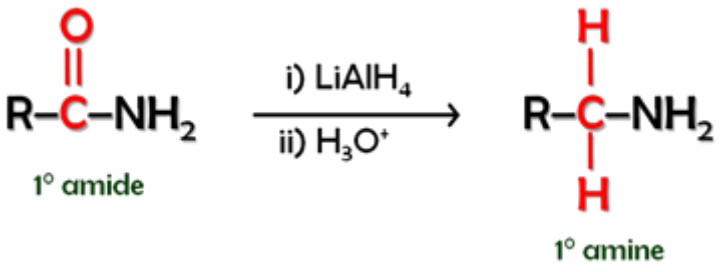
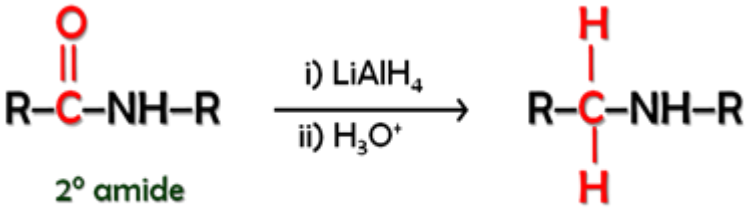
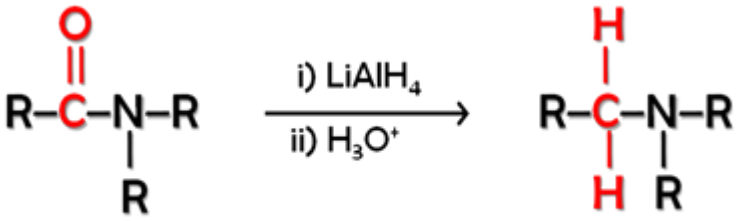
- Reduction of amides by **$LiAlH_4$** followed by **hydrolysis** produces **1°**, **2°** or **3°** amines.

General:





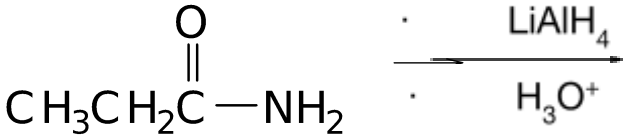
2° amide → 2° amine



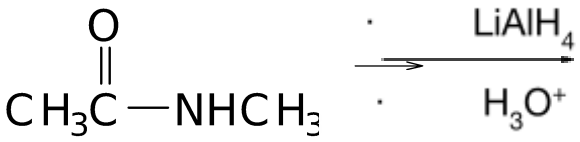
3° amide → 3° amine

Example:

1.



2.



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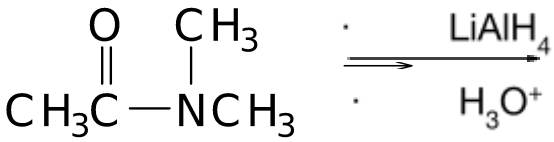

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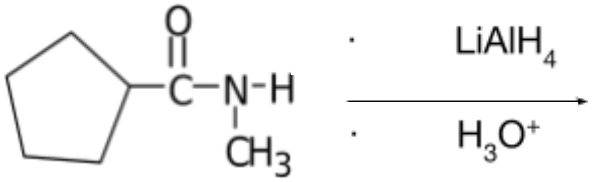
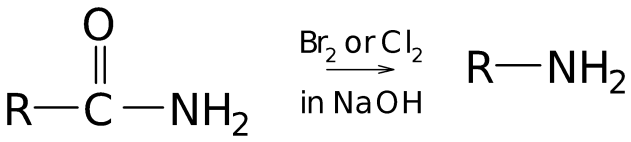


[redacted]

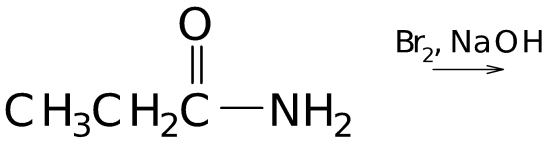
- **1° amides** reacts with **Br_2** or **Cl_2** in **NaOH** to produce **1° amines**



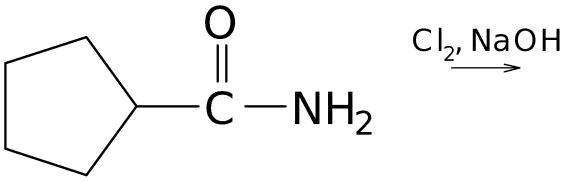
- The **carbonyl group** from the **amide** is **removed** and the **primary amine is formed.**

Example:

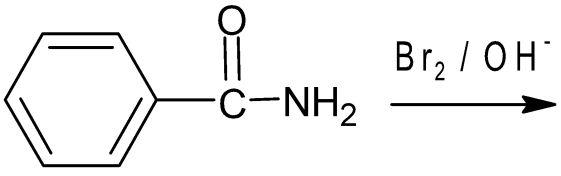
1.



2.

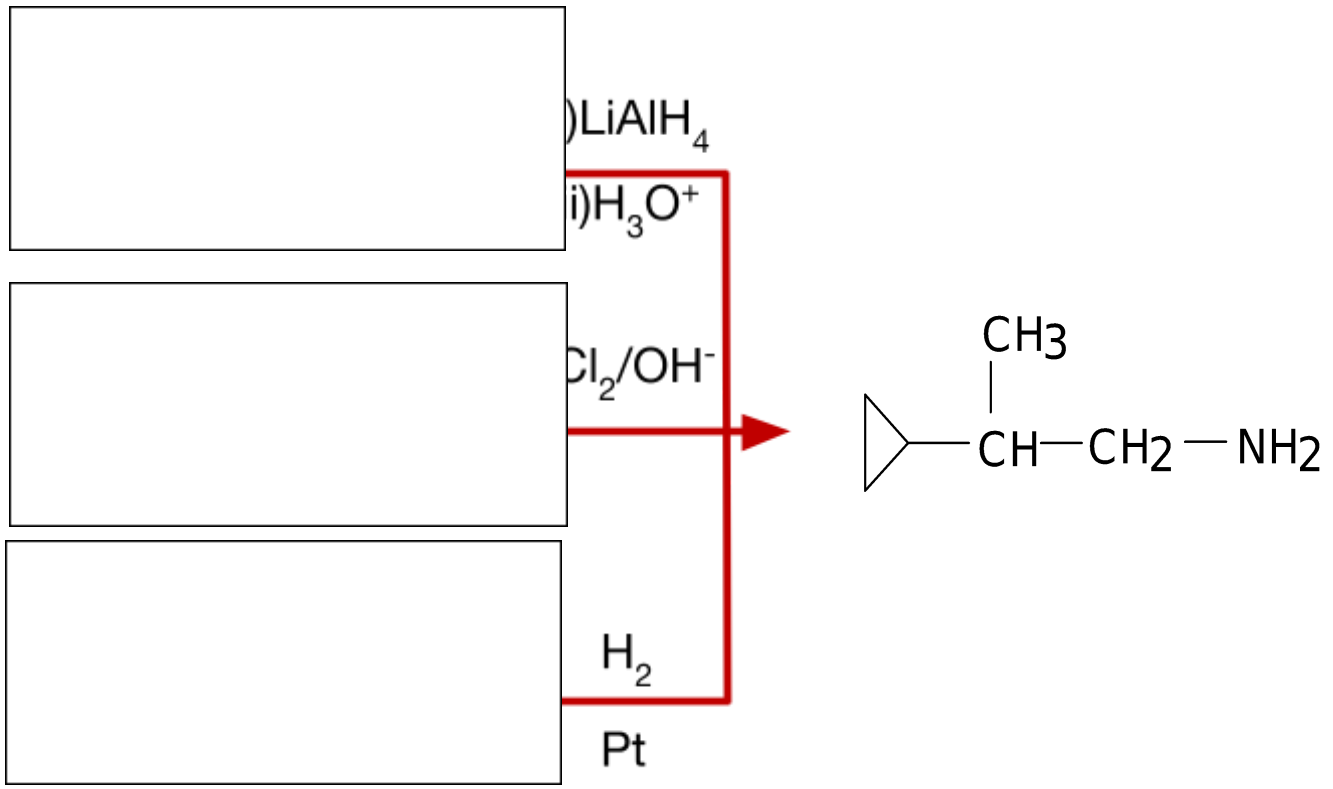


3.



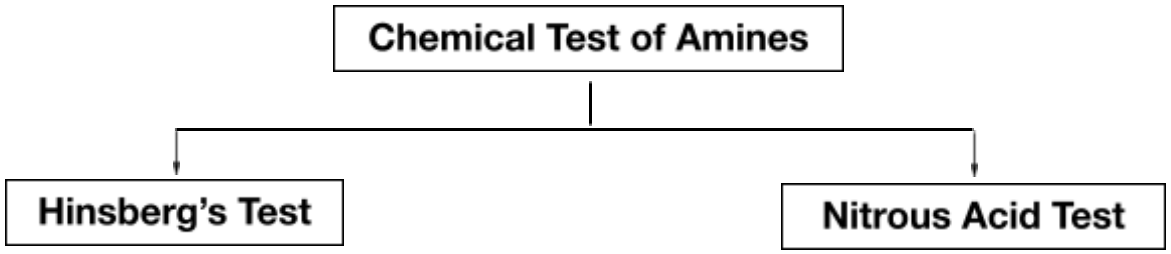
Exercise:

Test yourself.....



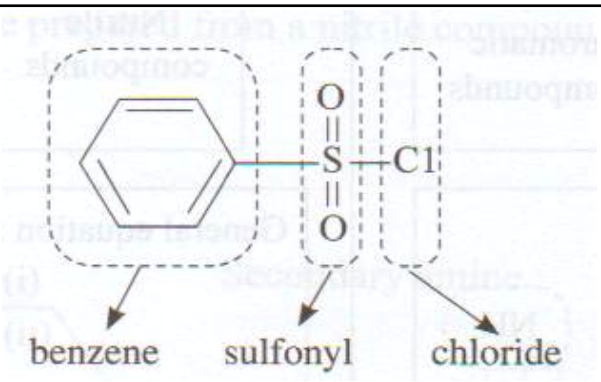
SUBTOPIC	LEARNING OUTCOMES	MAPPING COGNITIVE DOMAINS			
		C1	C2	C3	C4
11.5 Chemical Properties of Amines	a) Explain the reaction to distinguish classes of amine by using: i. Hinsberg's test ii. Nitrous acid test				√
	b) Distinguish classes of amines by using: i. Hinsberg's test ii. Nitrous acid test			√	
	c) Explain the identification test of aniline using bromine water		√		
	d) Explain the formation of dye by the coupling reaction of benzenediazonium chloride and phenol			√	
	e) Outline the synthesis of compounds related to reactions of amines				√

CHEMICAL PROPERTIES OF AMINES



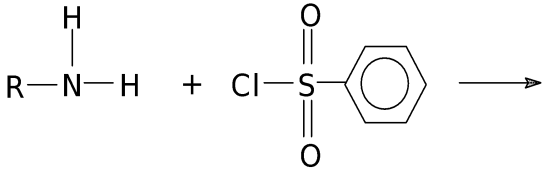
[redacted] ⇒ reaction with **benzenesulphonyl chloride**

Structure of benzenesulfonyl chloride is :



- Used to differentiate between 1°, 2° and 3° amines.
- Involves 2 steps:
  1) Amine + benzenesulfonyl chloride + excess KOH or NaOH.
  2) Then, the mixture is acidified by adding HCl.
- Each class of amine gives a different set of visible results after each of these 2 step.

1° amine

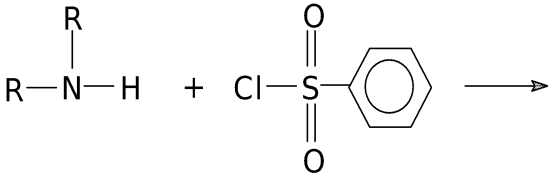


Excess NaOH → Clear solution (water soluble salt)

HCl → White precipitate

White precipitate

2° amine



Excess NaOH → No visible result

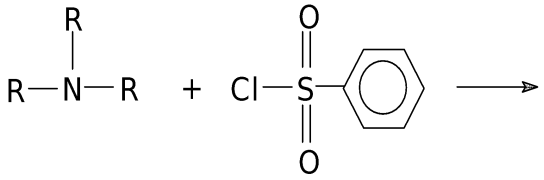
Insoluble white precipitate

HCl → No visible result

White precipitate remain

White precipitate

3° amine



No visible result
Clear solution

Excess
NaOH

No visible result
Clear solution

HCl

No visible result
Clear solution
(water soluble salt)

SUMMARY OF HINSBERG'S TEST

Hinsberg's Test	Step 1: Addition of benzenesulphonyl chloride	Step 2: Addition of excess NaOH	Step 3: Addition of HCl
1°	White precipitate formed	White precipitate formed dissolved and formed clear solution (water soluble salt)	White precipitate formed
2°	White precipitate formed	No visible reaction (Insoluble white precipitate)	No visible reaction (White precipitate remain)
3°	No visible reaction (clear solution)	No visible reaction (Clear solution)	No visible reaction (clear solution: water soluble salt)

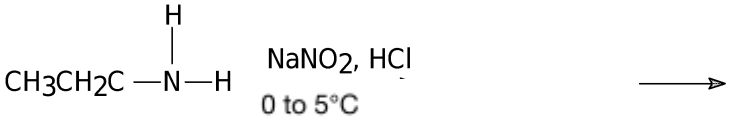
[redacted]

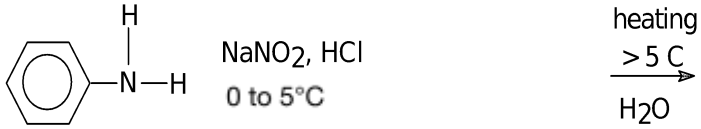
- Nitrous acid, HNO_2 is a weak, unstable acid.

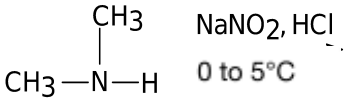
- HNO_2 is always prepared ***in situ***, by treating cold sodium nitrite (**$NaNO_2$**) with an aqueous solution of a **cold dilute hydrochloride acid** (0°C).

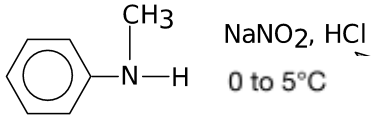
$$NaNO_2 + HCl \xrightarrow[0 \text{ to } 5°C]{} HNO_2 + NaCl$$

- This reaction can be used to differentiate:
  - 1°, 2° and 3° aliphatic amines.
  - 1°, 2° and 3° aromatic amines.
  - 1° aliphatic and 1° aromatic amines.

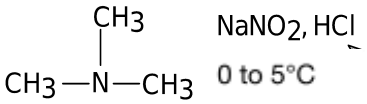
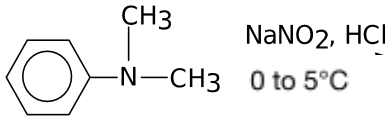
<table>
<tr><th colspan="2">1° amine</th></tr>
<tr><th>1° aliphatic amine</th><th>1° aromatic amine</th></tr>
<tr><td>1° aliphatic amines reacts with HNO_2 (0 to 5°C) to form diazonium salt. Diazonium salt is not stable. Will be decomposed to alkyl halide, alcohol, alkene and N_2 gas.
 

Observation: Bubble gas evolved (N_2 gas)</td><td>1° aromatic amines reacts with HNO_2 (0°C to 5°C) to form arenediazonium salts.
 

Observation: Clear solution formed Bubbles gas evolved upon heating</td></tr>
<tr><th colspan="2">2° amine</th></tr>
<tr><th>2° aliphatic amine</th><th>2° aromatic amine</th></tr>
<tr><td>2° aliphatic amines reacts with HNO_2 (0°C to 5°C) to form nitrosoamines
 

Observation: Yellow oil formed</td><td>2° aromatic amines reacts with HNO_2 (0°C to 5°C) to form nitrosoamines
 

Observation: Yellow oil formed</td></tr>
<tr><th colspan="2">3° amine</th></tr>
<tr><th>3° aliphatic amine</th><th>3° aromatic amine</th></tr>
</table>

When 3° aliphatic amines added to HNO_2 (0^0C to 5°C), it dissolves to form **trimethylammonium ion**, a **colourless solution**  Observation: **Clear solution formed**	3° aromatic amines reacts with HNO_2 (0°C to 5°C) by undergoing substitution at the **para position** of the benzene ring to form **nitrosoaniline.**  Observation: **Green precipitate formed**

SUMMARY OF NITROUS ACID

AMINE	OBSERVATION
1° aliphatic	gas bubbles evolved, $N_2(g)$ (and 3 products : R-OH + C=C & R-X)
2° aliphatic	Yellow oil formed
3° aliphatic	Colourless solution formed
1° aromatic	Clear solution formed and no gas bubbles at 0^0C to 5^0C evolved
2° aromatic	Yellow oil formed
3° aromatic	Green precipitate formed

IDENTIFICATION TEST OF ANILINE

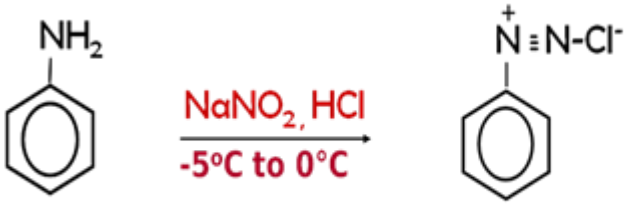
Chemical Test : **Test with bromine water**
Reagent : **Br, H_2O**
Reaction:

2,4,6-tribromoaniline

Observation:
Reddish brown colour of bromine decolourised and white precipitate formed

FORMATION OF DYE

- Primary aromatic amines react with HNO_2 to give arenediazonium salts which are stable at 0°C.

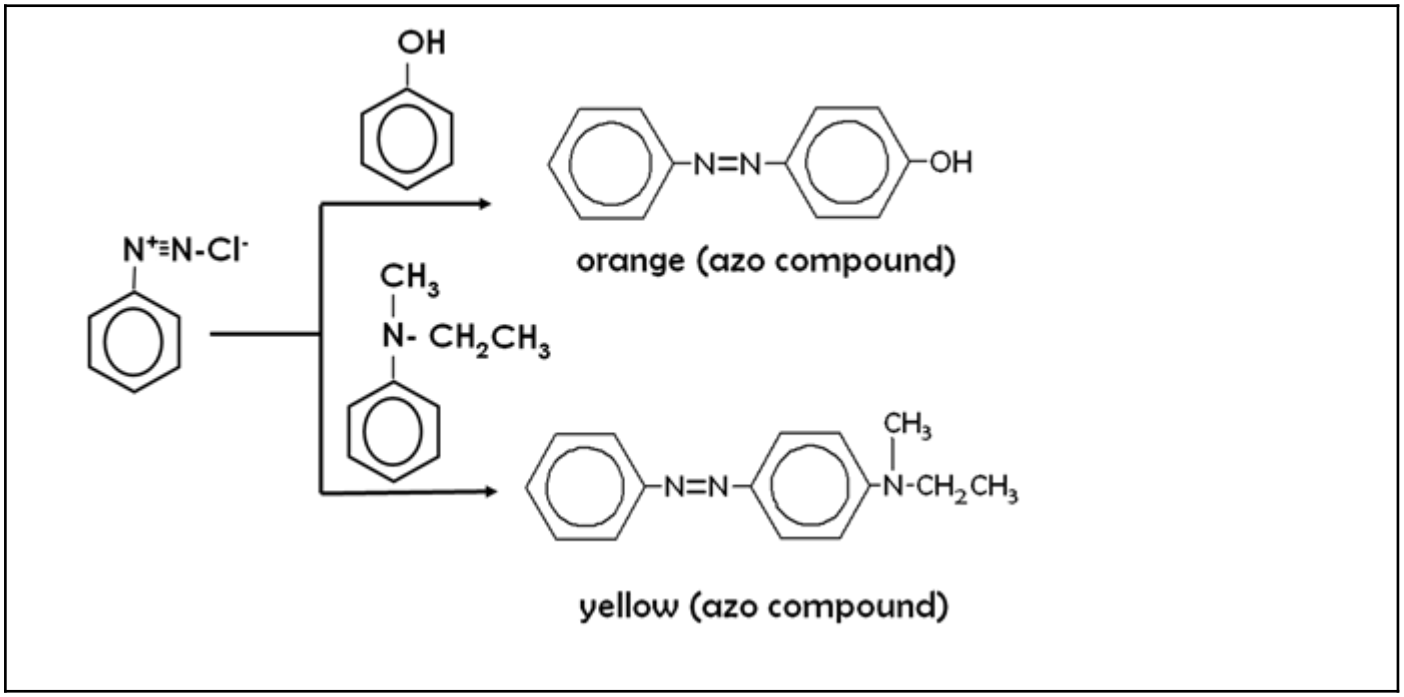


arenediazonium salts

- Arenediazonium salts also undergo **coupling reaction** with aromatic compounds with **strong EDG**, such as **–OH** and **–NR_2** at the **para position** to yield **azo compounds.**

- **Azo compounds – intensely coloured and relatively inexpensive compounds,** they are used as **dyes.**

Example:


OH
N=N
OH
orange (azo compound)
N+≡N-Cl-
CH3
N- CH2CH3
CH3
N=N
N-CH2CH3
yellow (azo compound)

Exercise:

1. Synthesis the following amines using ethene as the only source:

   a) Ethanamine

   b) Propanamine

   c) 2–butanamine

2. Outline the synthesis of butanamine from

a) Pentanamide

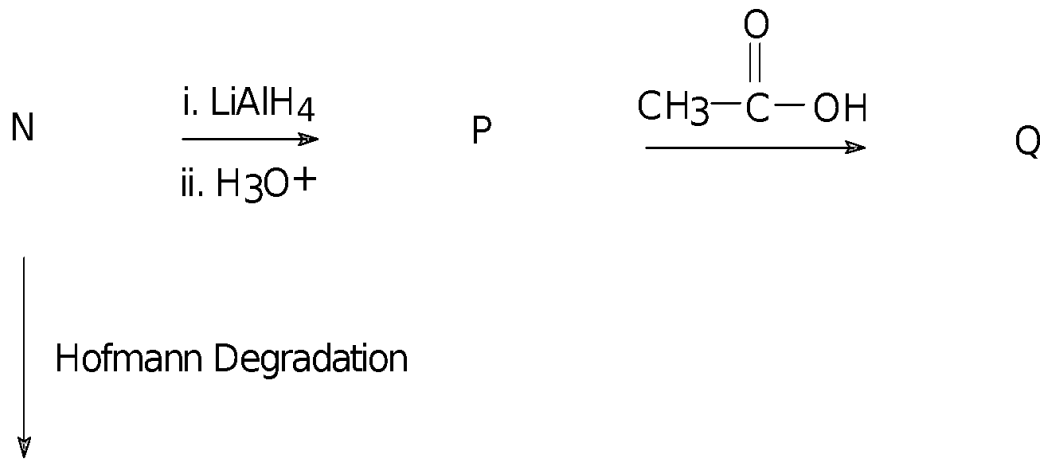
b) Propylnitrile

c) 1–butanol

d) Butanoic acid

3. Compound R, S and T are isomers of an organic compound C_3H_9N. The reaction between 1–bromoethane with sodium cyanide followed by treatment with $LiAlH_4$ and hydrolysis forms compound R. When compound S mixed with alkaline solution of benzenesulphonyl chloride, a precipitate U which does not dissolve upon acidification is formed. A two layer which dissolves upon acidification are formed when compound T mixed with alkaline solution of benzenesulphonyl chloride. Deduce the structure of R, S, T and U.

4. The reaction scheme for several organic compounds is shown as below:



a) Draw the structure of compound N, P and Q.
b) Give one chemical test to differentiate N from P. Write the reaction equations and state the observation involved.
c) Give the reagent used in the Hoffmann's Degradation reaction.