

# CHAPTER 11



**AMINES**

## 11.1 INTRODUCTION OF AMINES

At the end of the lesson, you should be able to:

- a) Give the name of aliphatic and aromatic amines according to the IUPAC nomenclature (parent chain  $\leq C_{10}$ ) **(C2)**
- b) State the common names of amines with parent chain  $\leq C_5$  **(C1)**
- c) Give the structural formulae of amines in 11.1 (a) **(C2)**
- d) Classify primary, secondary and tertiary amines. **(C2)**

# AMINES

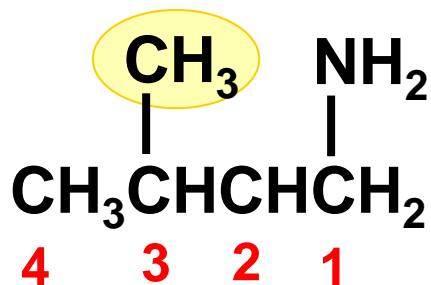
- In chemistry, amines are compounds and functional groups that contain a basic nitrogen atom with a lone pair.
- Amines are formally derivatives of ammonia ( $\text{NH}_3$ ), wherein one or more hydrogen atoms have been replaced by a substituent such as an alkyl or aryl group
- Amines have a distinctive odor and are commonly used in a variety of applications, including as solvents, bases, and intermediates in the production of pharmaceuticals and agrochemicals.

# Nomenclature of amines & Structural formulae of amines

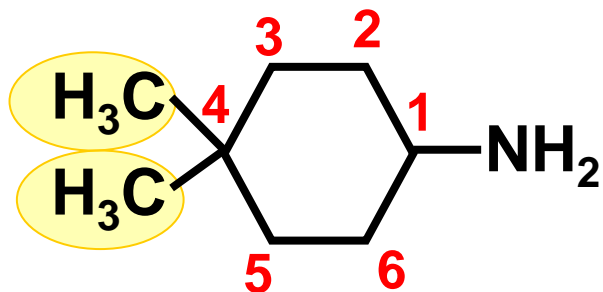
## IUPAC NAMES

- Determine the longest continuous chain of carbon atoms.
- The **-e** ending in the alkane name is changed to **-amine**, and a number shows the position of the amino group.
- Other substituents on the carbon chain are given numbers, and prefix **N-** is used for each **substituent**.

## EXAMPLE:

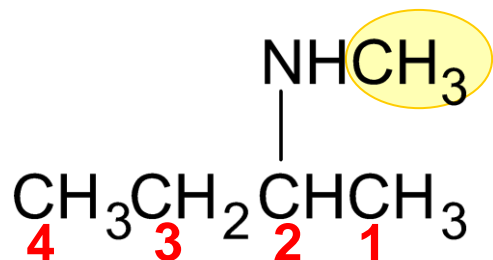


3-methyl-1-butanamine  
(1° amine)

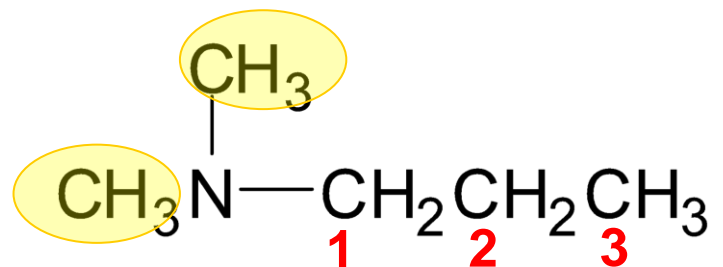


4,4-dimethylcyclohexanamine  
(1° amine)

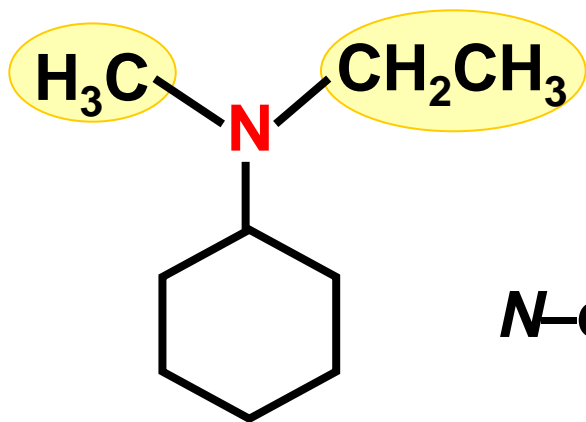
## EXAMPLE:



*N*-methyl-2-butanamine  
(2° amine)



*N,N*-dimethyl-1-propanamine  
(3° amine)

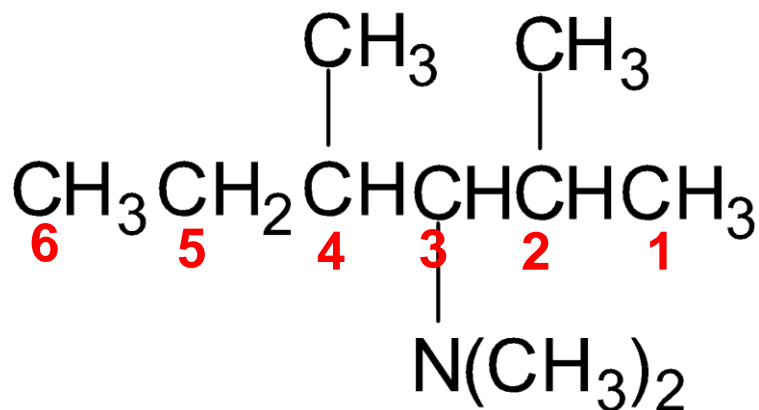


*N*-ethyl-*N*-methylcyclohexanamine  
(3° amine)

# Keep in mind!

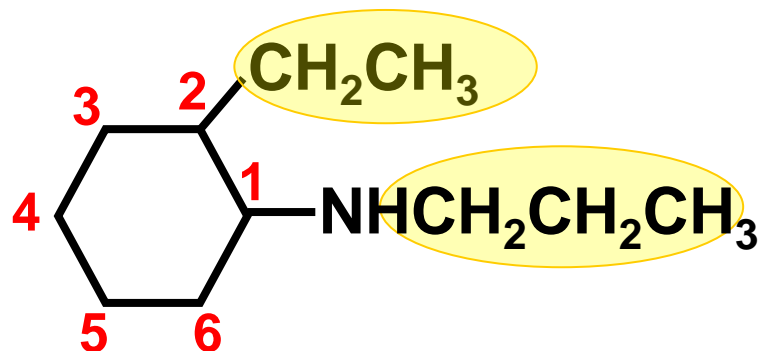
## For aliphatic amines:

- The non-numeric locant, *N*, is placed after the numeric locants when a list of them is needed.

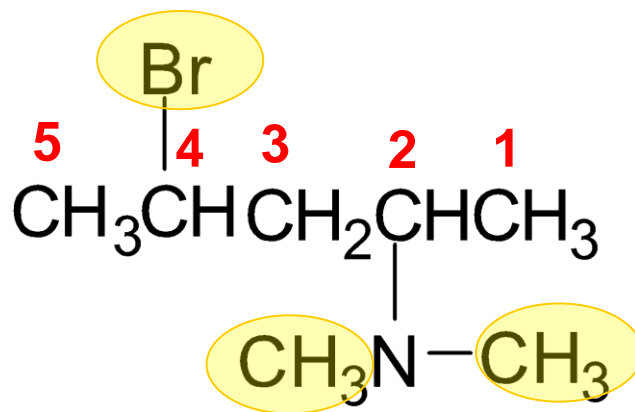


**2,4,*N,N*-tetramethyl-3-hexanamine**  
**(3° amine)**

## EXAMPLE:



2-ethyl-*N*-propylcyclohexanamine (2° amine)

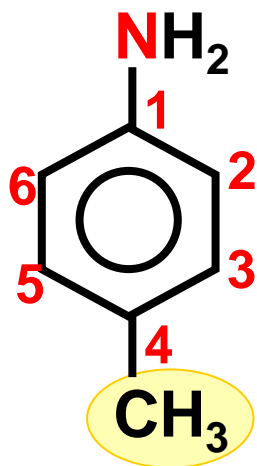


4-bromo-*N,N*-dimethyl-2-pentanamine (3° amine)

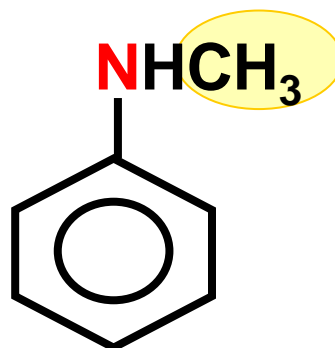


- Aromatic amines are named as **derivatives of aniline**.

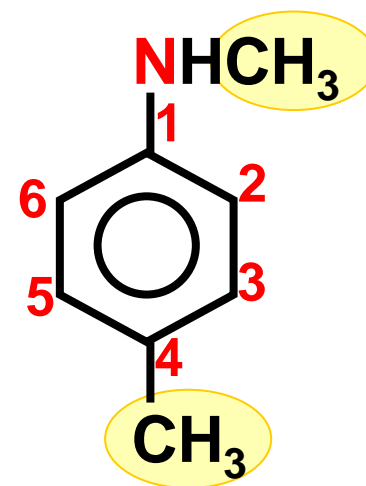
## EXAMPLE:



**4-methylaniline**  
**(1° aromatic amine)**



**N-methylaniline**  
**(2° aromatic amine)**



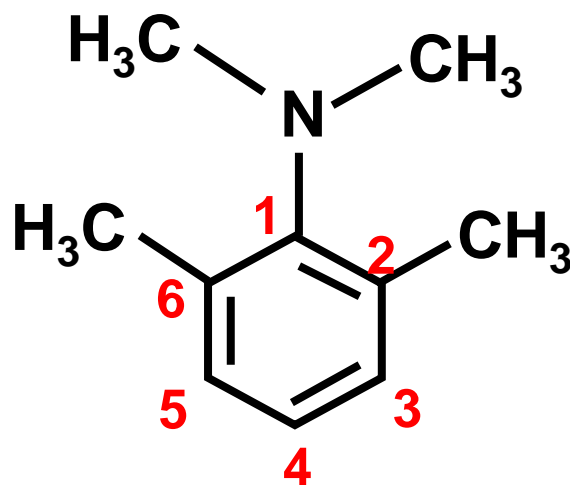
**N,4-dimethylaniline**  
**(2° aromatic amine)**

# Keep in mind!

## For aromatic amines:

- The non-numeric locant, **N**, is placed before the numeric locants when a list of them is needed.

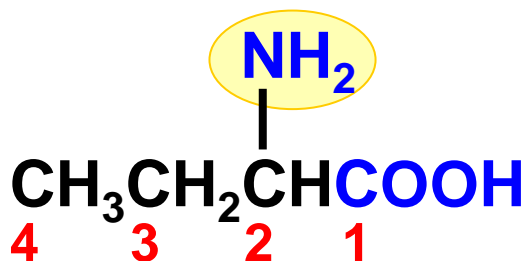
### EXAMPLE:



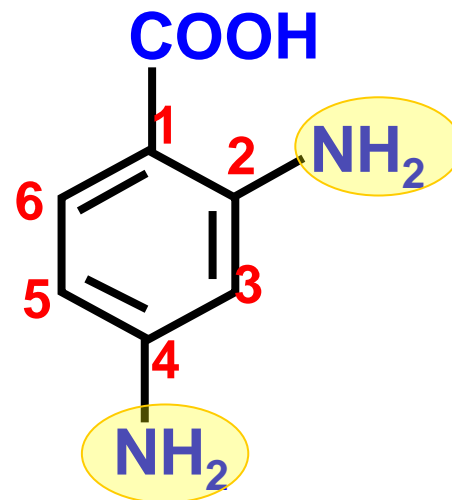
***N,N,2,6*–tetramethylaniline**  
(3° aromatic amine)

- When **multiple functional groups are present** and the **–NH<sub>2</sub> group does not take priority**, it is named as an **“amino” substituent**.

## EXAMPLE:

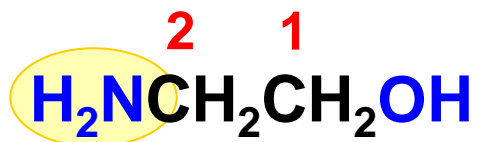


2-aminobutanoic acid

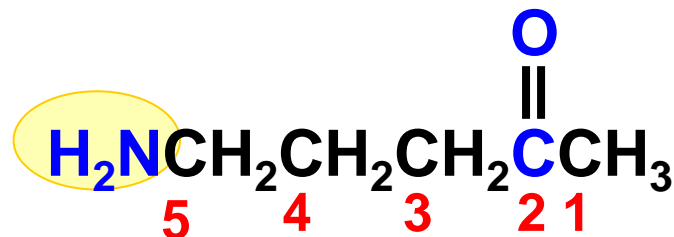


2,4-diaminobenzoic acid

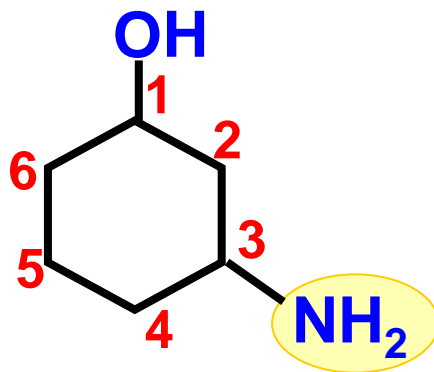
## EXAMPLE:



2-aminoethanol



5-amino-2-pentanone



3-aminocyclohexanol

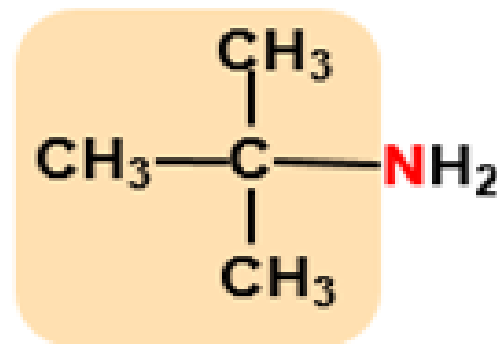
# Common names

- From name of **alkyl** groups **bonded to N**, followed by suffix **–amine**.
- The prefixes di-, tri-, and tetra are used to describe the number of identical substituents.

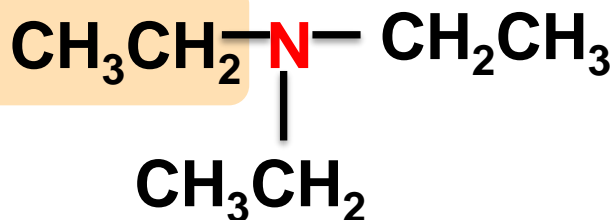
## EXAMPLE:



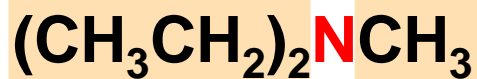
ethylamine



*tert*-butylamine



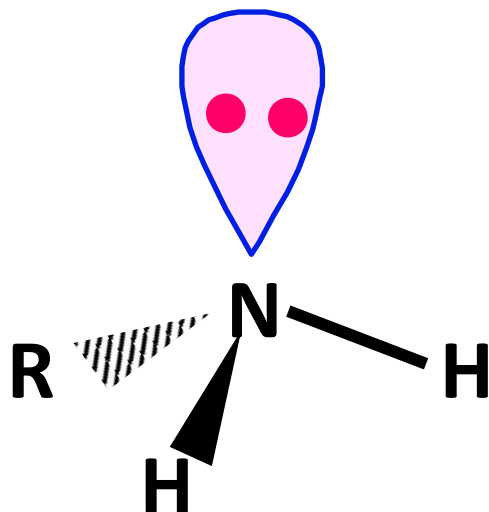
triethylamine



diethylmethanamine

# Classification of amines

- Amines are organic derivatives of ammonia,  $\text{NH}_3$ , with one or more alkyl groups bonded to the nitrogen atom.

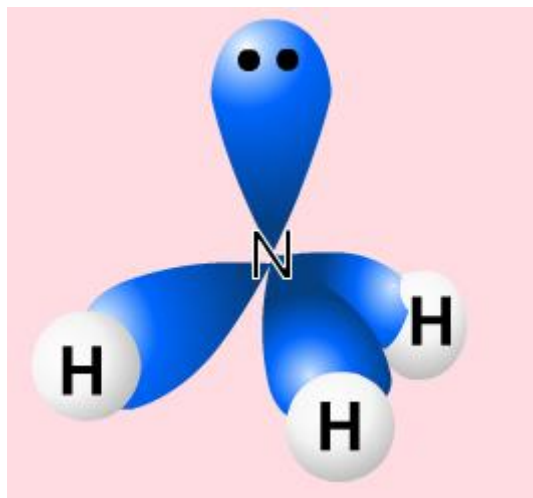


- General formula:  $\text{R-NH}_2$  (R= alkyl or aryl)
- Functional group:  $\text{NH}_2$  (amino group)

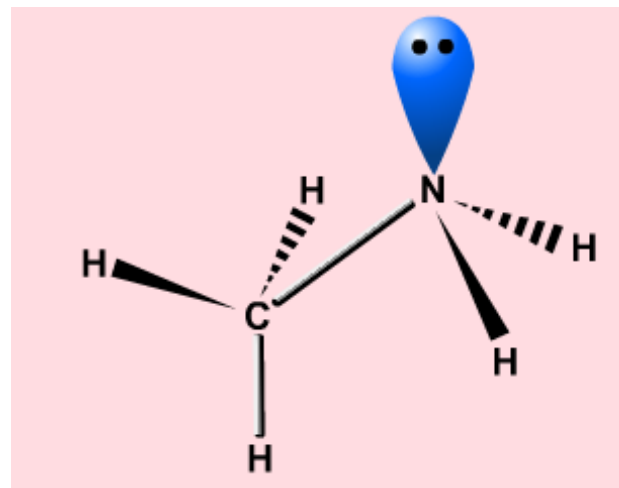


The chemistry of amines is dominated by the nonbonded **electron pair** on the **N** atom

- The lone pair electrons on N makes amines both **basic** and **nucleophilic**.

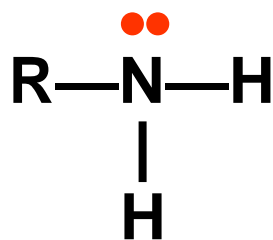


ammonia

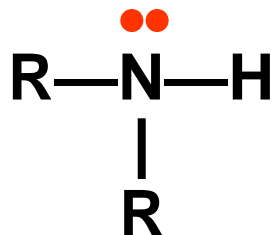


methylamine

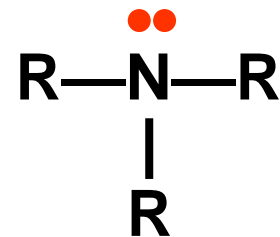
- Amines are classified as **primary (1°)**, **secondary (2°)**, or **tertiary (3°)**, corresponding to the number of **alkyl** or **aryl** groups **attached to N**.



**1° amine**



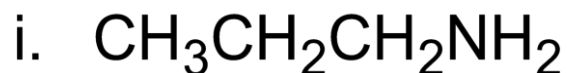
**2° amine**



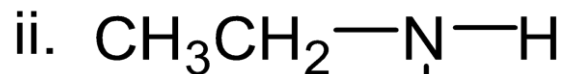
**3° amine**



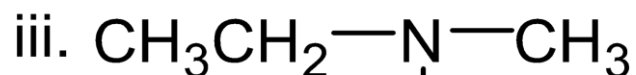
# Classify the following amines:



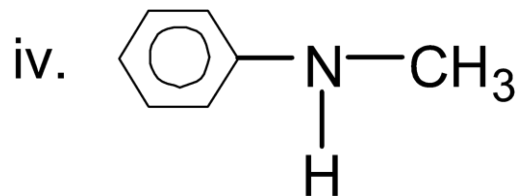
1°



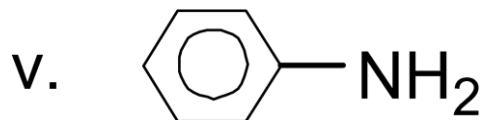
2°



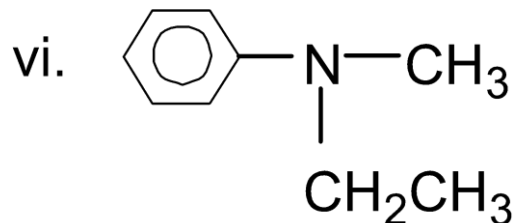
3°



2°



1°



3°

**Aliphatic amines**

**Aromatic amines**

## 11.2 PHYSICAL PROPERTIES OF AMINES

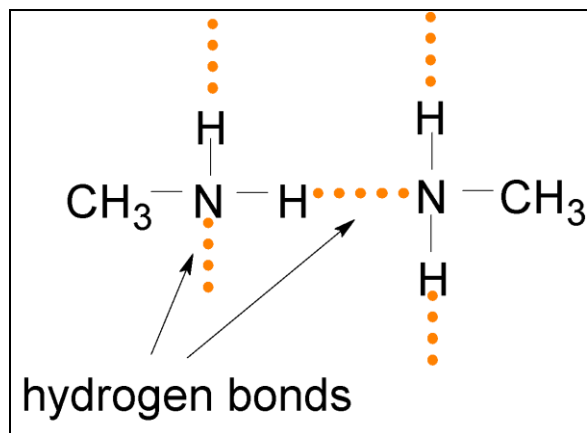
At the end of the lesson, you should be able to:

- a) Compare the physical properties of amines based on: **(C3 & C4)**
  - i. boiling points of:
    - primary, secondary and tertiary amines; and
    - amine with alkane, haloalkane, alcohol, carbonyl compound and carboxylic acid with comparable molar mass.
  - ii. solubility of primary, secondary and tertiary amines

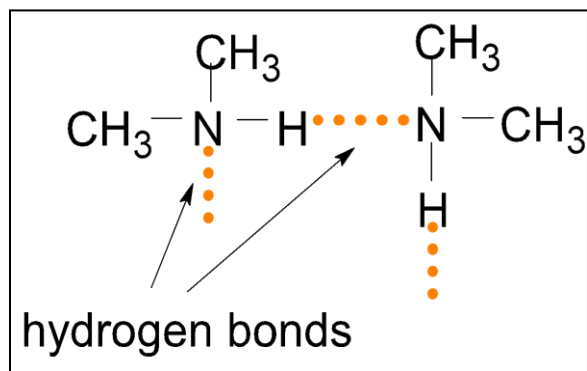
# Physical Properties Of Amines

## i. Boiling Point

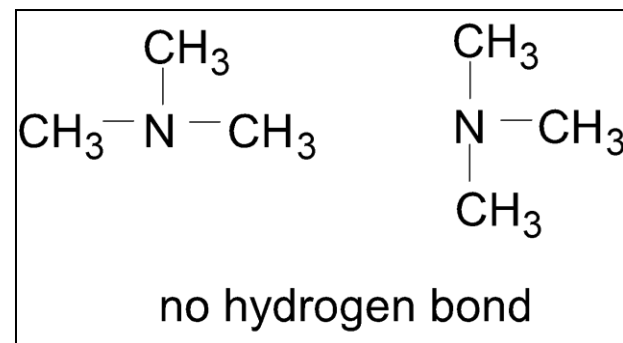
- Both **primary** and **secondary amines** can form intermolecular **hydrogen bonds**.
- Primary amines have **two N-H bond**, **hydrogen bonding is more significant** in primary amine than in secondary amine.
- Tertiary amines **cannot form hydrogen bonds** to each other.



$1^\circ$  amines



$2^\circ$  amines



$3^\circ$  amines

## EXAMPLE:

Amines	Class	Relative molecular mass	Boiling points/°C
$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$	1°	59	49
$\text{CH}_3\text{CH}_2\text{-NH-CH}_3$	2°	59	37
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{-N-CH}_3 \end{array}$	3°	59	4

Boiling Point :  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 > \text{CH}_3\text{CH}_2\text{NHCH}_3 > (\text{CH}_3)_3\text{N}$

**Explanation:** All the structures of amine have **same molecular mass** but the **boiling point** are different due to the **class of amine**. **1° amine > 2° amine > 3° amine**

- **Boiling point : carboxylic acid > alcohol > amine > haloalkane > alkane**

### **EXAMPLE:**

**Ethanoic acid > 1-propanol > propylamine > chloroethane > butane**

- **Only ethanoic acid, 1-propanol and propylamine can form hydrogen bond between molecules.**
- **Ethanoic acids have the highest boiling point because it forms a stable hydrogen-bonded dimer.**

- The hydrogen bonds of propylamine formed between its molecules are weaker than those between 1-propanol molecules since **nitrogen is less electronegative than oxygen**.
- Chloroethane is **polar** molecules (van der Waals forces between molecules), and hence **do not form** hydrogen bonds.
  - Butane is **non-polar** molecules (weak van der Waals forces between molecules), **do not form** hydrogen bonds.
  - The hydrogen bonds are stronger than van der Waals forces

## Examples

The table below compares the boiling points of **organic compounds** of comparable relative molecular mass.

Amines	Type	Relative molecular mass	Boiling points/°C
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ butane	alkane	58	-0.05
$\text{CH}_3\text{CH}_2\text{Cl}$ chloroethane	haloalkane	64.5	12.5
$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ 1-propanamine	amine	59	48.6
$\text{CH}_3\text{CH}_2\text{CHO}$ Propanal	aldehyde	58	48.8
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ 1-propanol	alcohol	60	97.2
$\text{CH}_3\text{COOH}$ ethanoic acid	Carboxylic acid	60	118

Boiling point : **Carboxylic acid > alcohol > carbonyl > amine > haloalkane > alkane**

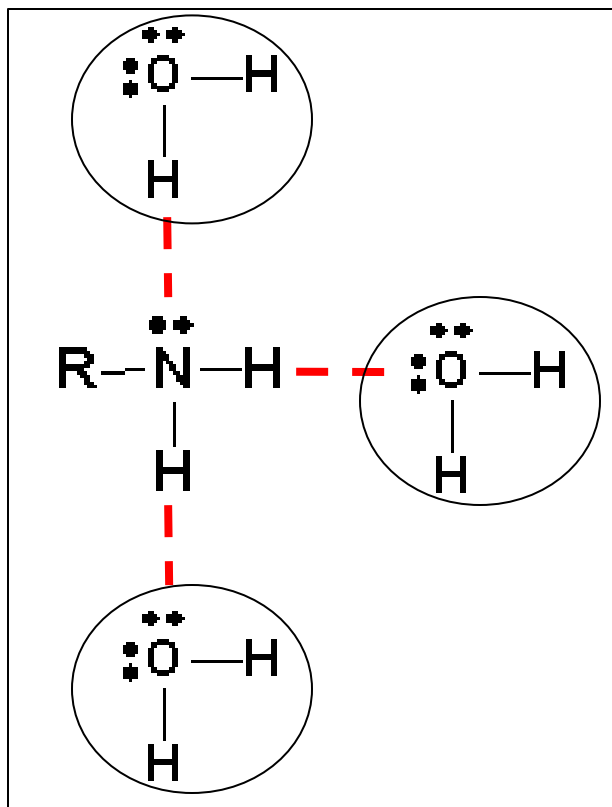


## ii. Solubility of 1°, 2°, 3° amines

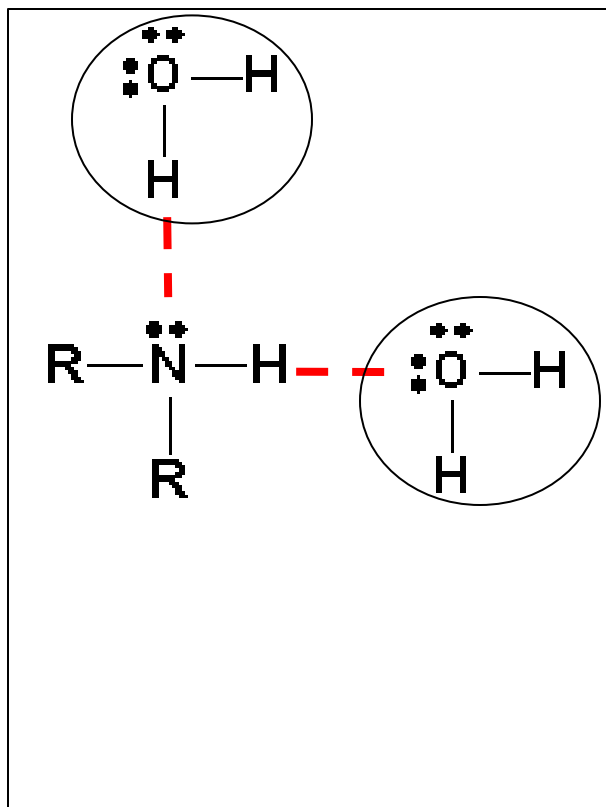
### In Water

- All amines having  $\leq 5\text{C}$ 's are **water soluble** because they can form hydrogen bond with  $\text{H}_2\text{O}$  molecules.
- Amines having  $> 5\text{C}$  are **water insoluble** because the alkyl portion (hydrophobic area) is too large to dissolve in the polar  $\text{H}_2\text{O}$ .
- Comparing amines with the same number of carbons, **1° amines are more soluble than 2° amines** because **1° amines** have two hydrogen atom that **can form** in hydrogen bonding.

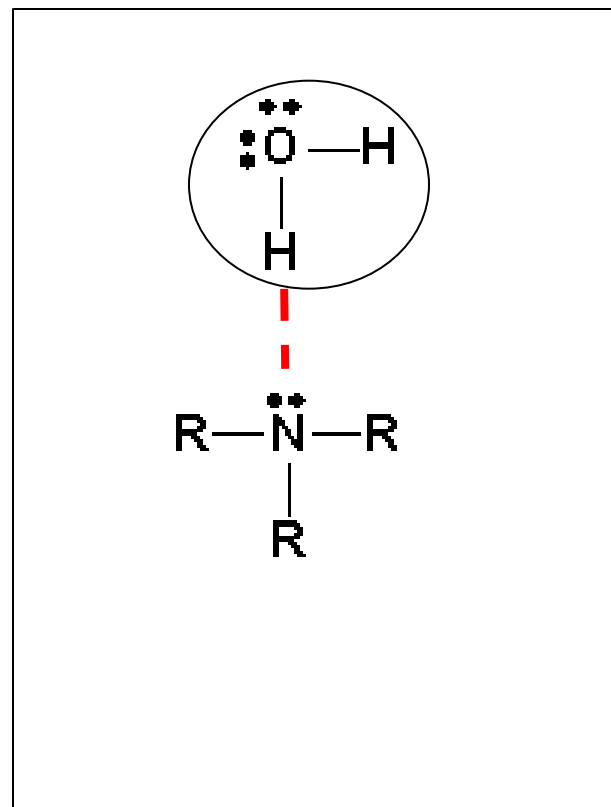
# Comparison the solubility between 1°, 2° and 3° amine in water



The most hydrogen bonds per 1° amine molecule



More hydrogen bonds per 2° amine molecule



The least hydrogen bond per 3° amine molecule

--- hydrogen bonds

$3^\circ < 2^\circ < 1^\circ$  amine

Increasing solubility

## 11.3 PREPARATION OF AMINES

At the end of the lesson, you should be able to:

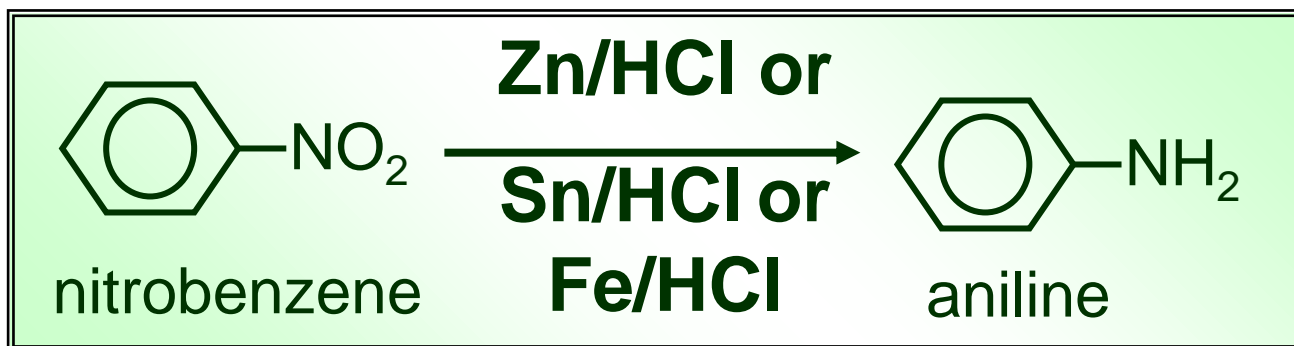
a) Explain the preparation of: **(C3 & C4)**

- i. aromatic amines by reduction of nitro compounds using Zn/HCl or Sn/HCl or Fe/HCl;
- ii. primary aliphatic amines by reduction of nitriles using  $\text{LiAlH}_4$  followed by  $\text{H}_2\text{O}$  or  $\text{H}_2$  with catalysts;
- iii. primary, secondary and tertiary amines by reductions of amides using  $\text{LiAlH}_4$ , followed by  $\text{H}_2\text{O}$ ;
- iv. primary alkyl and aryl amines by Hoffmann's degradation of primary amides.

# Preparation of amines

## i) Reduction of nitro compound

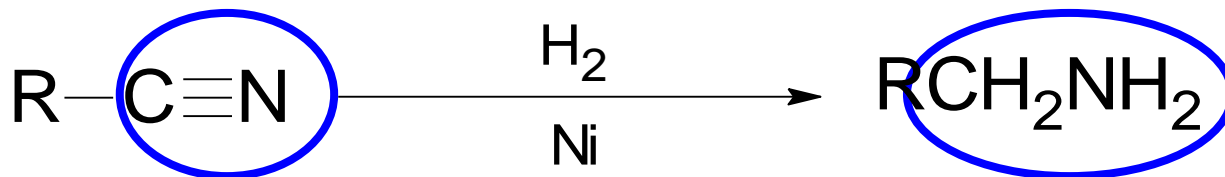
- Aromatic amines can be prepared by **reduction of nitro compounds** using **Zn/HCl** or **Sn/HCl** or **Fe/HCl**



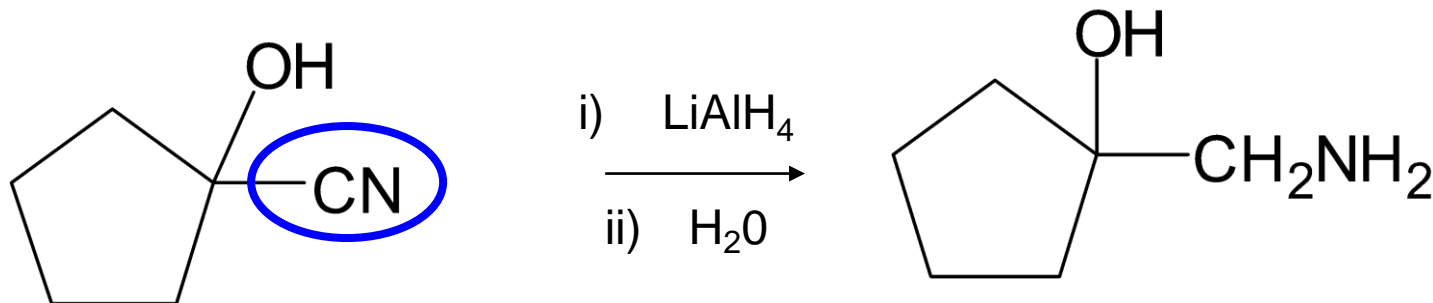
## ii) Reduction of nitriles

- Nitriles are reduced to primary amines by
  - $\text{H}_2$  / catalyst (Ni, Pt or Pd)
  - $\text{LiAlH}_4$  followed by  $\text{H}_2\text{O}$

General equation:



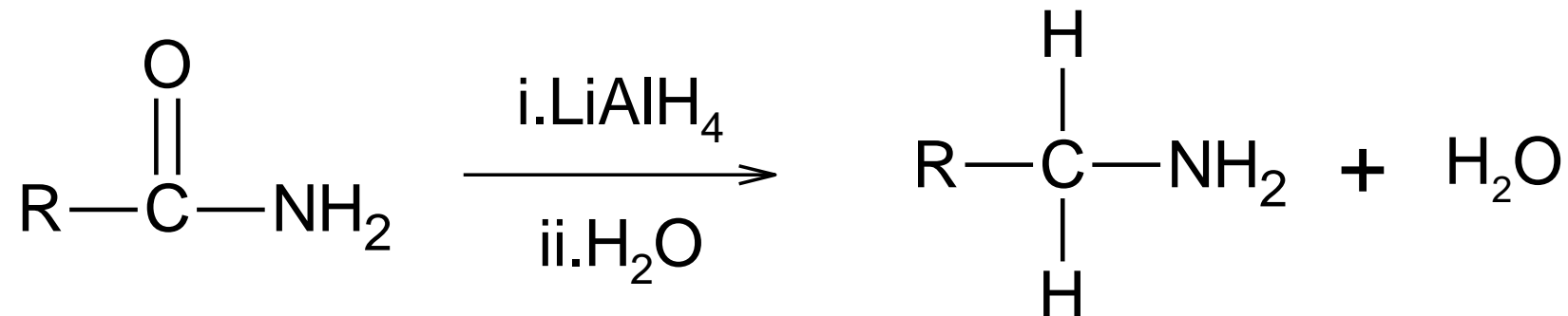
**EXAMPLE:**



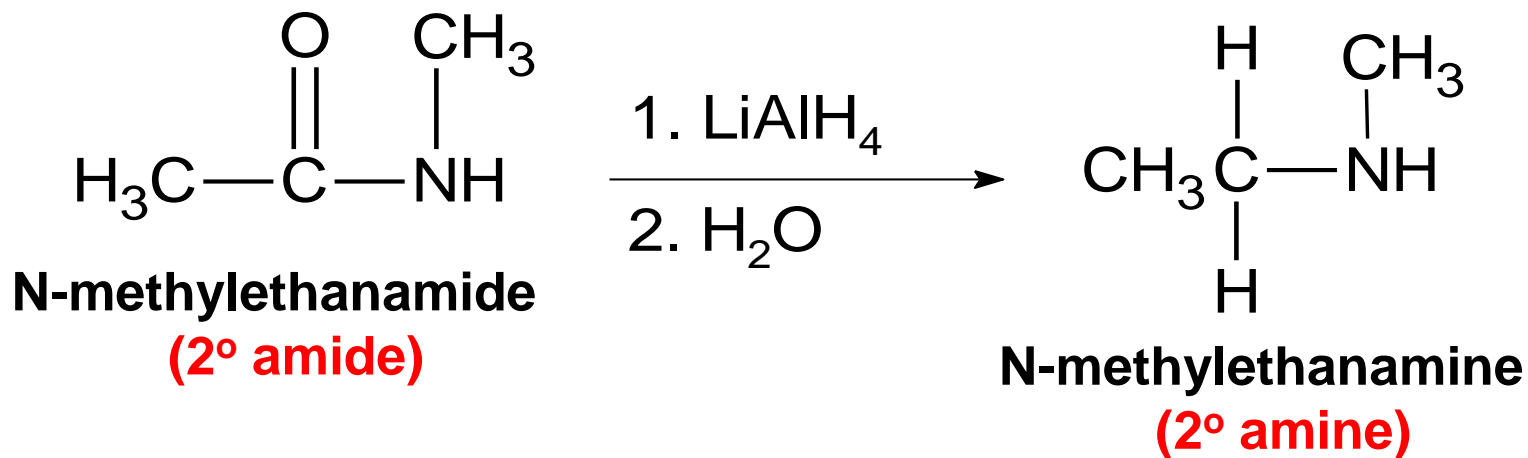
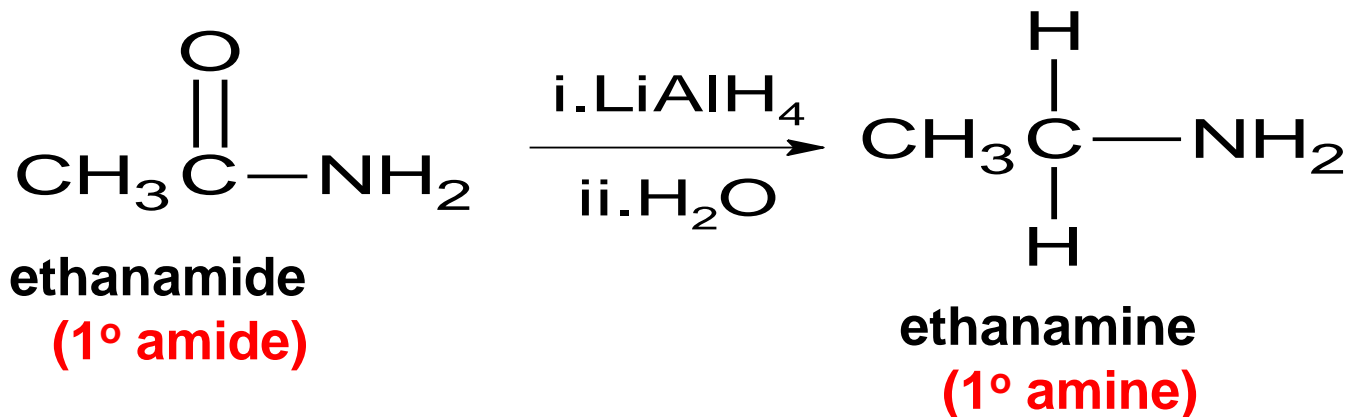
### iii) Reduction of Amides

- Reduction of an amide using  $\text{LiAlH}_4$  followed by  $\text{H}_2\text{O}$  can **yield a primary, secondary, or tertiary amine** depending on the type of amide used.

**General equation:**

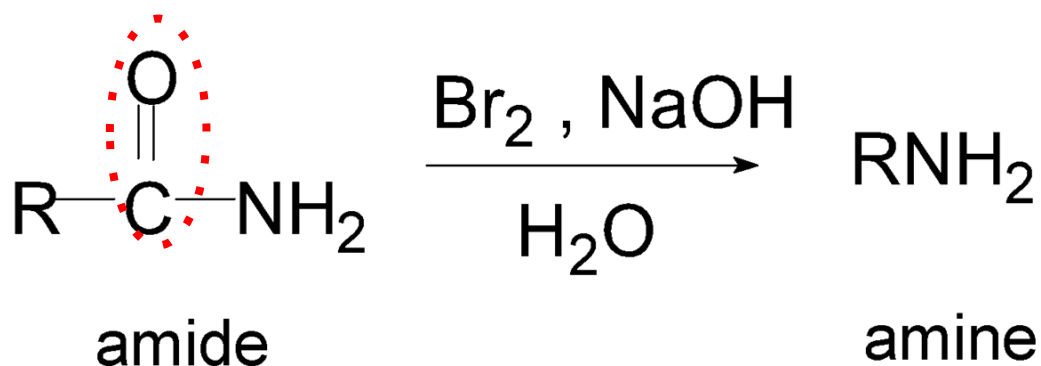


## EXAMPLE:



## iv) Hoffmann's Degradation of Amides

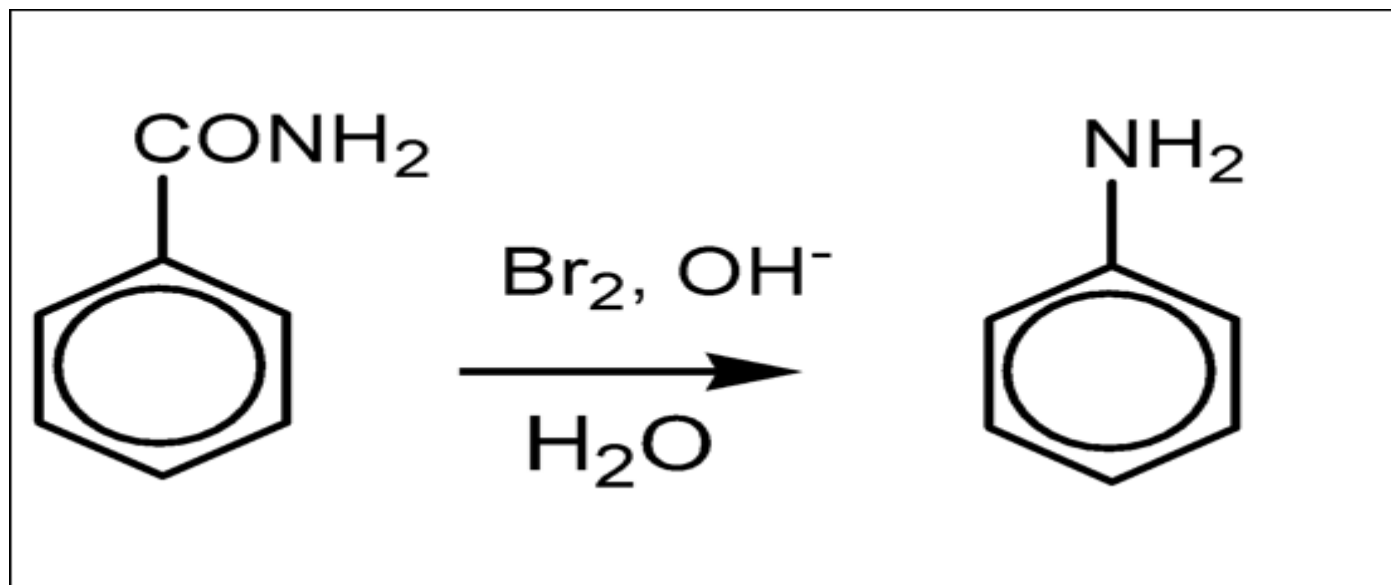
- On warming a primary amide with bromine in solution of NaOH, a **primary amine** is formed.
- This reaction is used to synthesis primary alkyl and aryl amines.



- Primary amide is converted to primary amine **with one carbon atom less.**



## EXAMPLE:



At the end of the lesson, you should be able to:

- a) Explain the reaction of amines with: **(C3 &C4)**
  - i. Hinsberg's reagent;
  - ii. nitrous acid.
- b) Distinguish classes of amines by using: **(C4)**
  - i. Hinsberg's test;
  - ii. nitrous acid.
- c) Explain the identification test of aniline using bromine water. **(C3 &C4)**
- d) Explain the formation of dye by the coupling reaction of benzenediazonium chloride and phenol. **(C3 &C4)**
- e) Outline the synthesis of compounds involving amines. **(C4)**  
*\*limit to maximum 4 steps only*

# 11.4 CHEMICAL PROPERTIES

## i) Reaction with Hinsberg's reagent

Hinsberg's reagent: benzenesulphonyl chloride

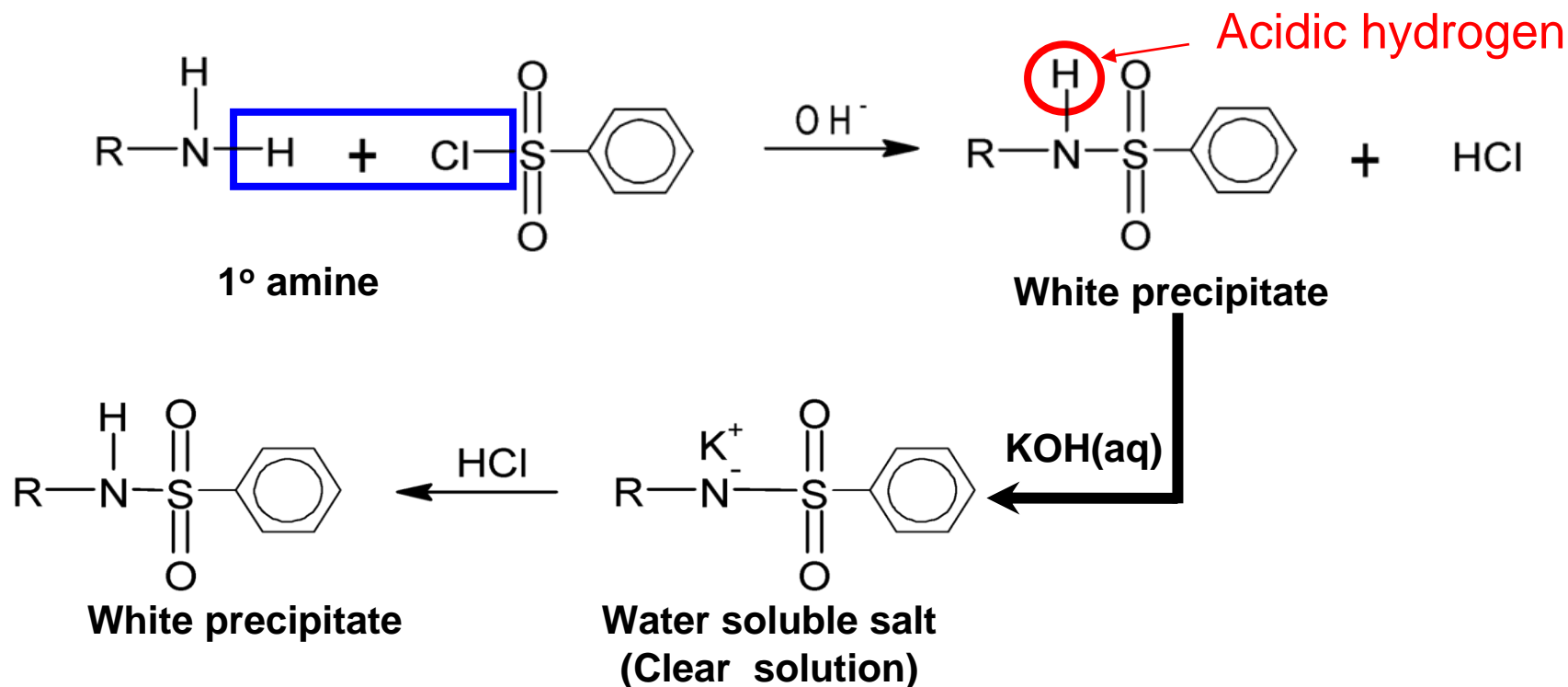
- **Involves two steps:**

1. Mixture of amine and benzenesulphonyl chloride with excess base (KOH @ NaOH).
2. The mixture then acidified with HCl.

- This reaction is used to **distinguish classes of amines.**
- In the test, **amines act as nucleophiles** and attack the electrophile (sulfonyl chloride). This leads to the displacement of the chloride and the generation of the sulfonamides.

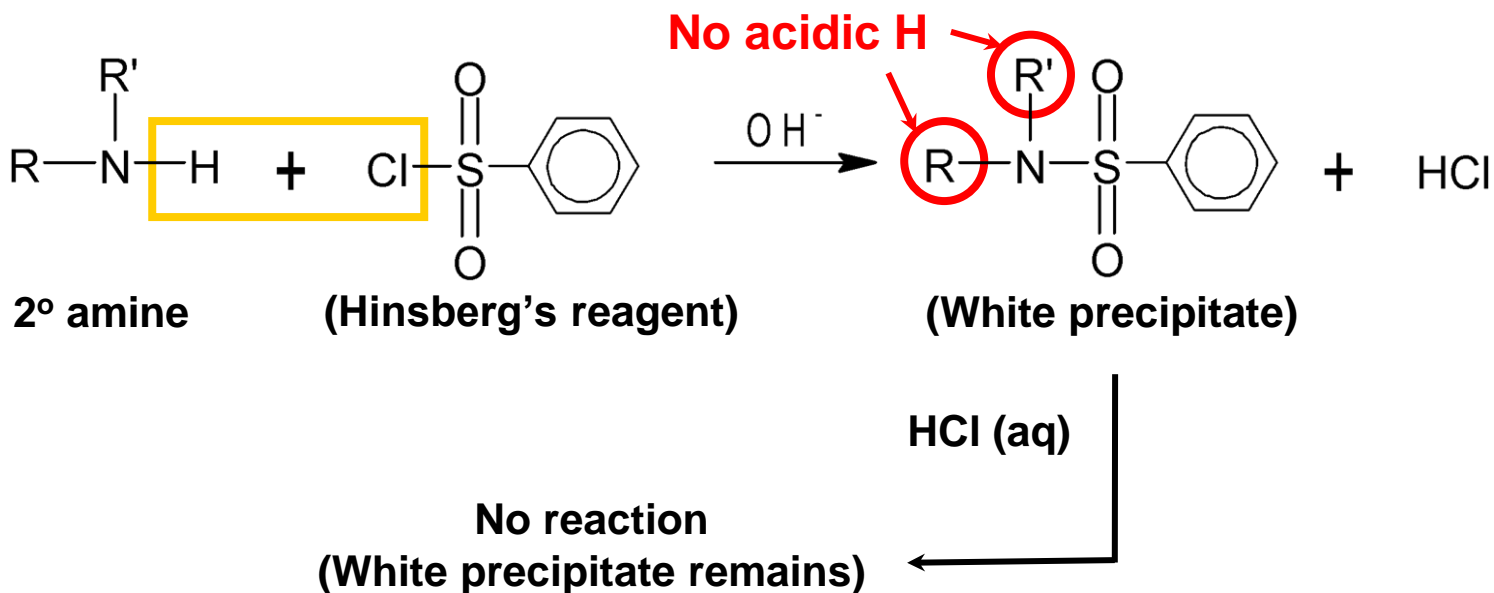
## 1° amine

- The reaction of the benzene sulfonyl chloride with primary amines gives a *N*-substituted benzenesulfonamide product that is soluble in excess base. **(clear solution form)**
- Addition of HCl will produce *N*-substituted benzenesulfonamides. **(white precipitate)**



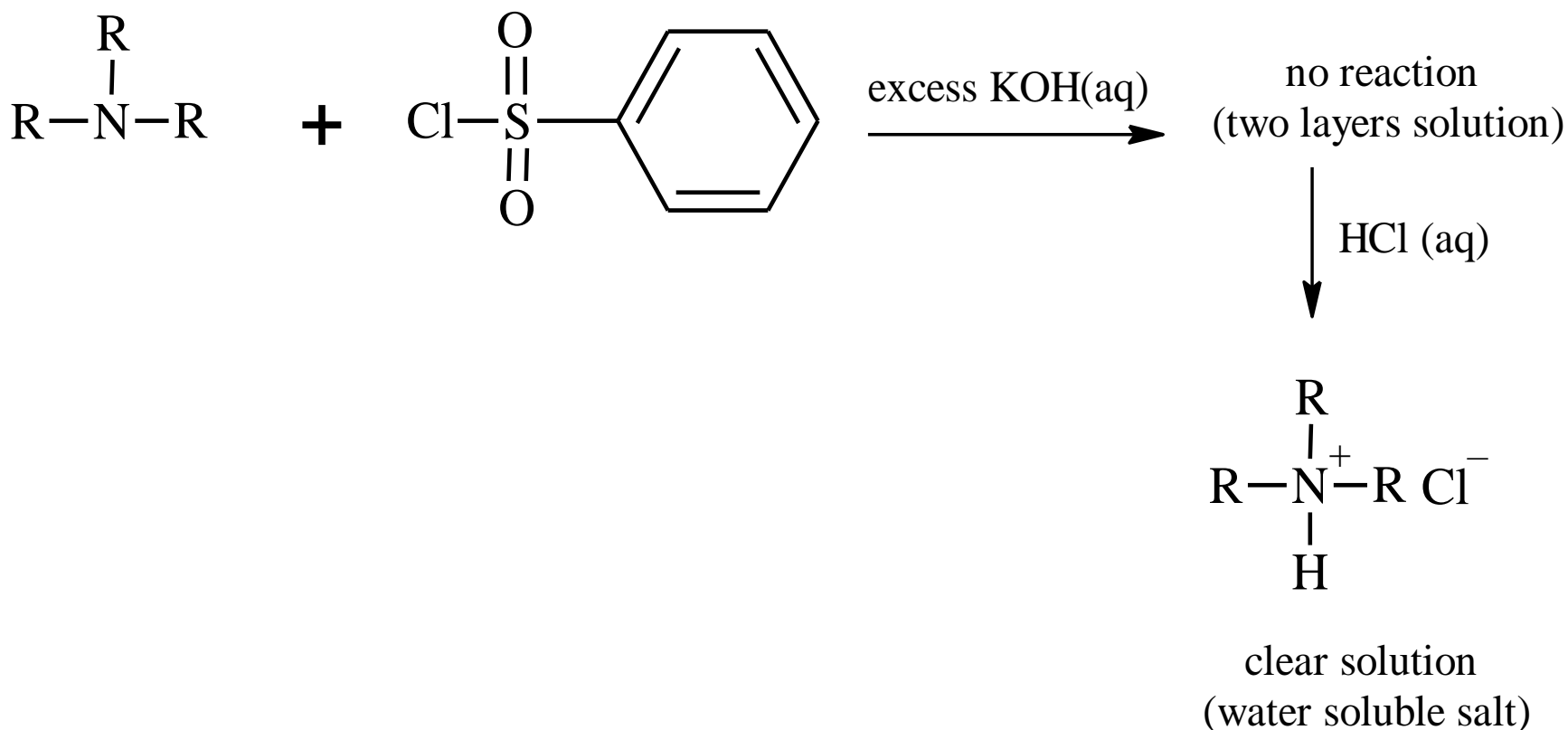
## 2° amine

- The reaction of the benzene sulfonyl chloride with secondary amines gives a *N,N*-disubstituted benzenesulfonamide product that is NOT soluble in alkali. **(white precipitate form)**
- No reaction occurs when HCl is added to *N,N*-disubstituted benzenesulfonamides h. **(white precipitate remain)**



## 3° amine

- No such reaction occurs between a tertiary amine and the benzene sulfonyl chloride reagent. **(two layers solution form)**
- Addition of HCl will produce soluble salt. **(clear solution form)**



# SUMMARY OF HINSBERG'S TEST

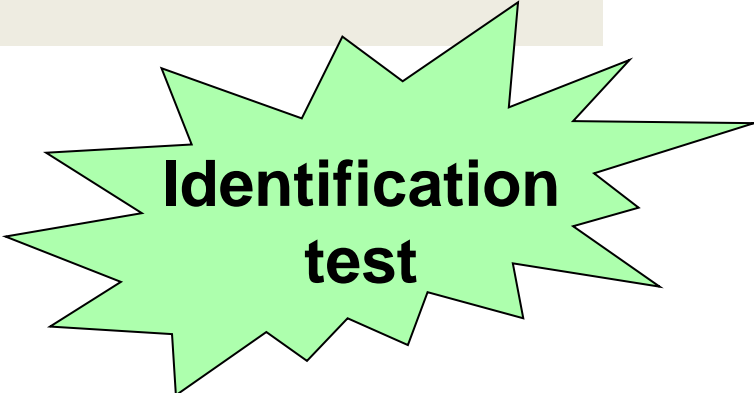
TYPE OF AMINE	Add KOH	Add HCl
1°	Clear solution	White precipitate
2°	White precipitate	(No change) Precipitation
3°	Two layer (no reaction)	Clear solution

## ii) Reaction with nitrous acid

- Nitrous acid ( $\text{HNO}_2$ ) is a weak and unstable acid.
- It is always prepared *in situ*, by treating cold sodium nitrite ( $\text{NaNO}_2$ ) with an aqueous solution of a cold dilute hydrochloride acid ( $-5^\circ\text{C}$ ).
- Nitrous acid reacts with all classes of amines.

### **Nitrous acid test can be used to distinguish:**

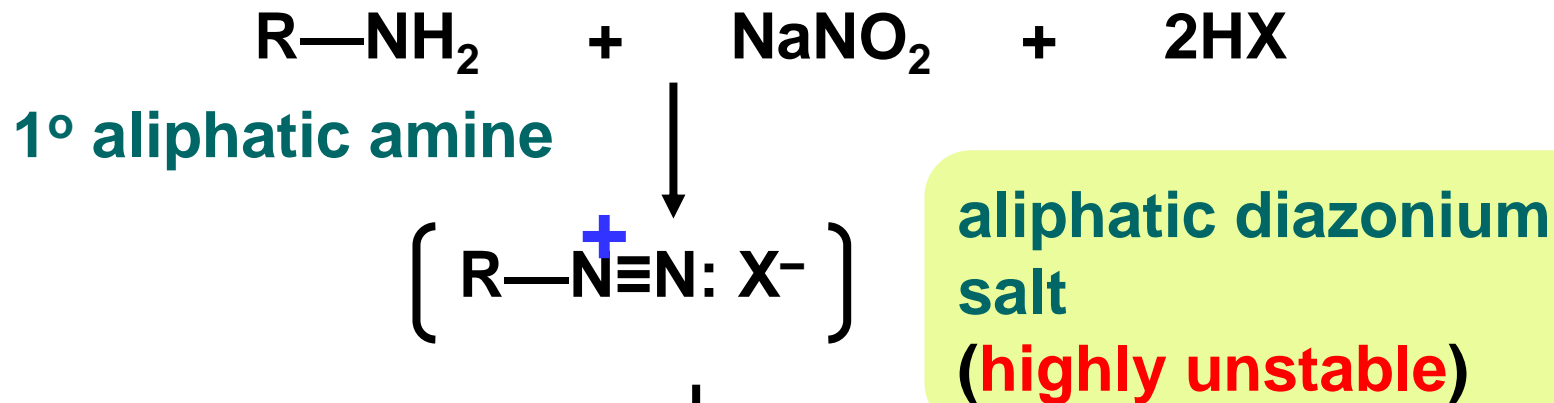
- $1^\circ$  aliphatic and  $1^\circ$  aromatic amines
- $1^\circ$  and  $2^\circ$  aliphatic amines



**Identification  
test**



# 1° AMINES (aliphatic)



release  $\text{N}_2$

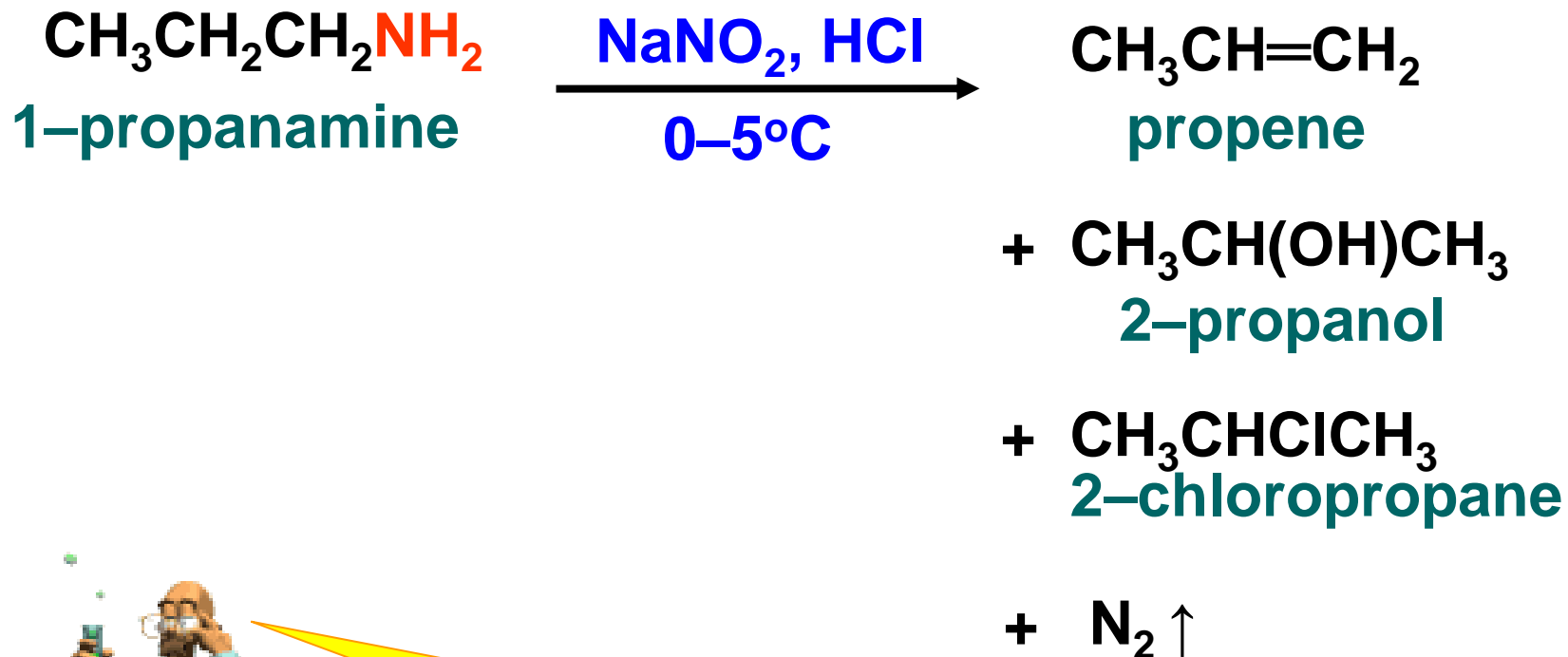


alkenes , alcohols , alkyl halide

Observation:  
Evolution of  $\text{N}_2$  gas



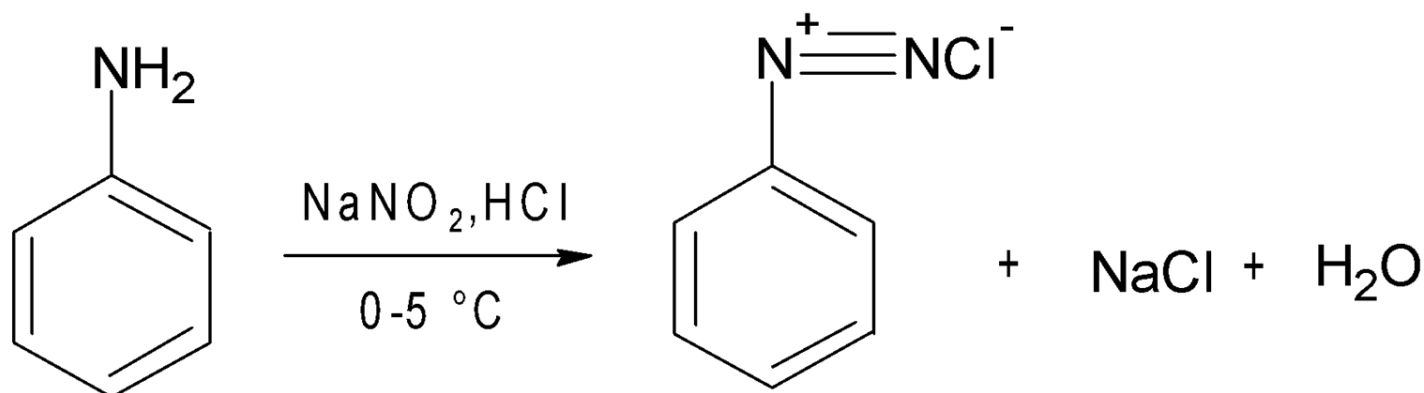
## EXAMPLE :



Even at **low temperature** **aliphatic diazonium salts** **decompose** spontaneously by **losing N<sub>2</sub>**

# 1° AMINES (aromatic)

- **Primary arylamines** react with nitrous acid to give **benzenediazonium salts**.
- Benzenediazonium salts only stable below 5° C.



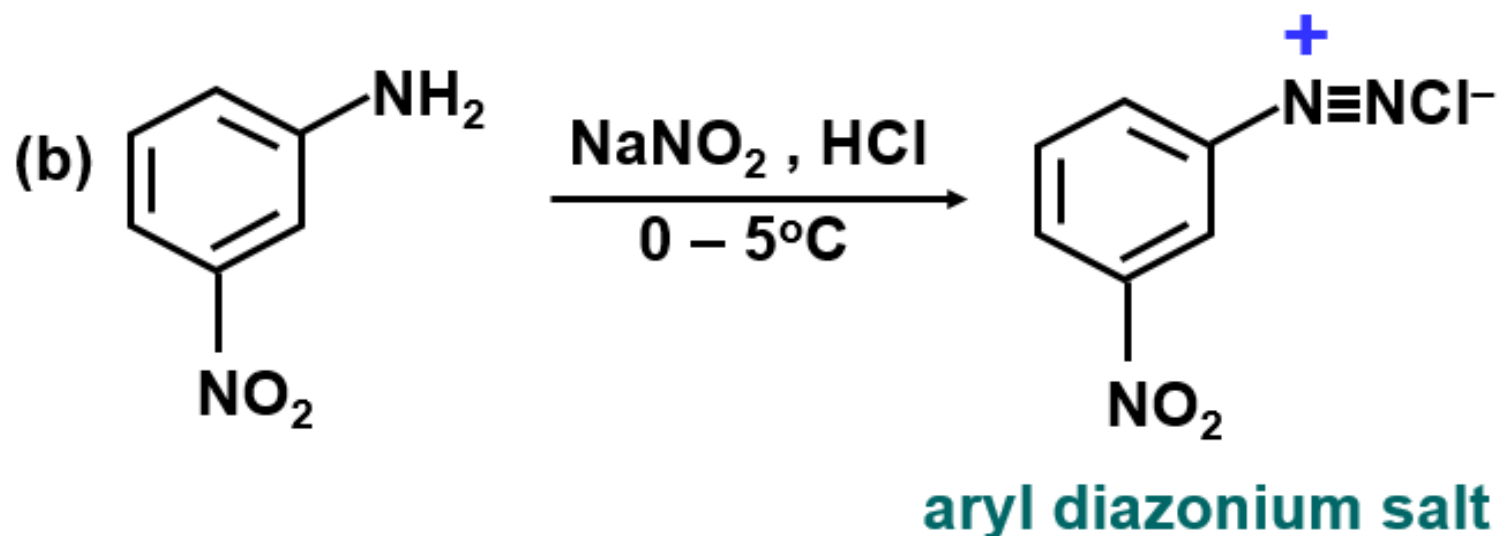
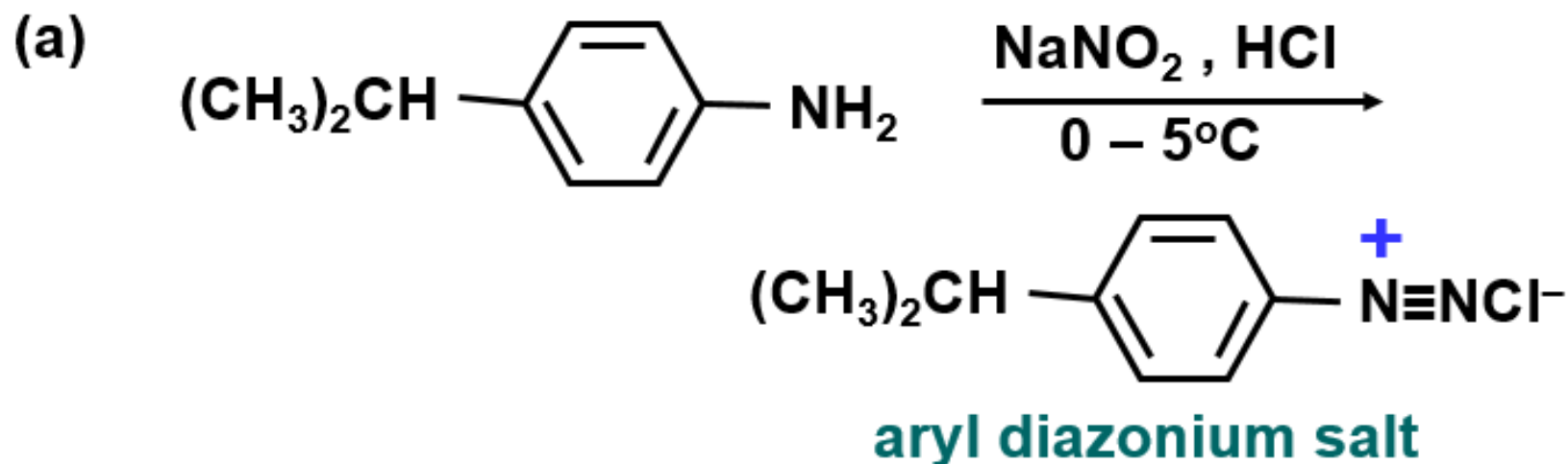
1° arylamine

**Benzenediazonium salt**  
(only stable < 5 °C)



**Observation:**  
No gas bubbles are  
formed below 5 °C

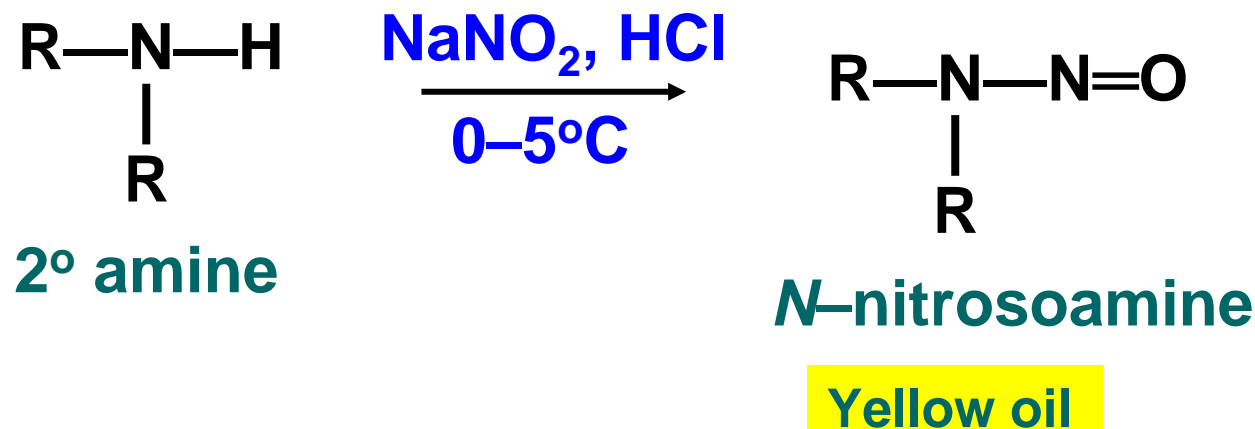
## EXAMPLE:



## 2° AMINES

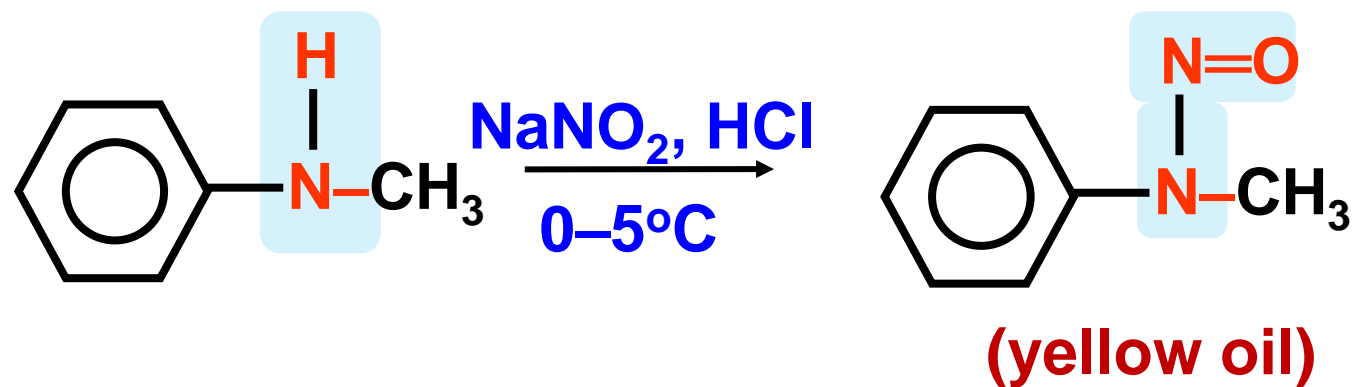
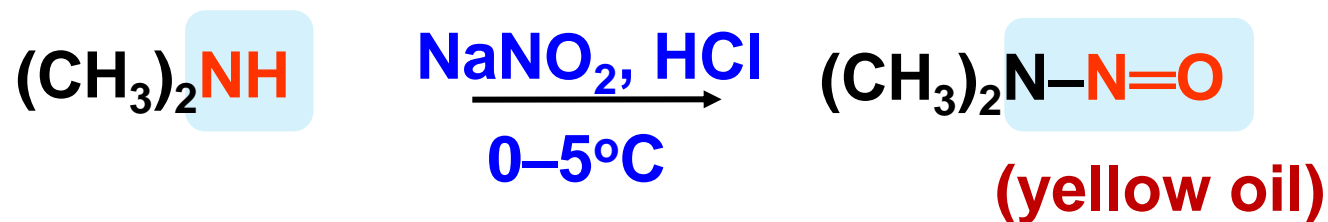
- Both **alkyl and aryl 2° amines** react with  $\text{HNO}_2$  to yield ***N*-nitrosoamines**.

General equation:



**Observation:**  
yellow oil of *N*-nitrosamine  
forms

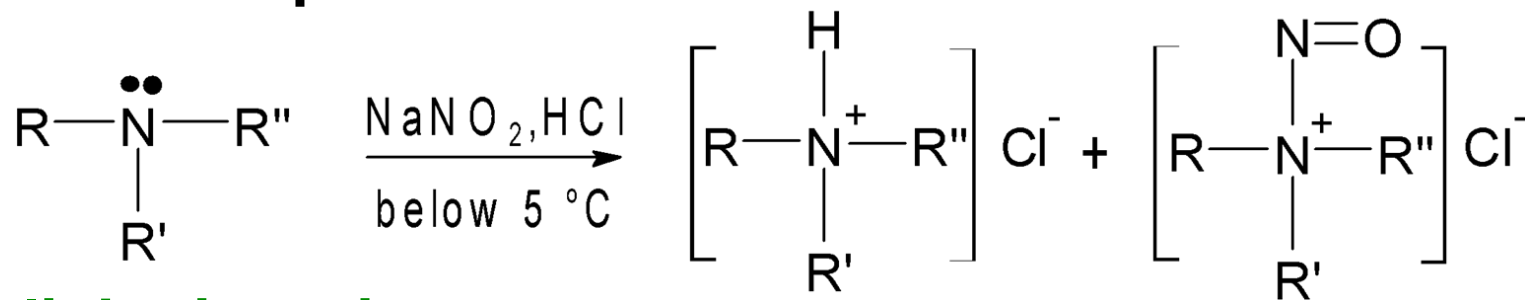
## EXAMPLE:



## 3° AMINES (Aliphatic)

- When **tertiary aliphatic amine** is mixed with nitrous acid, an equilibrium is established among the tertiary amine, its salt and an **N-nitrosoammonium compound**.

General equation:



3° aliphatic amine

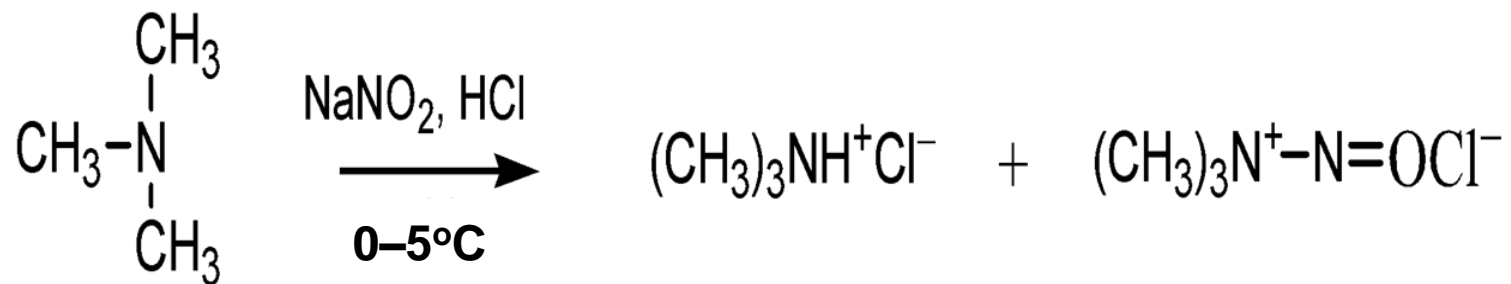
Water soluble salts  
(clear solution)



**Observation:**

**A clear solution is obtained**

## Example:

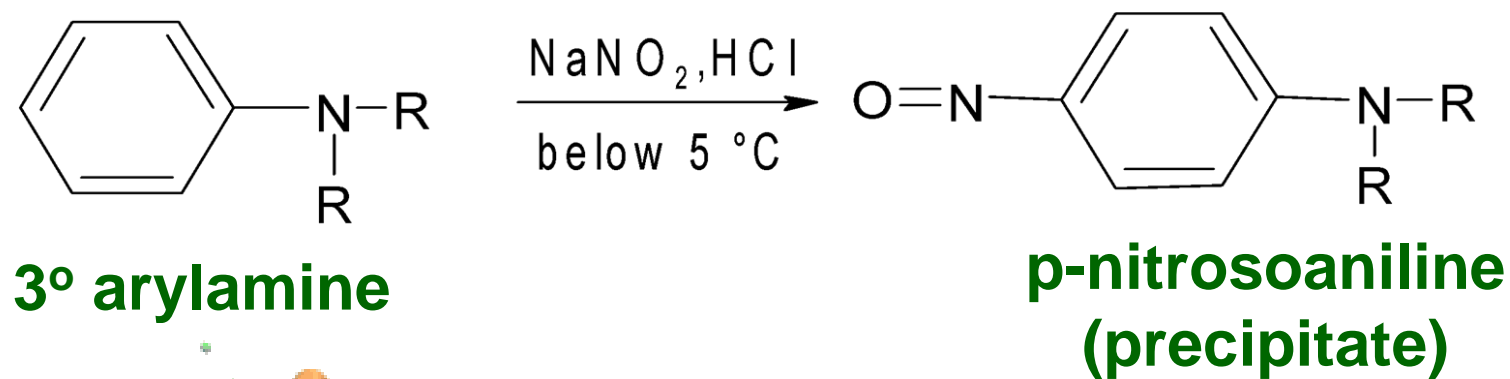




## 3° AMINES (Aromatic)

- Tertiary arylamines react with nitrous acid to give **green precipitate**.

**General equation:**



**Observation:  
Formation of precipitate**

## Distinguish 1° aliphatic amines from 2° aliphatic amines

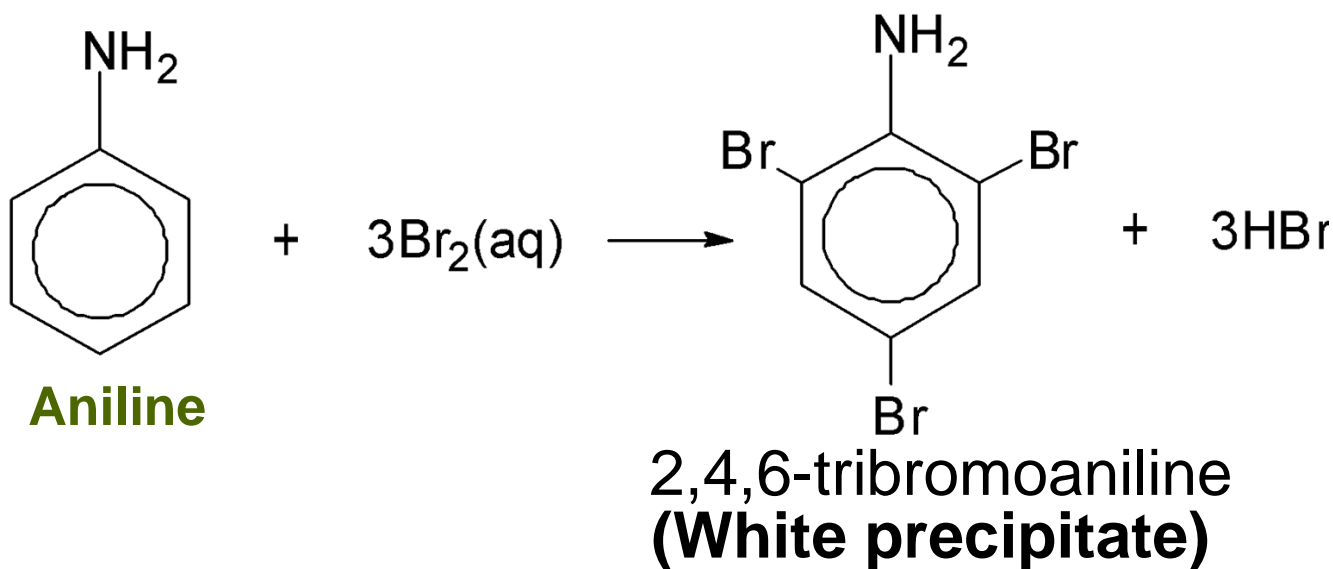
COMPOUND	OBSERVATION
Primary aliphatic amines	Form a mixture of <b>alkenes</b> , <b>alcohols</b> , <b>alkyl halides</b> and <b><i>nitrogen gas</i></b> .
Secondary aliphatic amines	Form <b>secondary N-nitrosamines</b> <b>as yellow oil</b> , which is stable under the reaction conditions (0-5°C).

## Distinguish primary aliphatic amines from primary aromatic amines

COMPOUND	OBSERVATION
Primary aliphatic amines	Form a mixture of <b>alkenes</b> , <b>alcohols</b> , <b>alkyl halides</b> and <b><i>nitrogen gas</i></b> .
Primary aromatic amines	<b><i>No gas bubbles (N<sub>2</sub>)</i></b> are evolved at temperature below 5 °C.

### iii) Reaction with bromine water

- Aniline reacts with aqueous bromine (bromine water) to yield **white precipitates**.



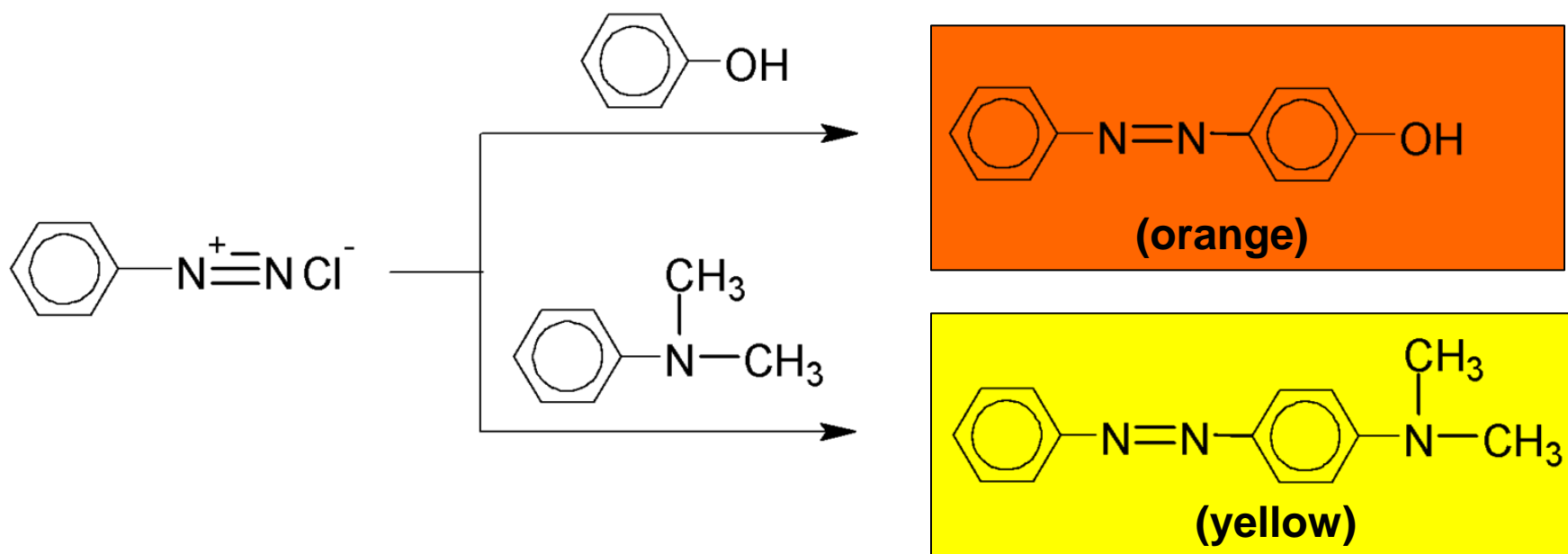
Identification  
test



**Observation:**  
**White precipitate is formed**

## iv) Formation of dye by coupling reaction

- Primary arylamines (aniline) react with nitrous acid to give arenediazonium salts which are **stable below 5 °C**.
- Arenediazonium salts also undergo **coupling reaction with aromatic compounds** with strong electron donating group, such as  $\text{-OH}$  and  $\text{-NR}_2$  at the **para position** to yield azo compounds.
- Azo compounds are usually intensely **coloured** and relatively inexpensive compounds, they are used as dyes.

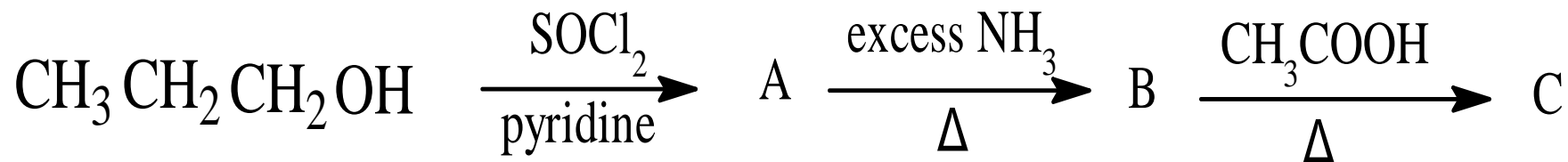


## v) Synthesis of compounds involving amines.

- Amines can be synthesized through various methods, including reduction of nitriles, alkylation of amides, and nucleophilic substitution reactions.
- One of the most commonly used methods of amine synthesis is the reaction between an alkyl halide and excess ammonia ( $\text{NH}_3$ ).
- This reaction produces an alkyl amine, which can then be further reacted to form other amine compounds.

## EXERCISE:

Complete the following reaction scheme.



ANSWER: