B. Sc. III – SEM- VI (2020-21)
Industrial Chemistry

UNIT-III

Manufacturing of Sugar and Jaggary

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Syllabus : UNIT IV – Manufacturing of Sugar and Jaggary

- Introduction , Importance of sugar industry,
- Manufacture of cane sugar- Raw materials, Extraction, Clarification and concentration of cane juice, Crystallization of sucrose, Centrifugation.
- Refining , Utilization of byproducts of sugar Industry.

Introduction and Importance of Sugar Industry

A wholesale **business** of **sugar** is a **profitable** venture, as the demand for this product is never going to fade away. **Sugar** is a highly demanded product. India has abundant production of **sugar**, so it is very easy to get **sugar** from the factories at a reasonable price and sell it at a higher price in the market.

1. Sugar Industry

- **Sugarcane** is most **important** commercial crop and it occupying 5.0 million hectares in area of the Indian nation. It contributes significantly to the socio economic development of the nation.

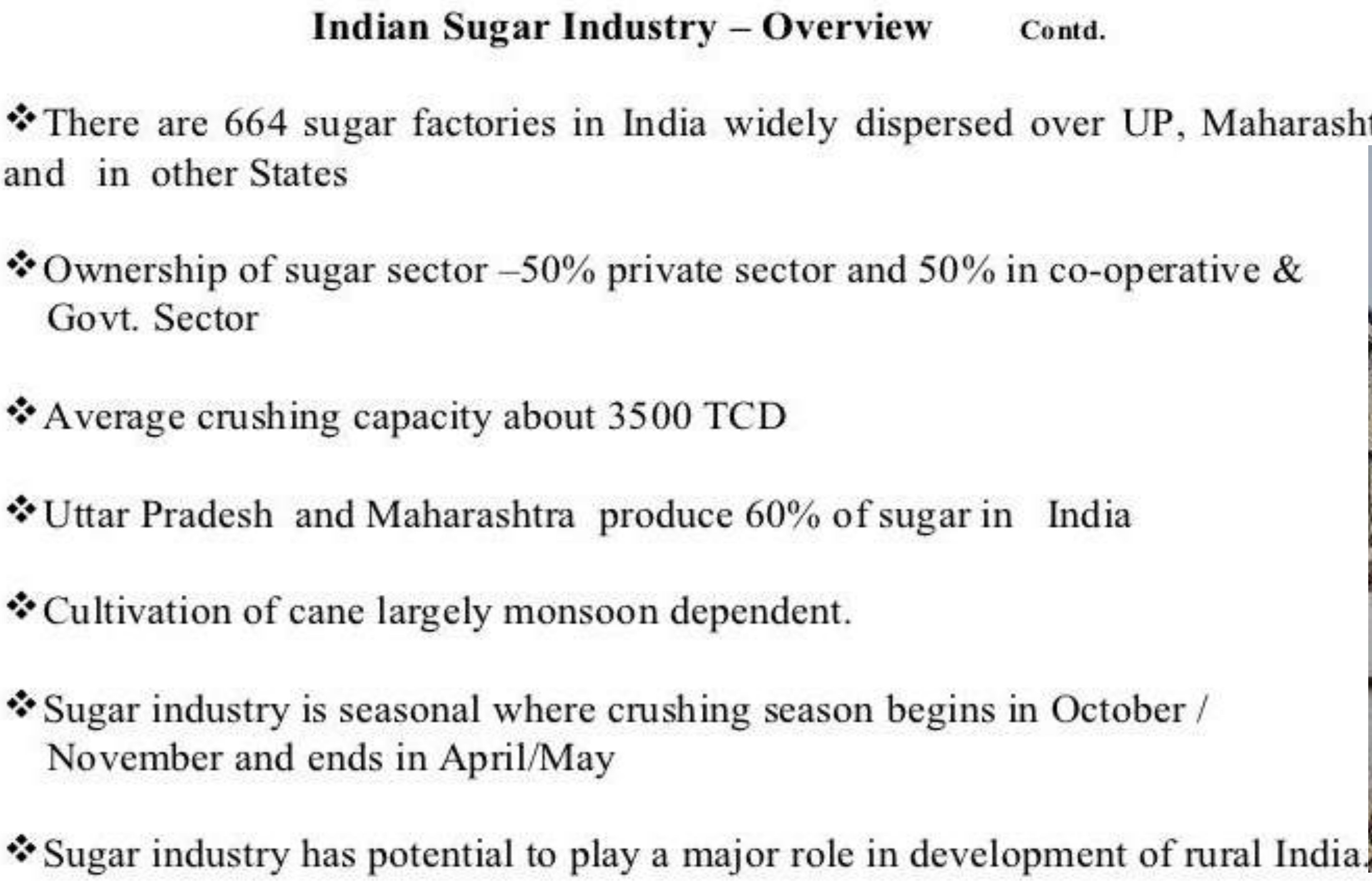
Introduction

A branch of the food-processing **industry** comprising specialized enterprises that manufacture white granulated **sugar** from sugar cane ,**sugar** beets and refined **sugar** from granulated **sugar**. **Sugarcane** is the principal raw material used in **sugar** processing in tropical and subtropical countries.

At **present**, this is the second largest agro-based **industry** of India after cotton textile **industry** is sugar Industry. India is the world's largest producer of sugarcane and second largest producer of **sugar** after Cuba. But India becomes the largest producer if gur and khandsari are also included.

The **largest sugar-producing** countries in 2019–2020 were Brazil, India, China, and Thailand. Brazil was the single **largest producer**, with 29.93 million metric tons of **sugar** produced in 2019–2020.

Overview of Indian Sugar Industry



Indian Sugar Industry – Overview Contd.

- There are 664 sugar factories in India widely dispersed over UP, Maharashtra and in other States
- Ownership of sugar sector –50% private sector and 50% in co-operative & Govt. Sector
- Average crushing capacity about 3500 TCD
- Uttar Pradesh and Maharashtra produce 60% of sugar in India
- Cultivation of cane largely monsoon dependent.
- Sugar industry is seasonal where crushing season begins in October / November and ends in April/May
- Sugar industry has potential to play a major role in development of rural India.

Overview continued…

Indian Sugar Industry – Overview

- **Located in rural heartland, directly contributes to rural economic development**
  - .Sector supporting 50 million farmers & their families – around Rs. 55,000 crores cane price paid in 2010-11
  - .Generates employment for around 12% of the entire rural population (in major 9 sugar producing States)
- **.One of the most environment friendly industry serving several requirements**
  - .Supplying eco-friendly bagasse based energy for consumption – approximate potential: 4000-5000 MW
  - .Mainstay of alcohol industry and eco-friendly Ethanol blending policy
- **.Significant position in the global sugar space**
  - .Largest consumer and second largest producer in the world
  - .World sugar prices impacted by India's Export/Import decisions

Importance of Sugar Industry

Economic Importance

- Sugarcane share is about 7% of total value of agriculture output.
- About 50 million farmers and their dependents and about 0.4 million skilled and unskilled workers are engaged in cultivation of sugarcane and sugar industries & its allied industries.
- Sugarcane provides raw material for the second largest agro-based industry after textile.
- Sugar industry playing an important role in socio economic development, mobilizing rural resources, generating employments, improvement farm income etc.

Continued…

- The **sugar industry** is an **important sector** to generate employment opportunities in the nation especially in the rural areas.
- Importance: India stands second as a world producer of sugar but occupies the first place in the production of gur-jaggary and khandsari. The raw material used in this industry is bulky.
- **Sugar industry** is an agro-based **industry**. **Maharashtra** has progressed a lot and captured first position from U.P. to emerge as the largest producer of **sugar** in India. Large **production** of sugarcane, higher rate of recovery and longer crushing period are some of the factors which have helped the state to occupy this enviable position .
- The **main** by-**products** are bagasse, molasses and press mud. The other **products** and their by-**products** of less commercial value are green leaves and tops, trash, boiler ash and effluent generated by **sugar industry** and distillery.

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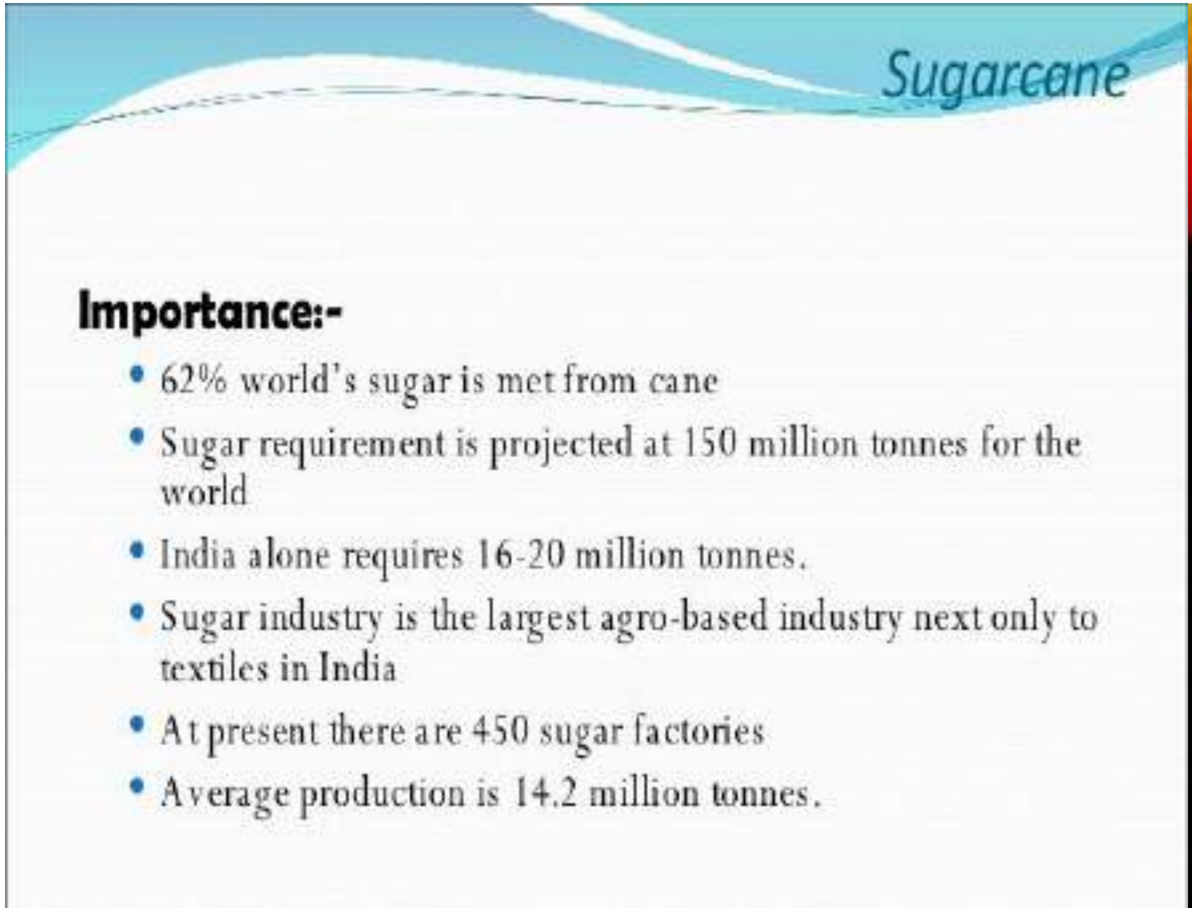
Sugar industry is a big business in **India**. Around 525 mills produced more than 30 million tones of **sugar** in the last crushing season, which lasted from October to April. This makes it the world's largest producer, unseating Brazil.



Sugarcane

Importance:-

- 62% world's sugar is met from cane
- Sugar requirement is projected at 150 million tonnes for the world
- India alone requires 16-20 million tonnes.
- Sugar industry is the largest agro-based industry next only to textiles in India
- At present there are 450 sugar factories
- Average production is 14.2 million tonnes.

IMPORTANCE OF SUGAR INDUSTRY

- THIRD LARGEST INDUSTRY IN INDIA
- GREAT EMPLOYMENT OF WORKERS
- IMPORTANT SOURCE OF EXCISE DUTY FOR CENTRAL GOVERNMENT

In Maharashtra, 181 sugar mills, which are in operation, have produced 51.55 lac tons till 15th January, 2021, as against 139 sugar mills which had produced 25.51 lac tons last year upto same period. This is 26.04 lac tons higher as compared to last season's production for the corresponding period.

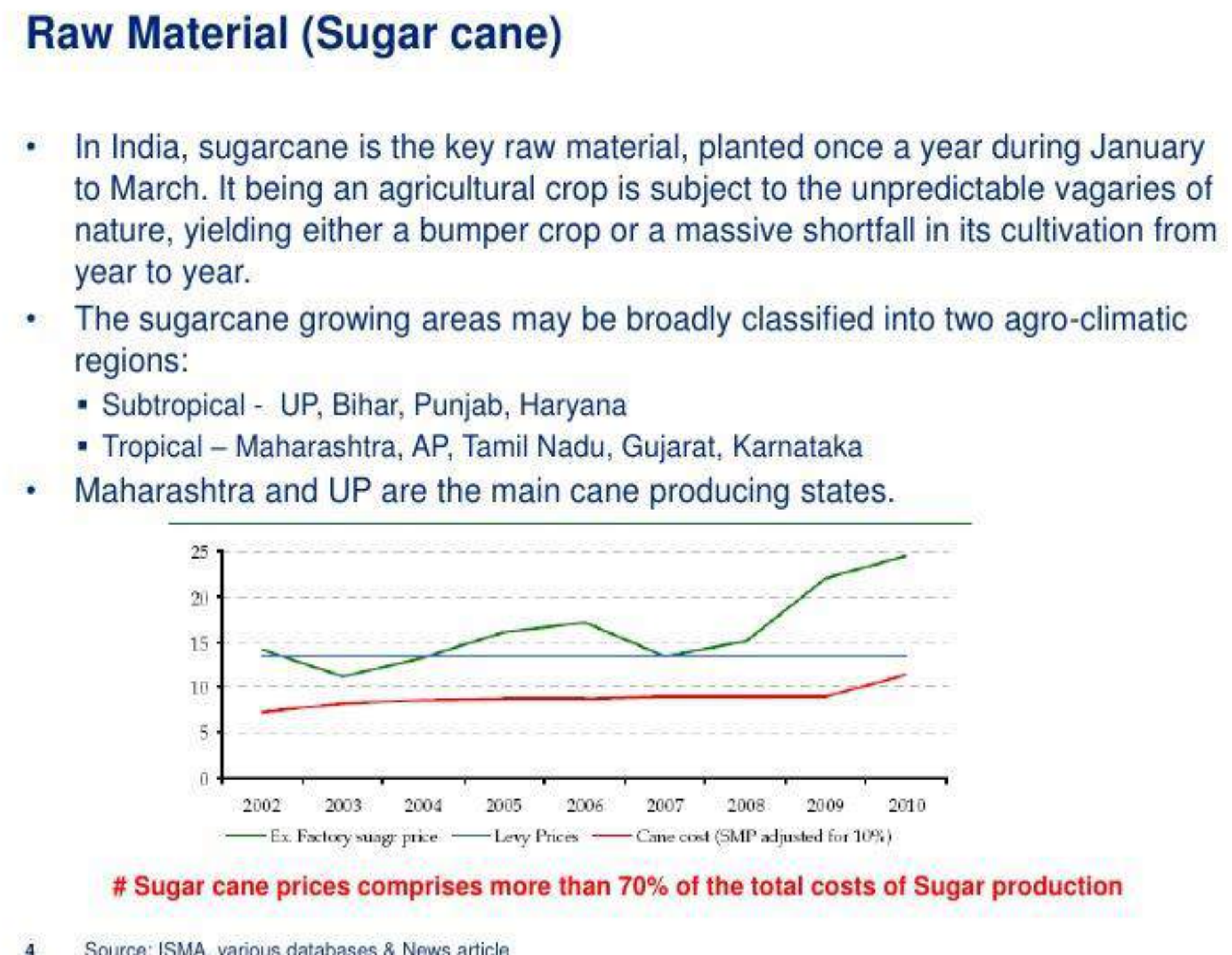
ROLE OF INDUSTRY IN THE ECONOMIC DEVELOPMENT

- The industries in india can be classified into :
- Organised industries
- Unorganised industries
- Both type of industries are important for large country with a huge size of population and plays an important role in the economy of the country.

Sugar Manufacturing Process:

1. Growing & Harvesting the Cane.
2. Cane preparation for Milling.
3. Milling.
4. Clarification.
5. Evaporation.
6. Crystallization.
7. Centrifugation.
8. Drying.
9. Refining.

Raw material for sugar industry



Raw Material (Sugar cane)

- In India, sugarcane is the key raw material, planted once a year during January to March. It being an agricultural crop is subject to the unpredictable vagaries of nature, yielding either a bumper crop or a massive shortfall in its cultivation from year to year.
- The sugarcane growing areas may be broadly classified into two agro-climatic regions:
  - Subtropical - UP, Bihar, Punjab, Haryana
  - Tropical – Maharashtra, AP, Tamil Nadu, Gujarat, Karnataka
- Maharashtra and UP are the main cane producing states.

 # Sugar cane prices comprises more than 70% of the total costs of Sugar production

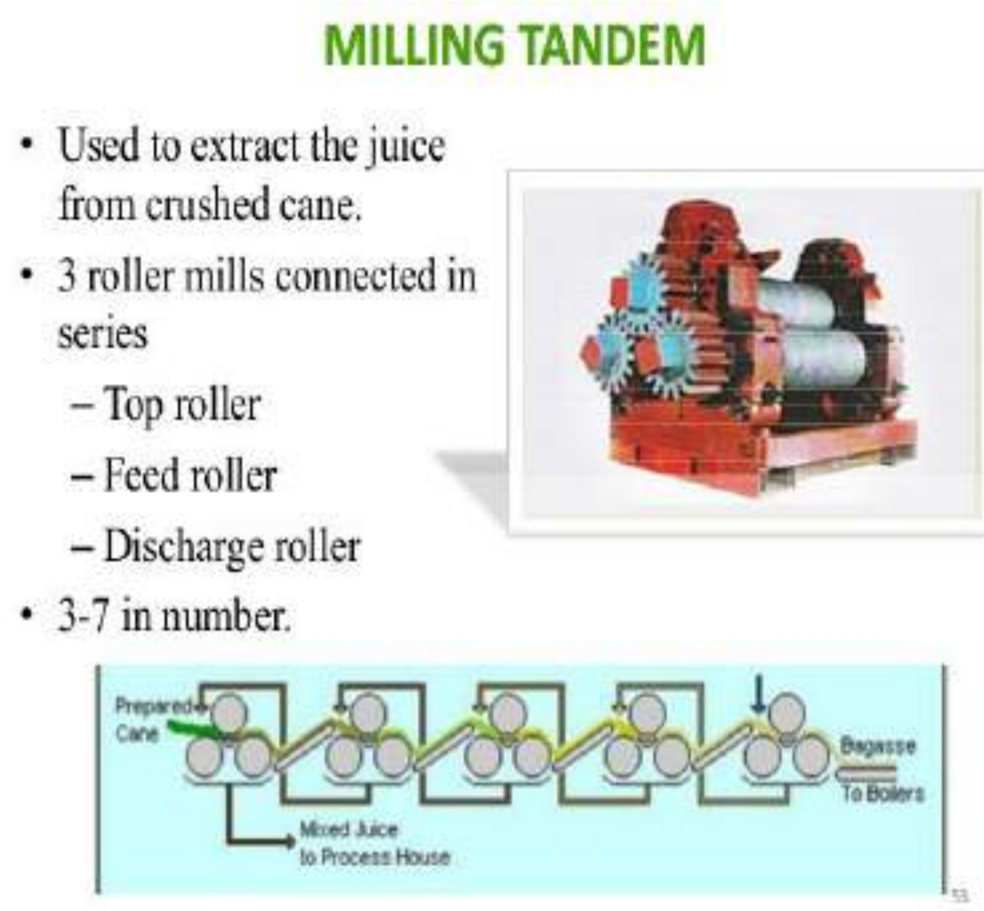
Source: ISMA, various databases & News article

1. Extraction of Juice

- **Cutting of Canes** :Sugar canes are first washed using huge amount of water and then loaded onto a conveyor table. It passes through various sugar equipment including a shredder, which uses a series of knives to chop the cane into smaller lengths and shred it into fine pieces. This process exposes the inner material of the sugarcane and prepares it for efficient juice extraction.
- The shredded cane then proceeds to a crusher, which uses a set of roller mills to extract the juice. A countercurrent stream of maceration water is used to remove the juice from the crusher.
- **Crushing of sugar canes and Extraction of Juice :** Sugar cane must be crushed to extract the juice. The crushing process must break up the hard nodes of the cane and flatten the stems. The juice is collected filtered and sometimes treated and then boiled to drive off the excess water. The dried cane residue (bagasse) is often used as fuel for this process.

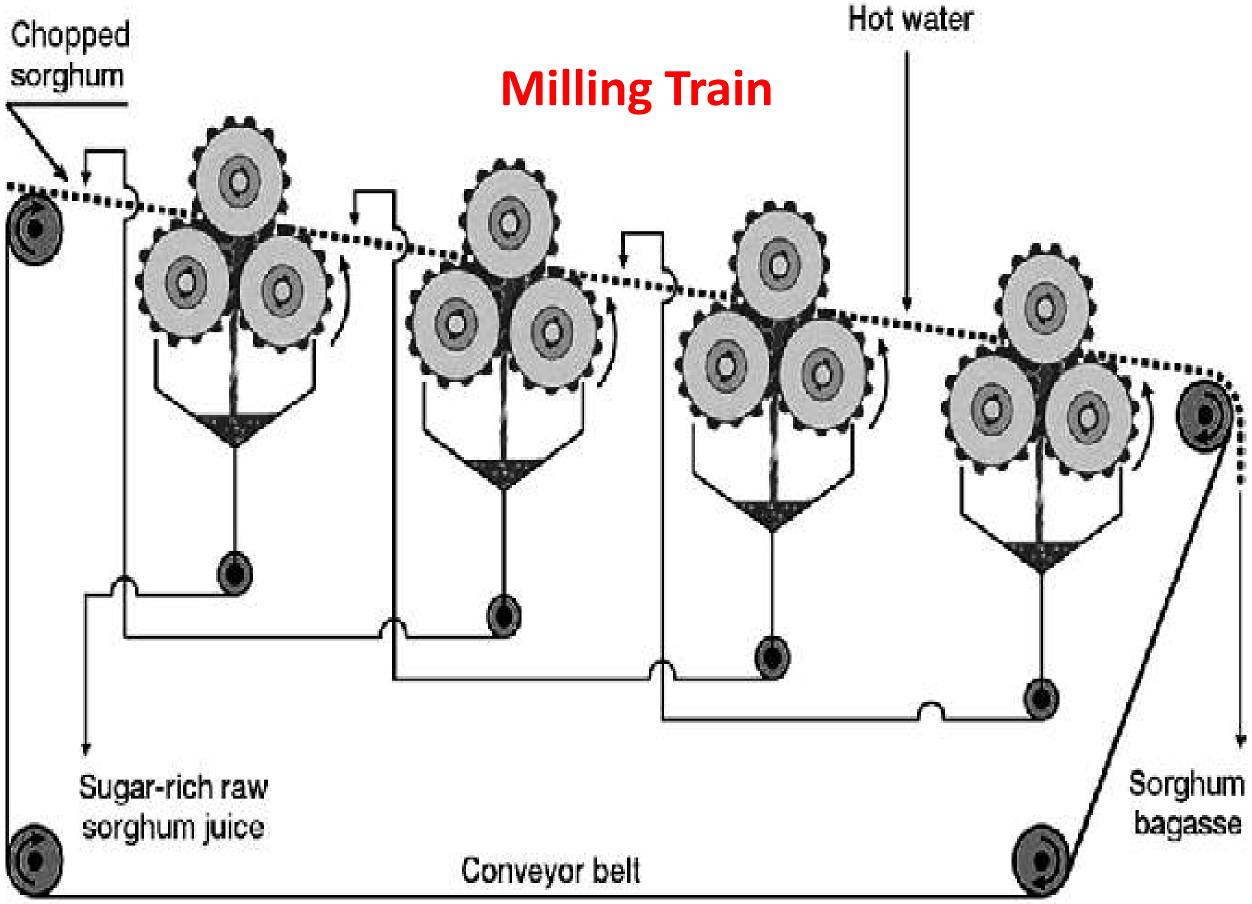
Sugar cane Crushers- Three roller Mills for extraction of juice

Cane **Crusher** Mills are widely used for the extraction of juice by crushing **sugar** canes. Features: High efficiency of extraction. Provided with a hydraulic system. Easy to assemble or dismantle.



MILLING TANDEM

- Used to extract the juice from crushed cane.
- 3 roller mills connected in series
  - Top roller
  - Feed roller
  - Discharge roller
- 3-7 in number.



Milling Train

Working of three roller mills

- Working :

Three roller traditional sugarcane **juice** extractor, **crushers**.Using these **three** sugarcane **crushers** the amount of **juice extracted** is 79 per cent of **juice** is expressed in **sugar mills** by this crusher. A series of sugar **cane crushers** are ideal for extracting sugar **cane** juice for jaggary plant and mini sugar plants. These machines have higher extraction rate of **sugarcane** juice reducing the wastage.

The **crush** unit consists of **three rollers**, one big **roller** and two tiny **rollers**. The improved cane preparation and increasing crushing, provision of high imbibition water have increased juice quantity in the mill.

If this increased juice is not drained effectively, then it affects the mill extraction adversely and will demand extra hydraulic load increasing the power demand in the mill. The pressure feeding equipments, lotus rollers are used in the mill to ideal with this increased juice.

Continued…

- To have the maximum extraction of juice.

a) To press and squeeze the prepared cane in 1st mill and bagasse in other mills for juice extraction.

b) To drain the **juice effectively from mill.**

c) To mill the bagasse is exposed to imbibition and juice maceration plays important role in achieving better mill extraction. Imbibition water dilutes the juice in bagasse and reduces it viscosity.

The characteristics of low viscosity of juice increases the flow of juice through bagasse. The hot water further helps in reducing the viscosity of the juice. However higher temperature of water sometime leads to slippage of bagasse in the mill. The higher imbibition water is restricted due to capacity of boiling house and availability of steam and therefore it restrains to increase crushing rate. further processed to get the uncut juice cells broken to help to increase the extraction in the following mill.

d) To drive the bagasse through the mill effectively.

Continued…

Imbibition and juice maceration plays important role in achieving better juice extraction. Imbibition by water dilutes the juice in bagasse and reduces it viscosity. The characteristics of low viscosity of juice increases the flow of juice through bagasse.

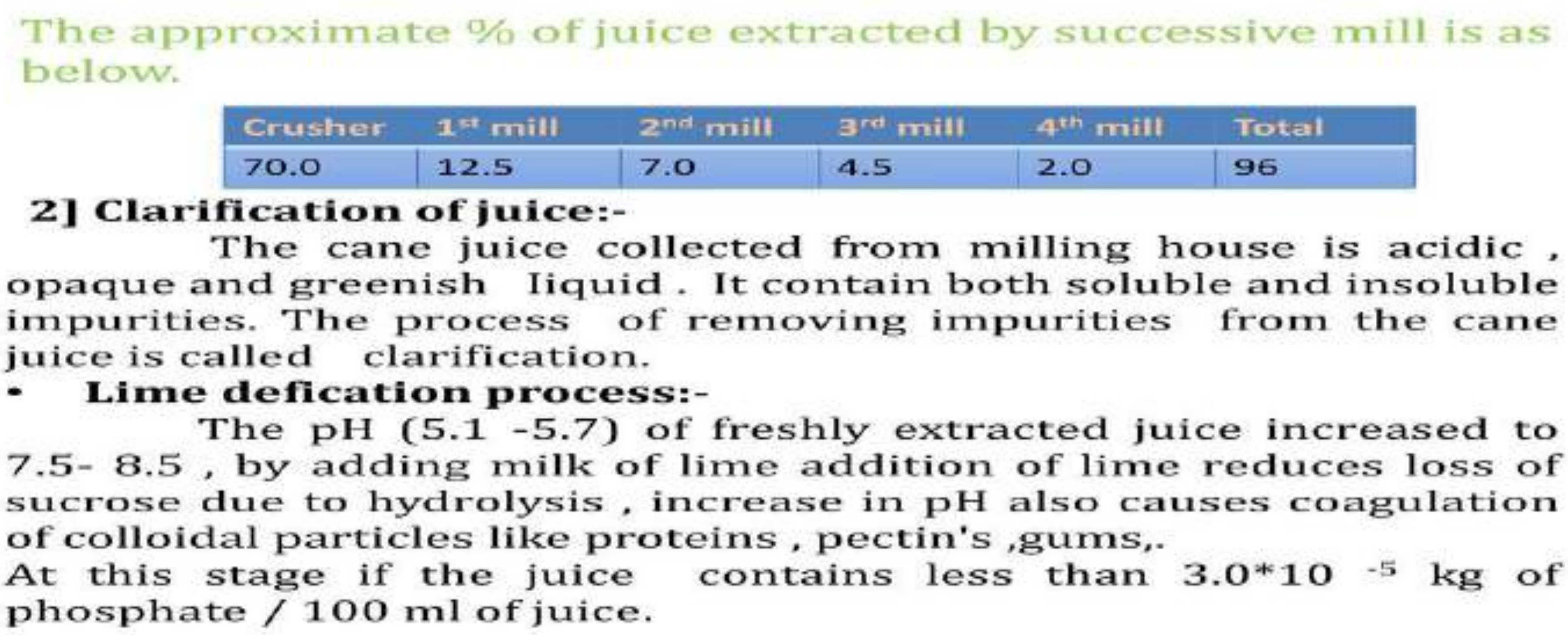
The hot water further helps in reducing the viscosity of the juice. However higher temperature of water sometime leads to slippage of bagasse in the mill.

The higher imbibition water is restricted due to capacity of boiling house and availability of steam and therefore it restrains to increase crushing rate.

2. Clarification of Juice…

The purpose of the **clarification process** is to remove as many nonsugar components as possible, improve the purity of the juice, and reduce its viscosity and color values. This is necessary for providing high-quality, concentrated **sugar** syrup crystals into the boiling stage.

The **clarification** of sugar **cane juice** occurs by coagulation, flocculation, and precipitation of the colloids and pigmented substances, which are later eliminated by decanting and filtration, i.e., an insoluble precipitate which absorbs and drags such compounds from the **juice** is formed.



The approximate % of juice extracted by successive mill is as below.

Crusher	1st mill	2nd mill	3rd mill	4th mill	Total
70.0	12.5	7.0	4.5	2.0	96

2] Clarification of juice:-

The cane juice collected from milling house is acidic , opaque and greenish liquid . It contain both soluble and insoluble impurities. The process of removing impurities from the cane juice is called clarification.

- **Lime defication process:-**

The pH (5.1 -5.7) of freshly extracted juice increased to 7.5- 8.5 , by adding milk of lime addition of lime reduces loss of sucrose due to hydrolysis , increase in pH also causes coagulation of colloidal particles like proteins , pectin's ,gums,.

At this stage if the juice contains less than $3.0*10^{-5}$ kg of phosphate / 100 ml of juice.

Continued…

- Purpose of clarification

The limed raw **juice** entering the **clarifier** should be heated in heaters to 104°C (220°F), slightly above the boiling point of **cane juices** of 13—16° Brix. At this temperature the viscosity of **cane juices** is reduced, and when **juice** passes through the flash tank, the occluded gases are eliminated.

The purpose of the **clarification process** is to remove as many nonsugar components as possible, improve the purity of the juice, and reduce its viscosity and color values. This is critical for providing high-quality, concentrated **sugar** syrup crystal to the boiling stage.

Removal of **impurities** (soluble and insoluble non-sugar compounds) from cane sugar **juice** by clarification is an essential part of the process of raw sugar manufacture. Rapid flocculation and sedimentation of suspended particles in primary cane sugar **juice** is achieved using high molecular weight anionic polymers

Clarification of Juice- continued…

- The **clarification process** was required to reduce particles in **sugarcane juice** before heating to **produce syrup**.
- The **syrup** from **juice** treated with 3% bentonite and 0.3% activated carbon gave the lowest absorbance value at 420 nm corresponding to the lightest color with 52.4% sucrose i. e. juice get purified. Dark colour is due to presence of impurities.

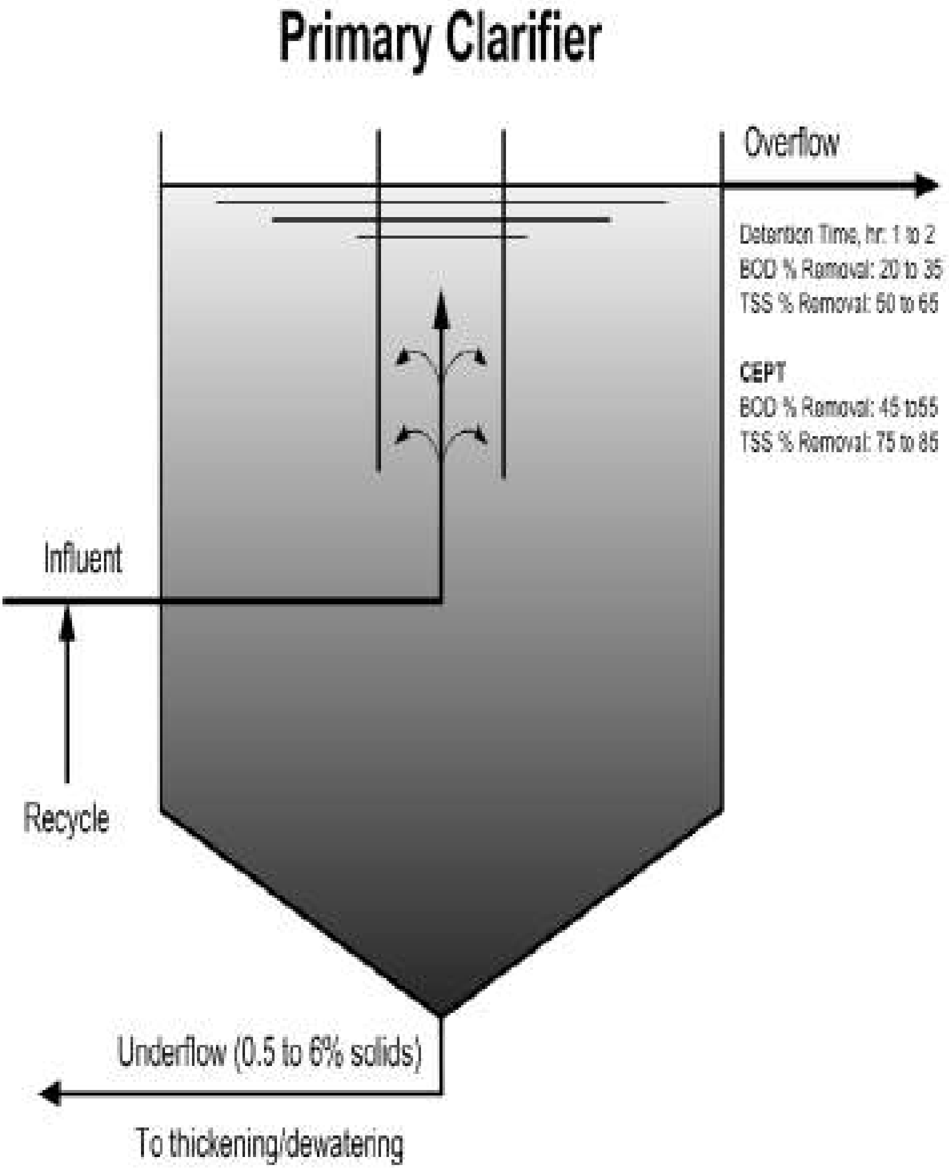
The analysis of turbidity, color, pH and sensory evaluation is done to determine

the clarification effect due to three clarifying agents: lime, bentonite and activated

carbon and SO2.

- The study of clarification by liming showed that adding lime to pH 7 reduced the turbidity more effective than those to pH 8 and 9, and the study of adding bentonite at 3% (w/w) resulted in turbidity that was not significantly different ($p>0.05$) from those adding at 4 and 5% (w/w).
- Further clarification by powder activated carbon at 0.1 0.2 and 0.3% (w/w) after liming to pH 7 and 3% bentonite indicated that the increase in activated carbon content led to the decrease in turbidity and colour.
- **A kind of absorbent clay formed by breakdown of volcanic ash, used especially as a filler** which are hydrous aluminum silicates containing iron and magnesium as well as either sodium or calcium.

Clarifier in Sugar Industry



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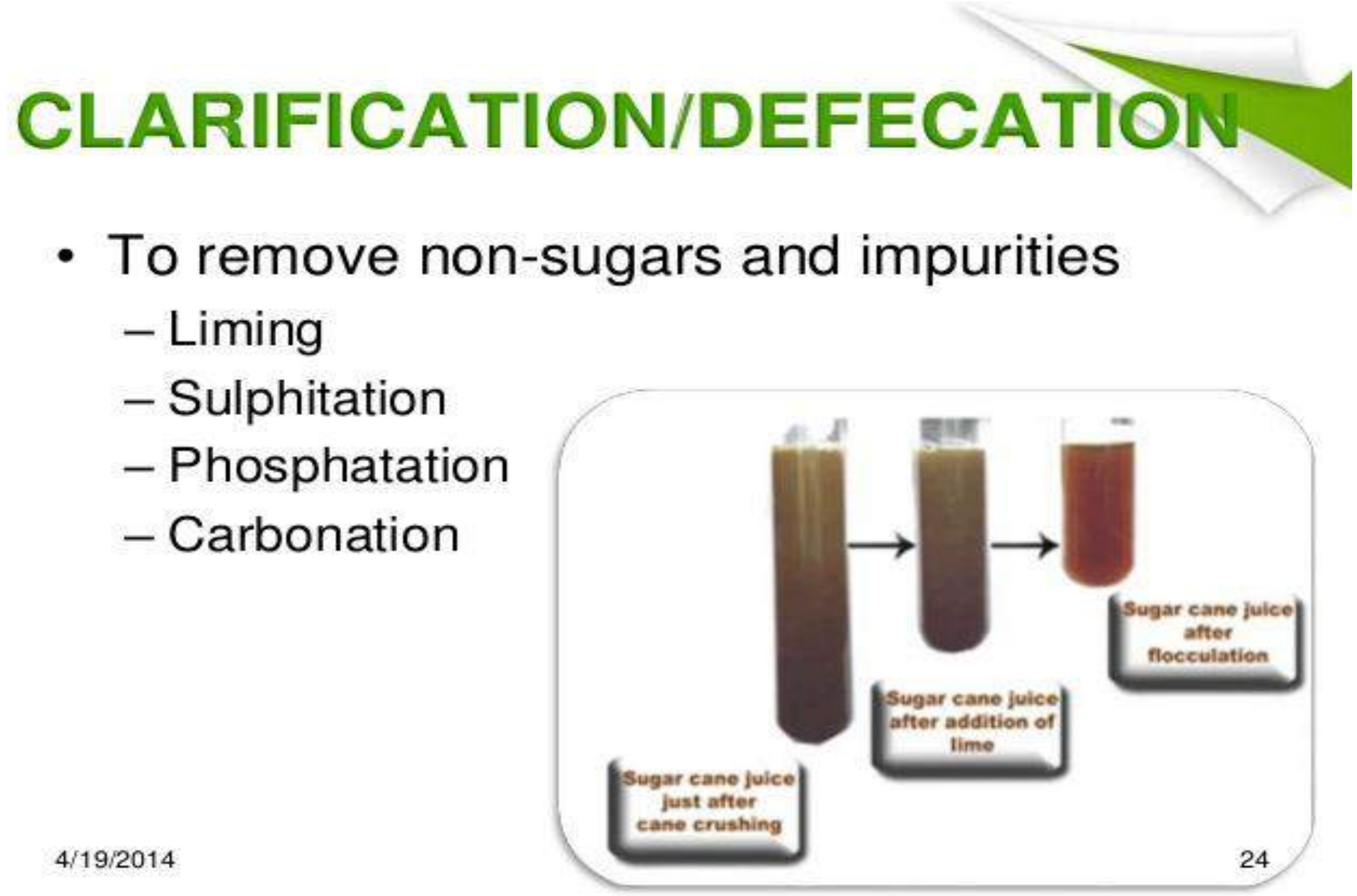
- A **clarifier** is used to separate out the solids suspended in the cane **juice**. These solids originate from sand adhering to the cane stalks as well as from material inherent in the cane stalk. The separation takes place by allowing the solid particles to settle out onto a tray. Then following steps are carried out.



CLARIFICATION/DEFECATION

- To remove non-sugars and impurities
  - Liming
  - Sulphitation
  - Phosphatation
  - Carbonation

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SCHEMATIC ARRANGEMENT FOR JUICE CLARIFICATION

Raw Juice pH 5.0

↓

Heated to 65^{0}C on Juice Heaters

↓

Simultaneous Liming and Sulphitation and the final pH is kept around 7.0/7.2

↓

Heated to 102 ^{0} C on Juice Heaters.

↓

CLARIFIER

Subsequently juice is allowed to settle for 2.5 hours. The CLEAR supernatant juice is separated for further processing. The non-sugars precipitated as calcium sulfite complex compounds are further treated on Rotatory Vacuum Filters (RVF) for futher extraction of residual juice.

Continued…

Phosphoric acid is **added** to the sugar **cane juice** and heated to 70°C, lime is **added** and the limed **juice** is further heated to 105°C. The **juice** is degassed and a flocculent polymer **added** to **remove** insoluble **impurities**. The decanted **juice** is filtered and the clarified **juice** concentrated in multiple evaporators.

Electrophilic Substitution Reactions of Aniline

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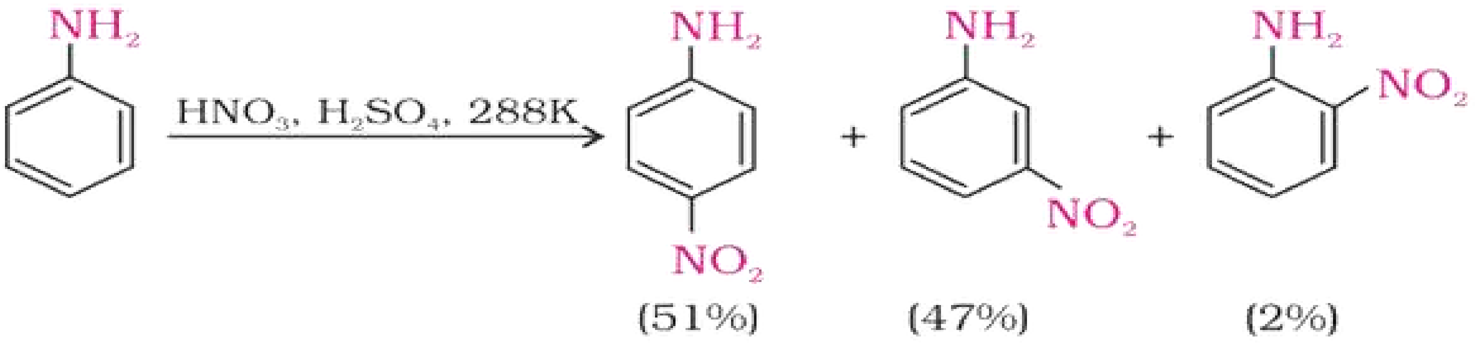
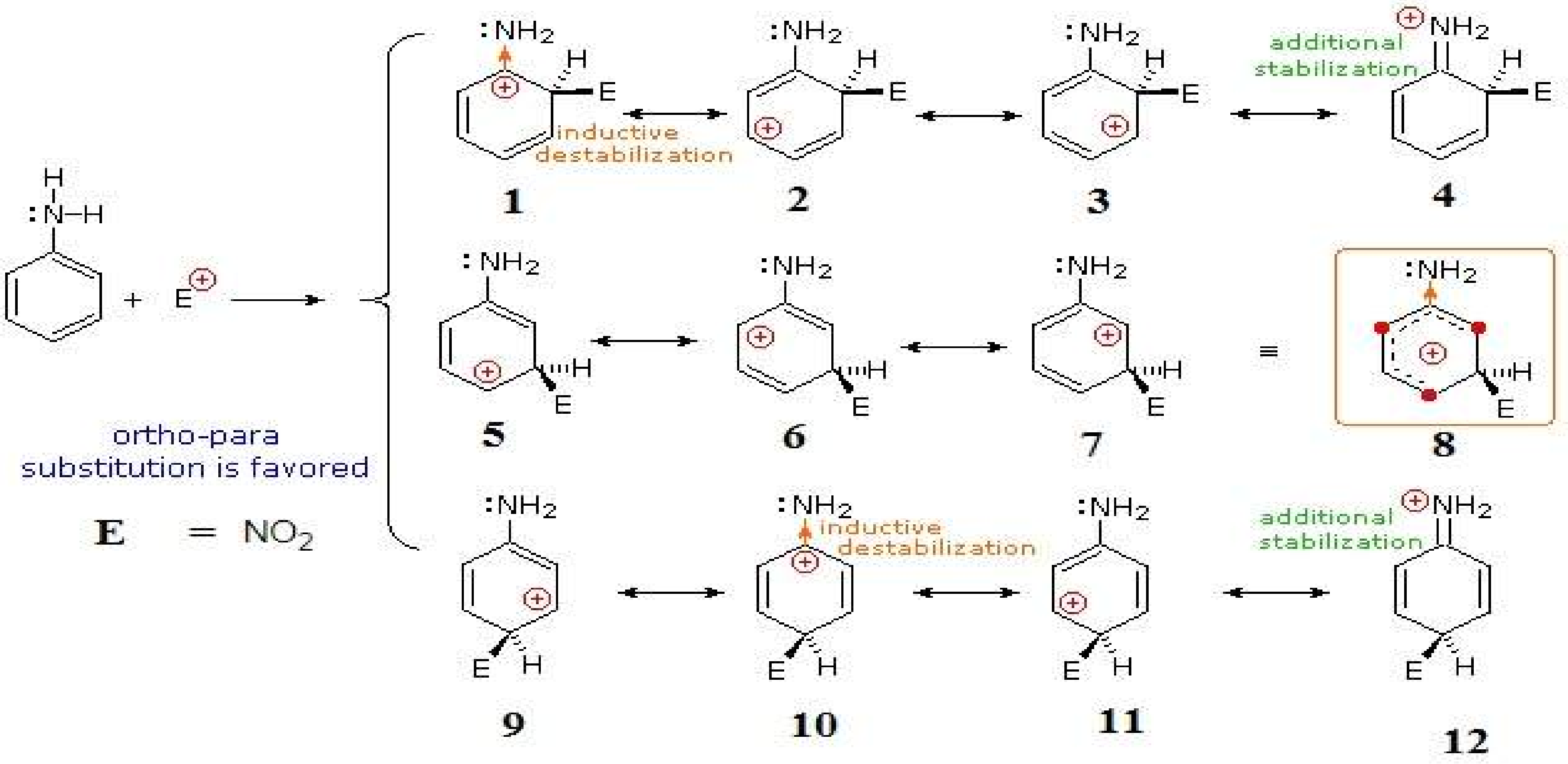
- 1. Nitration of Aniline
- **Electrophilic substitution reaction** refers to the reaction in which an electrophile substitutes another electrophile in an organic compound. Anilines undergo the usual electrophilic reactions such as halogenation, nitration and sulphonation.
- A mixture **of concentrated sulphuric and nitric acids**, used to introduce a nitro group (–NO_2) into an organic compound.
- Nitration is **a process in which there is the replacement of a hydrogen atom (organic compound) with one or more nitro groups (single bond NO_2)**. The reaction usually occurs with high temperatures or we can say that the reaction is exothermic.



Mechanism :

- o- and p- substituted products are more stable products due to more resonating structures giving rise to stable product.



Mechanism of Nitration :

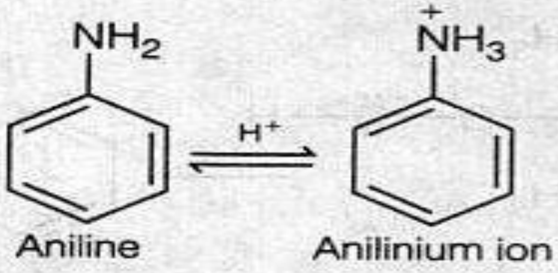
In case of nitration in aniline, the **Nitric Acid protonates the aniline to form the Anilinium ion**. Now since the nitrogen atom has no lone pair to conjugate, it has no mesomeric effect on the ring, but as nitrogen is now protonated, it has a high negative inductive effect.

Direct nitration of aniline yields **(p-nitroaniline) a mixture of ortho, meta, and para nitroanilines**. In an acidic medium the -NH_2 group is protonated to the -N^+H_3 group which is meta-directing and deactivating. Hence, a considerable amount of m-nitroaniline is obtained.

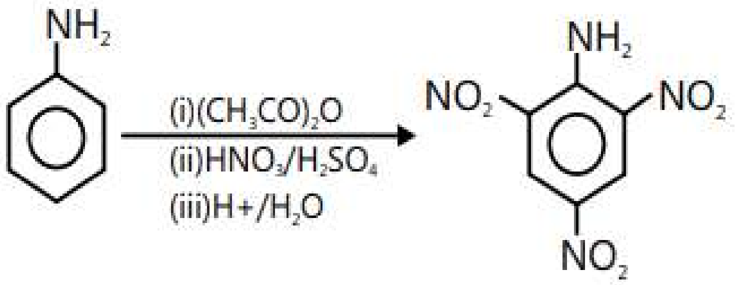
Continued…

Nitration: Direct nitration of aniline yields **(p-nitroaniline) a mixture of ortho, meta, and para nitroanilines**. In an acidic medium the -NH_2 group is protonated to the -N^+H_3 group which is meta-directing and deactivating. Hence, a considerable amount of m-nitroaniline is obtained. Aromatic sulfonation is an organic reaction in which a hydrogen atom on an arene is replaced by a sulfonic acid functional group in an electrophilic aromatic substitution. Aryl sulfonic acids are used **as detergents, dye, and drugs**.

(*d*) In strongly acidic medium, aniline is protonated to form the anilinium ion.

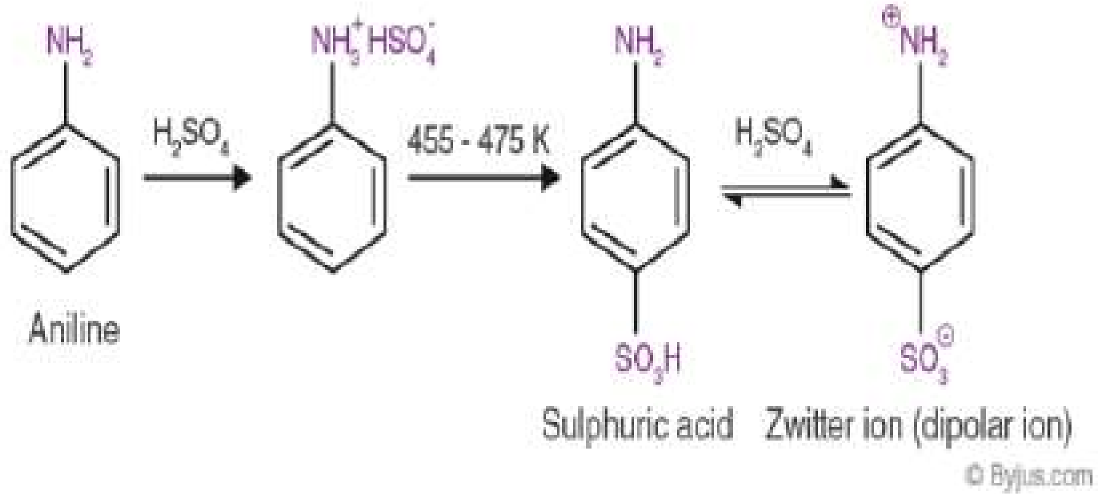


Since, anilinium ion so formed is *meta* directing, thus besides *ortho* and *para* derivatives, significant amount of *meta* derivative is also formed.



2. Sulfonation of Aniline

- Sulphonation. Sulphuric acid reacts vigorously with aniline to form **anilinium hydrogen sulphate** which on heating produces sulphanilic acid which in turn also has a resonating structure with zwitter ion as shown in the figure.



Aniline

Sulphuric acid Zwitter ion (dipolar ion)

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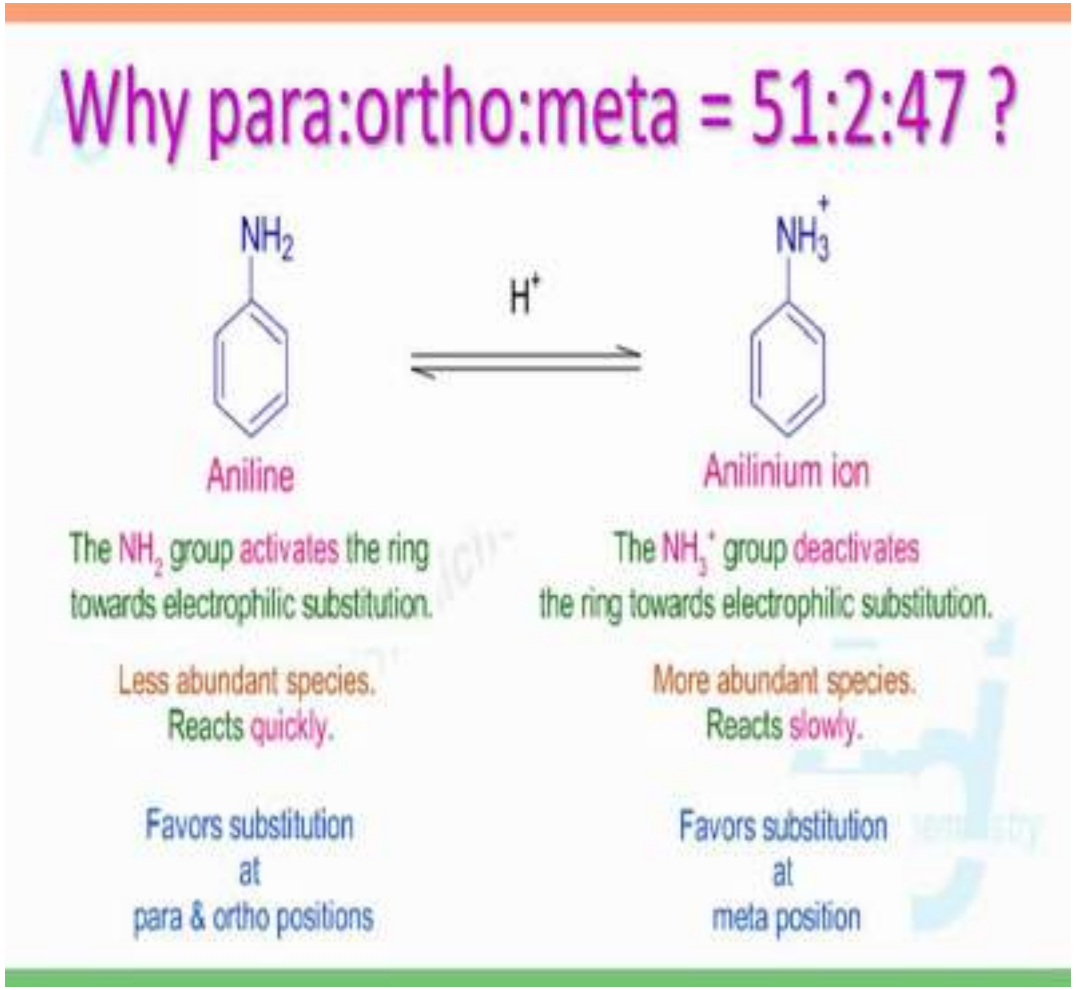
The electrophile is sulphur trioxide, and this arises in one of two ways depending on which sort of acid you are using. Concentrated sulphuric acid contains traces of SO3 due to slight dissociation of the acid.



Why para:ortho:meta = 51:2:47 ?

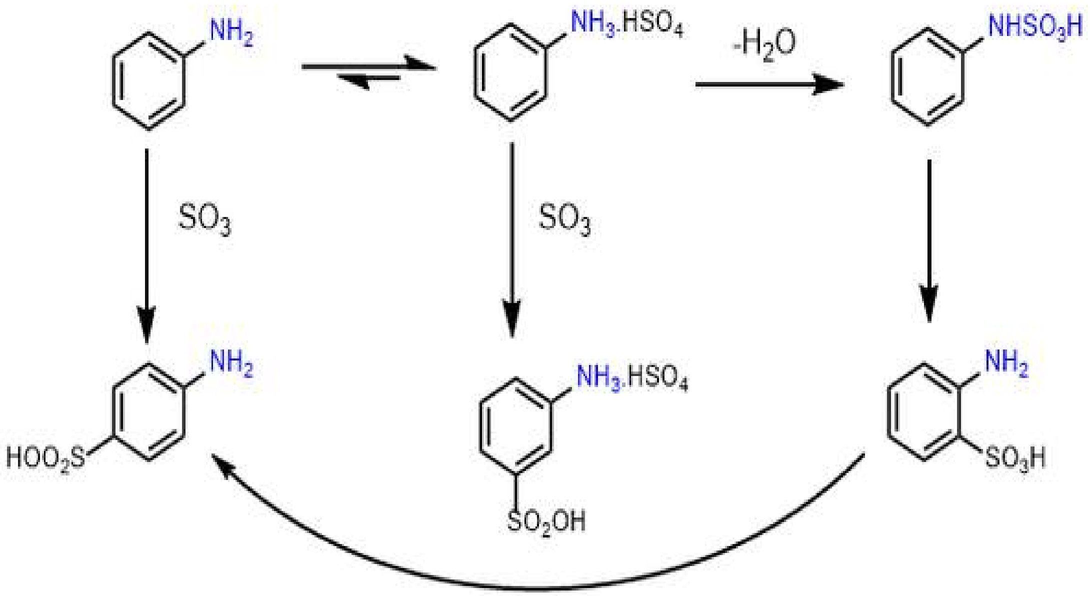
Aniline	Anilinium ion
The NH_2 group activates the ring towards electrophilic substitution.	The NH_3^+ group deactivates the ring towards electrophilic substitution.
Less abundant species. Reacts quickly.	More abundant species. Reacts slowly.
Favors substitution at para & ortho positions	Favors substitution at meta position

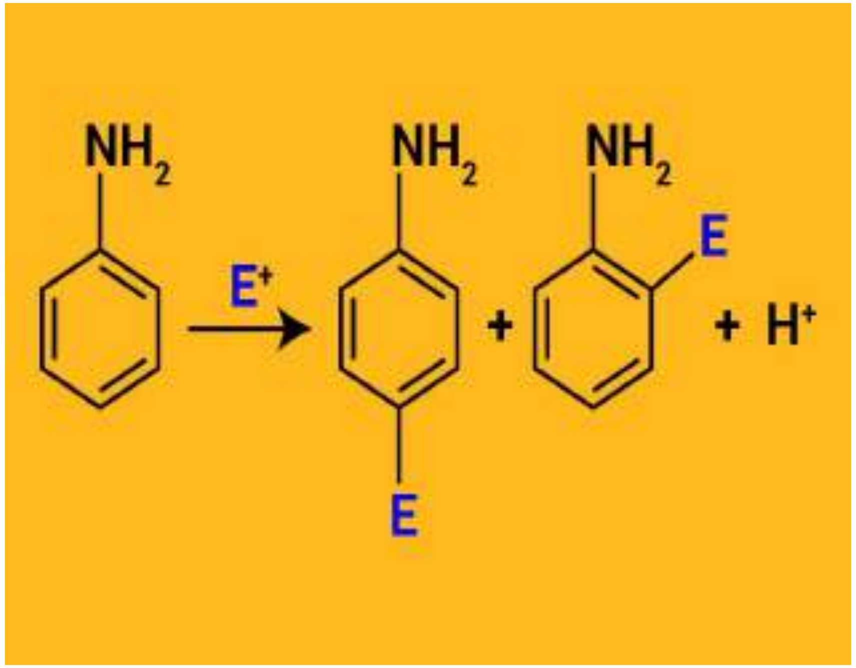
Continued…

- What is Sulphonation ?

The sulfonation process is a direct process in which **SO3 gas** is diluted with very dry air and reacted directly with the organic feedstock. (aniline)The source of the SO3 gas may be either liquid SO3 or SO3 produced by burning sulfur.

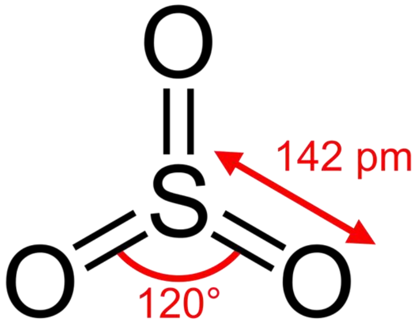
Sulfonation is a reversible reaction that **produces benzenesulfonic acid by adding sulfur trioxide and fuming sulfuric acid**. The reaction is reversed by adding hot aqueous acid to benzene sulfonic acid to produce benzene.

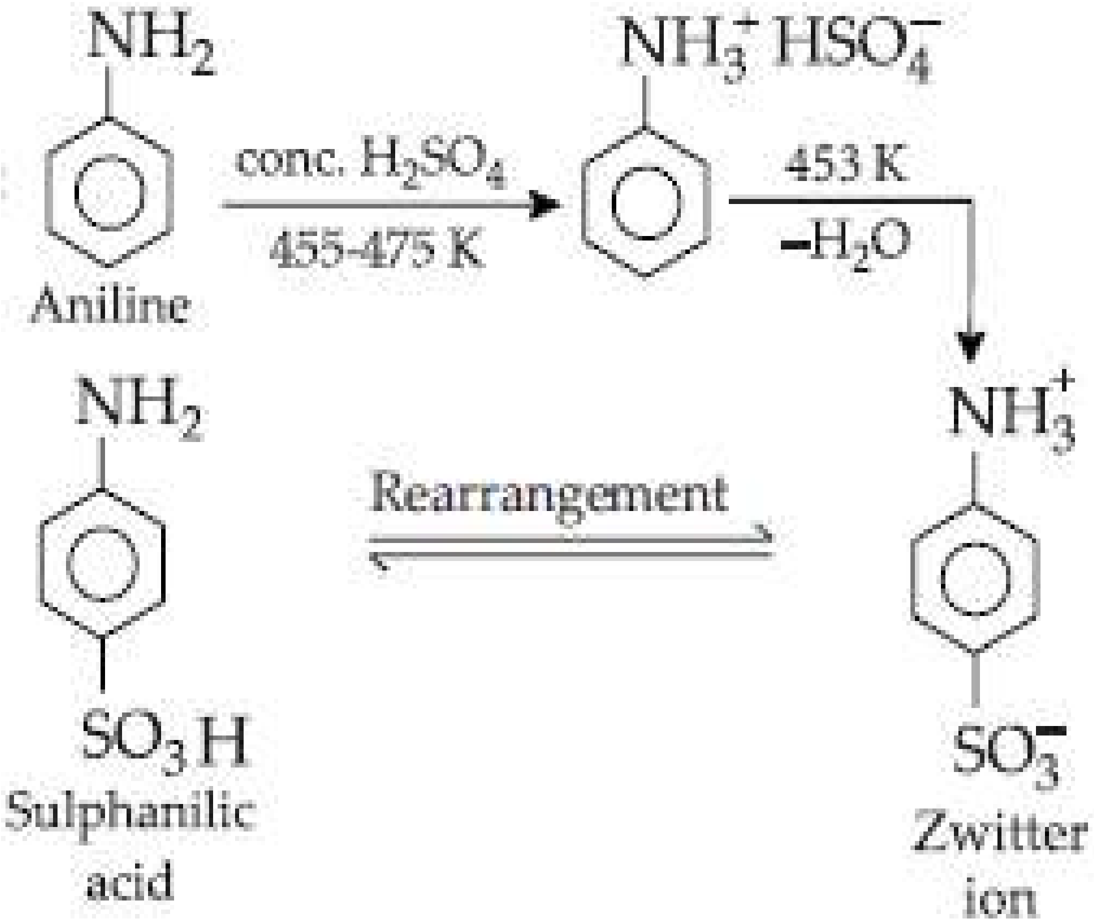




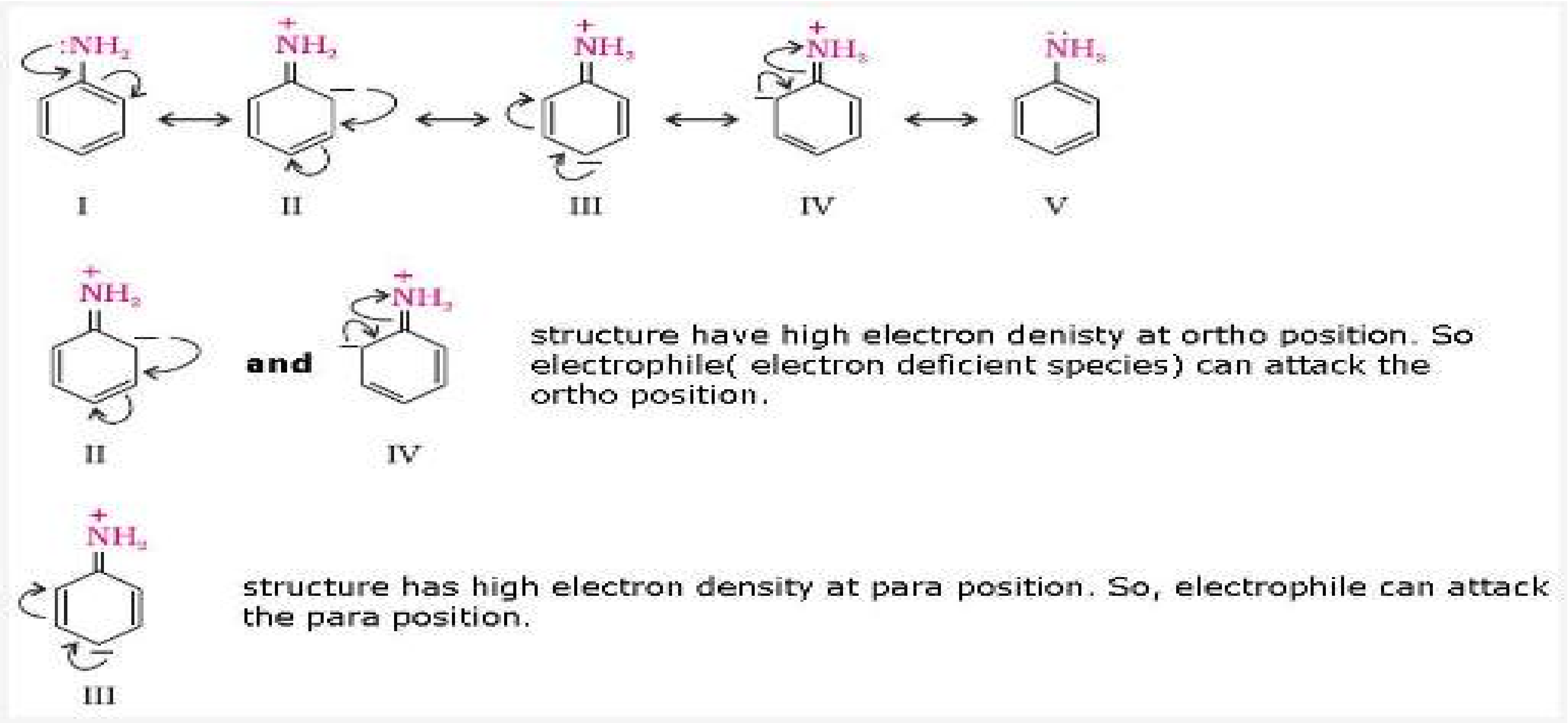
SULPHONATION

- SO_3 is an aggressive electrophilic reagent that rapidly reacts with any organic compound containing an electron donor group.
- Sulfonation is a difficult reaction to perform on an industrial scale because the reaction is rapid and highly exothermic, releasing approximately 380 kJ/kg SO_3 (800 BTUs per pound of SO_3) reacted.





In Aniline, o- and p- positions are electron rich due to resonance phenomenon, as follows hence they attract the electrophile at those positions and form o- and p- substituted products.



structure have high electron denisty at ortho position. So electrophile(electron deficient species) can attack the ortho position.

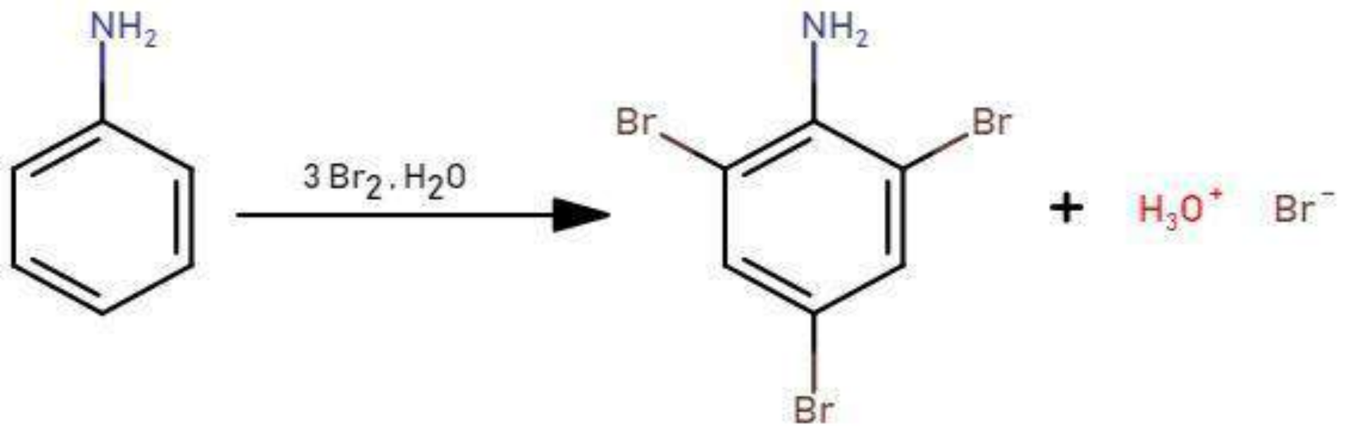
structure has high electron density at para position. So, electrophile can attack the para position.

3. Bromination in Aniline :

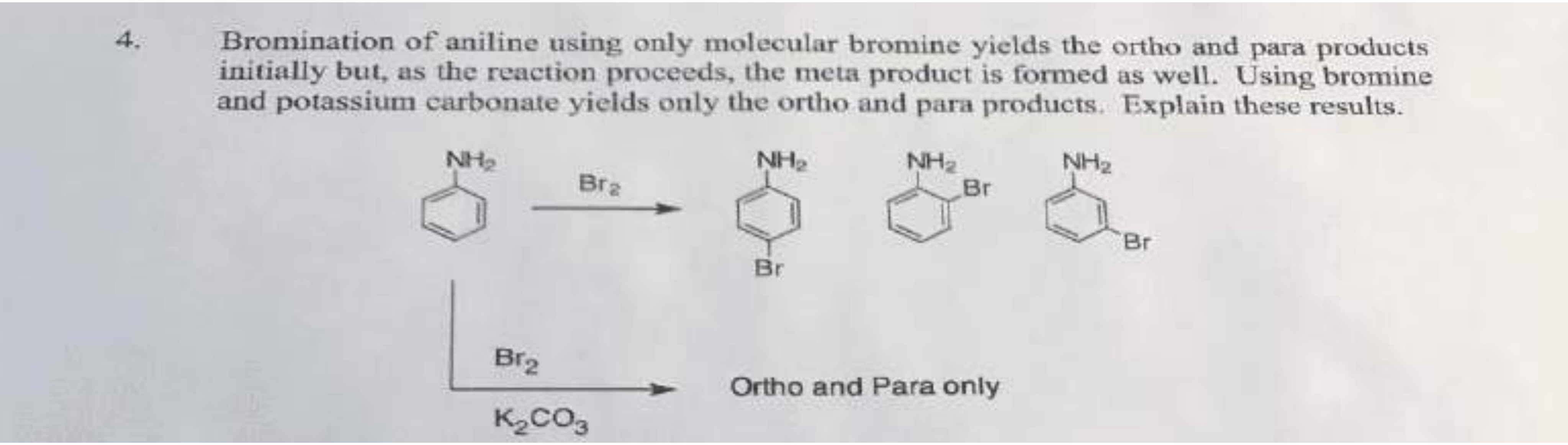
Aniline reacting with bromine water at room temperature produces a white-coloured precipitate called **2,4,6-tribromoaniline**. This is because the polarity is developed within the bromine molecule where bromine then acts as an electrophile as it has slightly positive charge.

When aniline treated with bromine water, **the bromine water gets decolourized and white precipitate is formed**. This reaction results in the formation of 2,4,6-tribromo phenylamine. This reaction is an example of bromination.

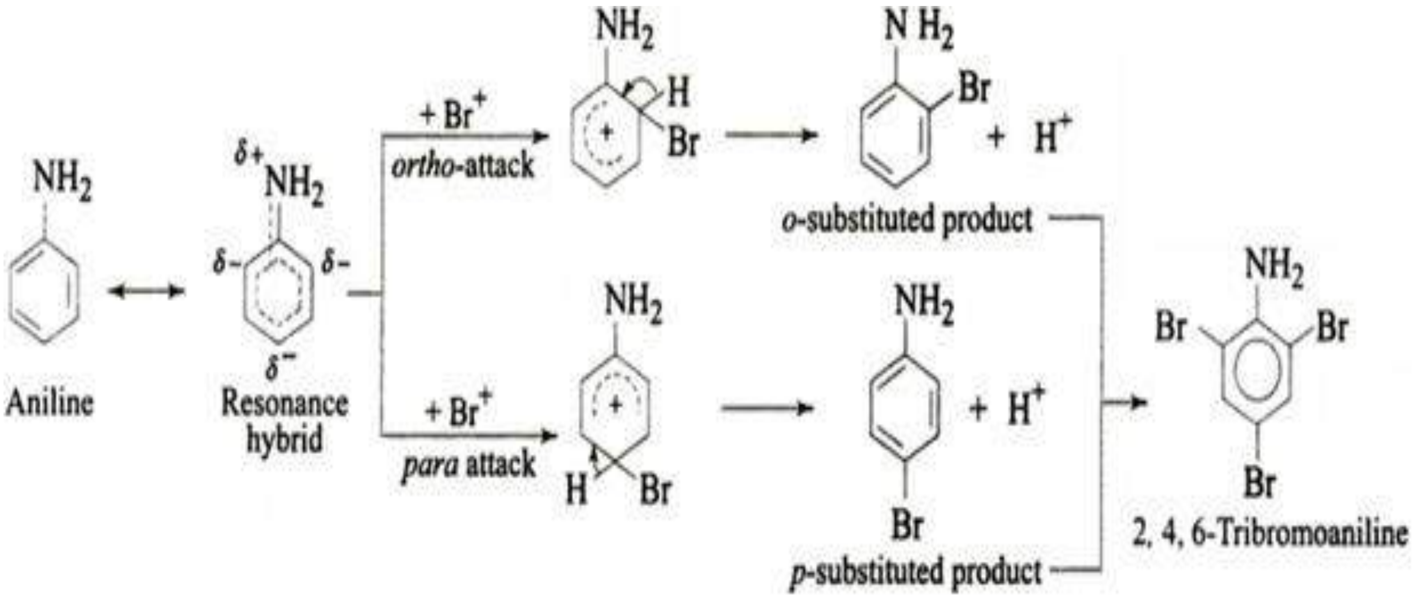
This is because **NH_2 group in aniline is highly activating group**. So, aniline reacts with bromine water at room temperature to give a white precipitate of 2,4,6 - tribromoaniline. Aniline reacts with excess bromine in aqueous solution to give major product as. **2, 4, 6-tribromoaniline**.

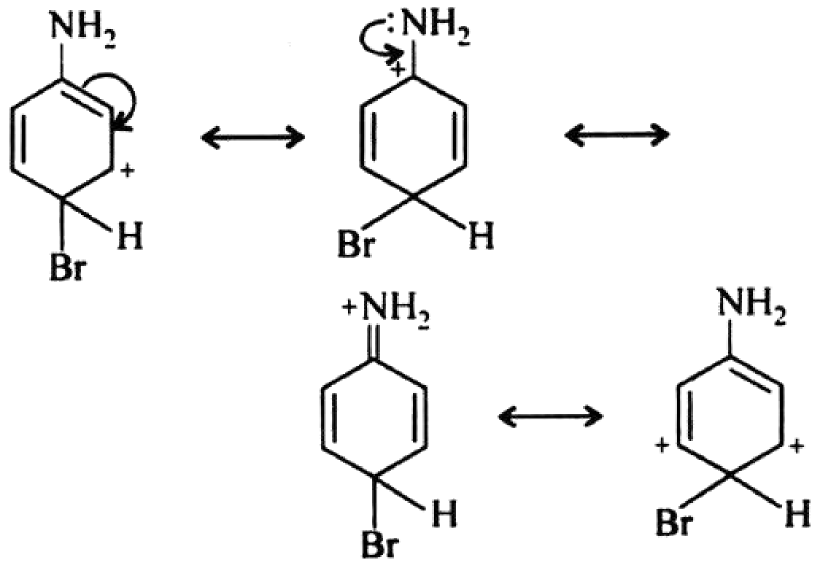


Reaction of aniline with bromine molecule :



4. Bromination of aniline using only molecular bromine yields the ortho and para products initially but, as the reaction proceeds, the meta product is formed as well. Using bromine and potassium carbonate yields only the ortho and para products. Explain these results.





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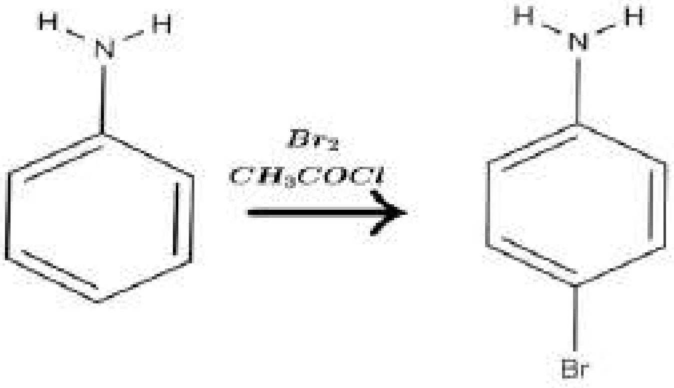
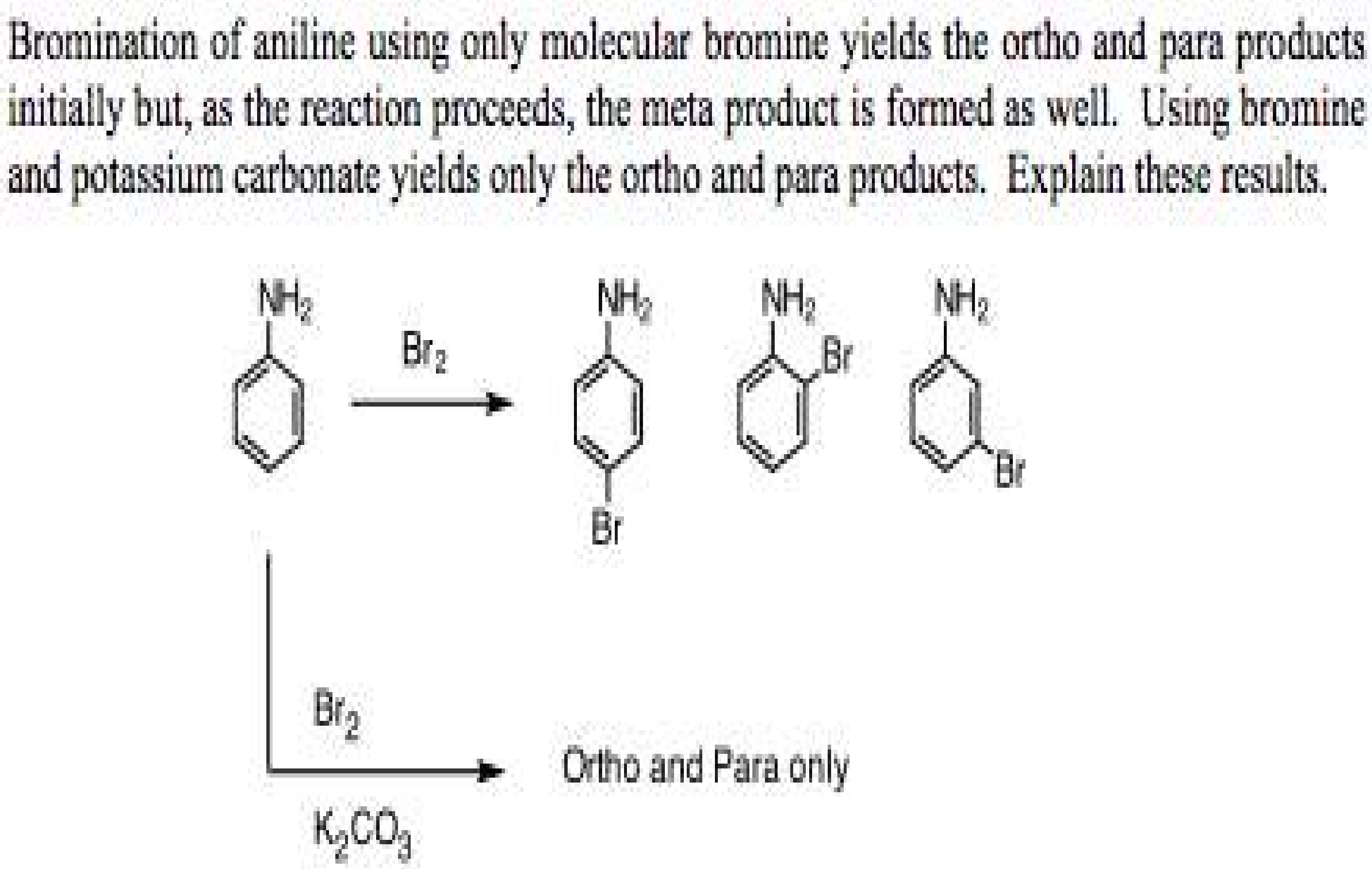
Aniline reacts with excess bromine in aqueous solution to give major product as. **2, 4, 6-tribromoaniline**. **NH_2 group in aniline is highly activating group**. So, aniline reacts with bromine water at room temperature to give a white precipitate of 2,4,6 - tribromoaniline. .




Bromine water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Gomberg’s reaction

- What is this reaction ?

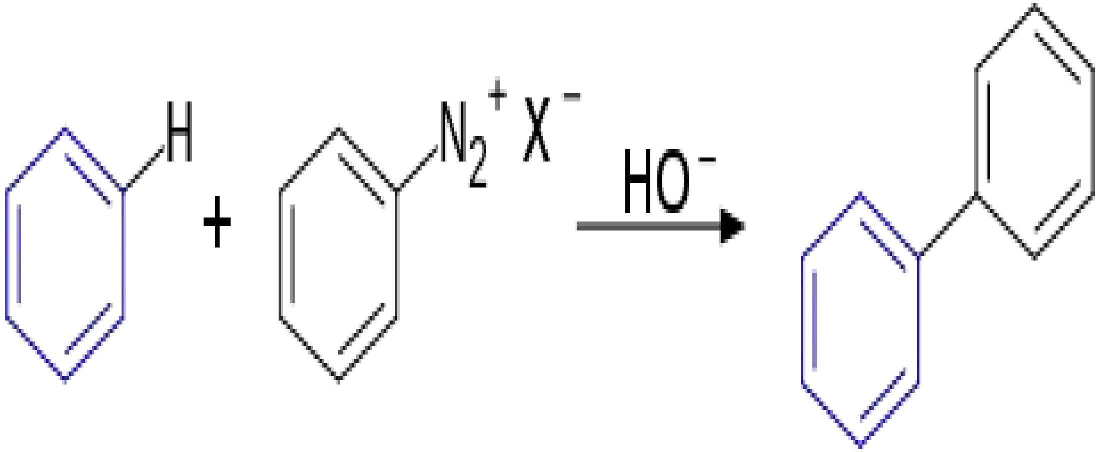
In the **first step diazonium salt derivative is reacted with hydroxide ion and forms diazonium oxide which further reacts with PhN2+ and forms a double ring compound**.

Gomberg reaction is known by the name of Gomberg-Bachmann reaction as this reaction is discovered by two scientists known as Gomberg and Bachmann. It is an aryl-aryl coupling reaction with the help of diazonium salt.

Gomberg reaction basically start with the starting reactant diazonium salt as a common functional group represented by R−N2+X−R−N2+X− where R can be any organic group may be alkyl or aryl and X is halogen. The mechanism of Gomberg-Bachmann reaction can be explained as follows:

Continued…

The **Gomberg–Bachmann reaction**, named for the Russian-American chemist Moses Gomberg and the American chemist Werner Emmanuel Bachmann, It is an aryl-aryl coupling reaction via a diazonium salt.



Gomberg’s reaction :

- Mechanism :

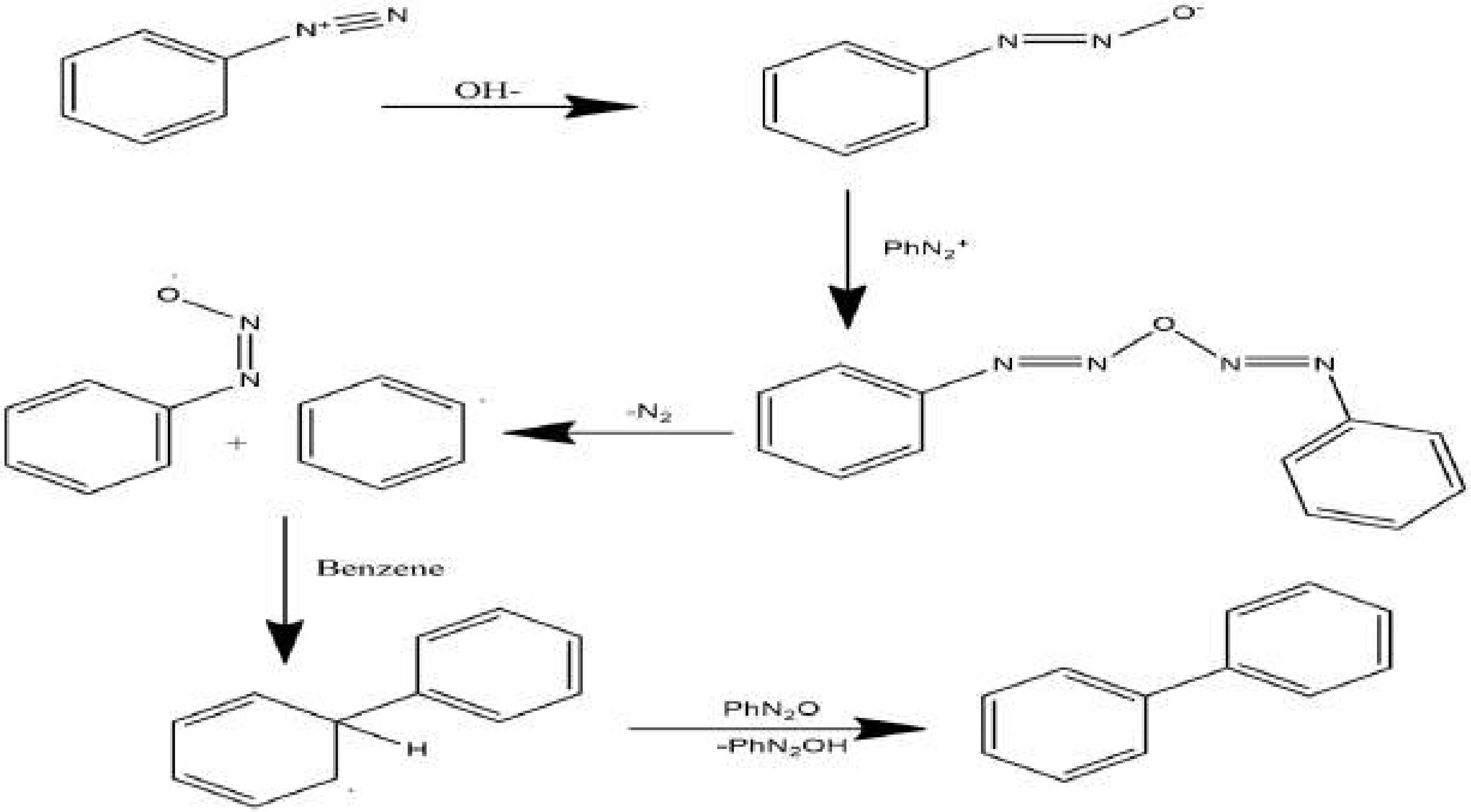
1.In the first step diazonium salt derivative is reacted with hydroxide ion and forms diazonium oxide which further reacts with PhN2+ and forms a double ring compound.

2. After this, loss of nitrogen gas takes place which dissociates the molecule into two fragments out of which one is diazonium oxide and other onother is a radical form of benzene.

3. After that diazonium oxide reacts with benzene group and forms a biaryl group with the presence of aryl intermediate in this product i.e. H ion is present in this compound.

Continued…

- 4. This H atom reacts with PhN2O which immediately form PhN2OH which readily get eliminated from the compound and it forms a biaryl product. Mechanism can be shown as follows:



M. Sc. II(Organic Chemistry) Sem-I
Advanced Synthetic Methods :
Use of following in Organic Synthesis

Dr S. D. Shirke

Department of Chemistry

Vivekanand College, Kolhapur

1. Microwave Oven :

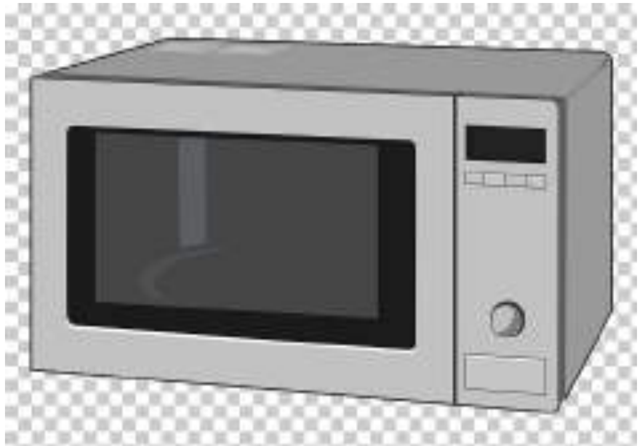
Principle : Microwaves are produced inside the **oven** by an electron tube called a magnetron. The **microwaves** are reflected within the metal interior of the **oven** where they are absorbed by food. **Microwaves** cause water molecules in food to vibrate, which produce heat that cooks the food. A microwave oven is a kitchen appliance that heats ,bakes and cooks the food.

- Microwave ovens convert electrical energy into a form of electromagnetic radiation called microwaves.
- Microwaves are radio waves with frequencies 2500 MHz and the radio waves at this frequency has an important characteristic property. The food particles that contain water, fats and sugars absorb microwave radiation through atoms and molecules of food and absorption of this radiation gives them energy and make to move significantly, collide and due to the friction they produce heat for warming and cooking the food material. Microwave is electromagnetic radiation spectrum.

Microwave oven

- **History :**

1.History: It was invented accidently in 1945 by Dr. Percy LeBaron Spencer.
2. During world war II, two scientist made the magnetron, a tube that produce microwaves.
3. In 1967 the first countertop, domestic oven was introduced.
4. By 1975 sales of microwave ovens exceeded - Percy Spencer's microwave oven.



Radarange, the first commercially available microwave oven.
Technical Design ➤ Basic design of a Microwave oven.
- The basic design of a microwave oven is simple.

Accessories :A transformer, a magnetron, a stirrer, a waveguide and a control panel is located on the external casing where oven cavity is normally bolted. There is a front panel on the oven body by which user can control/program the machine.

Structure of Microwave oven

- Parts of MW oven :

1. Magnetron •Magnetron is a high-powered vacuum tube which generates microwave. •It's a diode type electron tube. •There's a cathode at the center of a magnetron. •A ring shaped anode surrounds the cathode. A Magnetron. Here the yellow part in the middle is cathode and the surrounding bronze part is anode._

2. Waveguide •A waveguide is a structure that guides microwaves. A rod shaped metal waveguide. •Generally waveguide is made of brass, copper, silver, aluminum, or any metal that has low bulk resistivity.

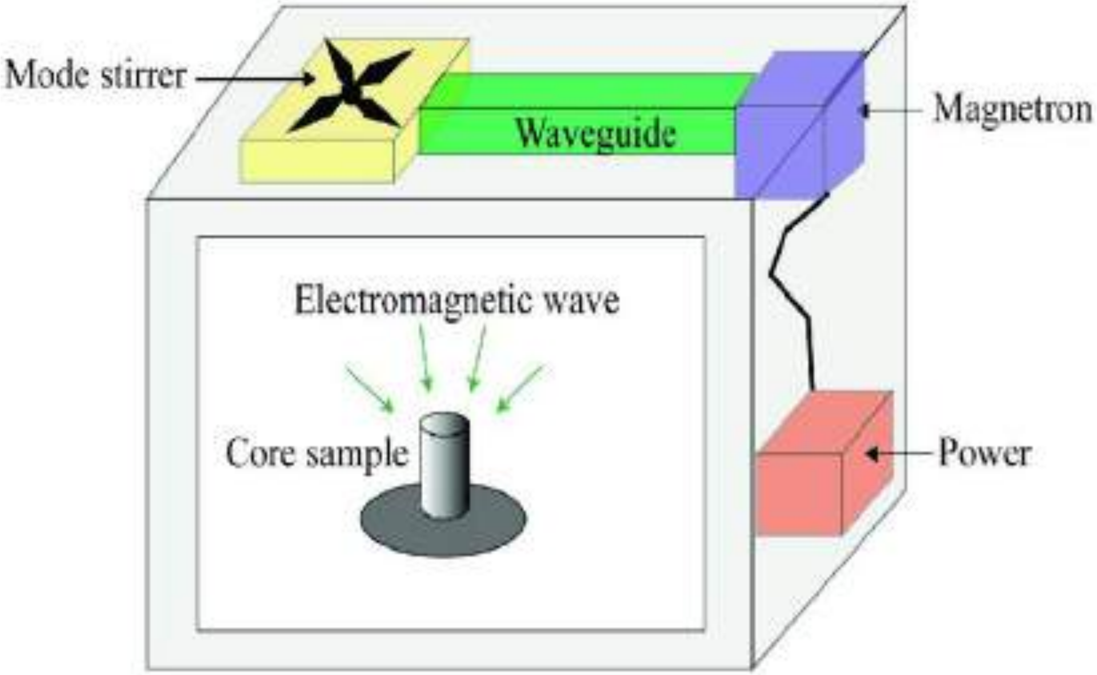
_3. Stirrer. •Looks like a fan. •Usually situated at the top of the cavity. •Moves the microwaves around the cavity.

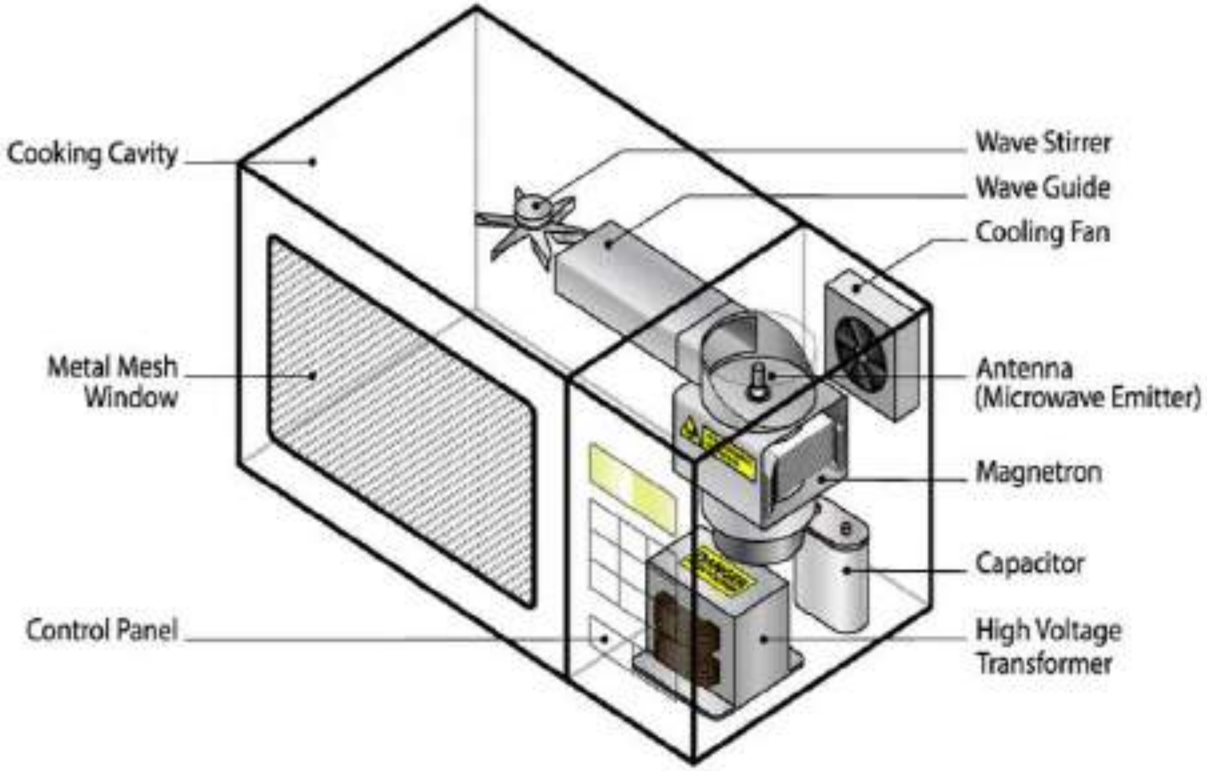
_ Main part is A microwave oven. •The main chassis is placed on the pallet, and the cavity is screwed on to the chassis. And the door is attached next to the cavity. •A front panel that allows the operator to select the various settings and features available for cooking is attached to the chassis. •This is the place where every parts of a microwave oven is organized.

Internal structure of Microwave oven :

Microwaves are generated in a magnetron which feeds via a waveguide into the cooking chamber. This cuboid chamber has metallic walls and so acts as a Faraday cage. The front door, made of glass, and the light bulb cavity are both covered by metal grids.

Magnetron tube has tank circuits in it •Streams of electrons amplify tank oscillations •A loop of wire extracts energy from tanks. •A short wave antenna emits the microwaves



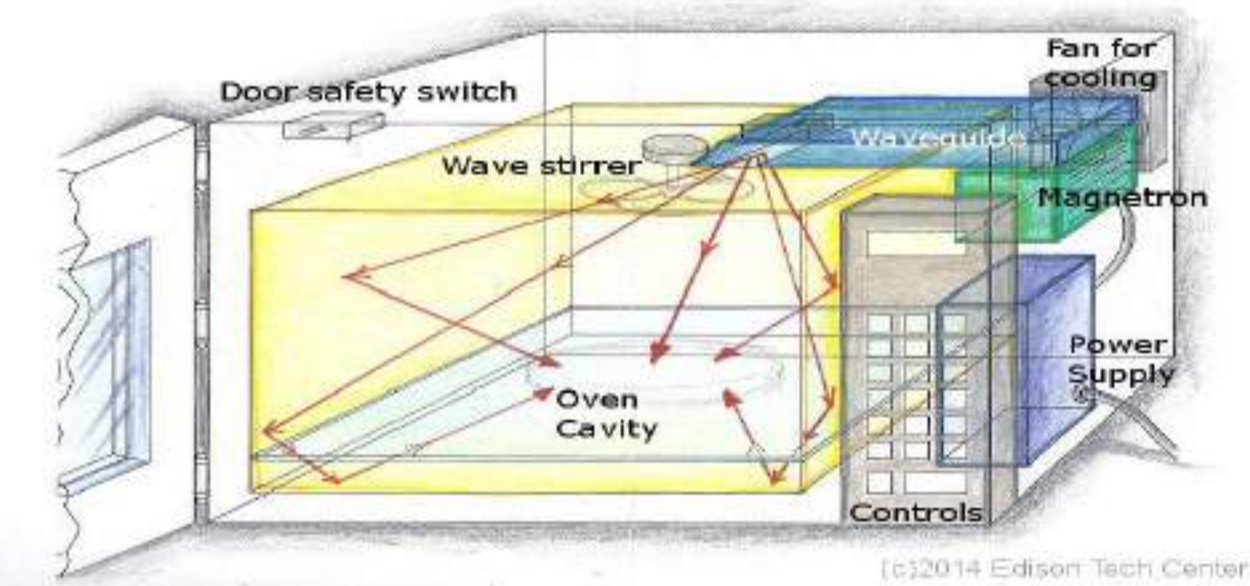


Continued…

- . A complex design of a microwave oven. .How it Works!

Working Principles : Microwave oven works by passing non-ionizing microwave radiation , usually at a frequency 2.45 GHz(a wavelength of 12.24 cm), through the food…water, fat & other substances in the food absorb energy from the microwaves in a process called dielectric heating .

Many molecules (water) are electric dipoles, meaning that they have "+"charge at one end & - charge at other end therefore rotate as they try to align themselves & this rotation put them into motion which creates heat through friction among the molecules.

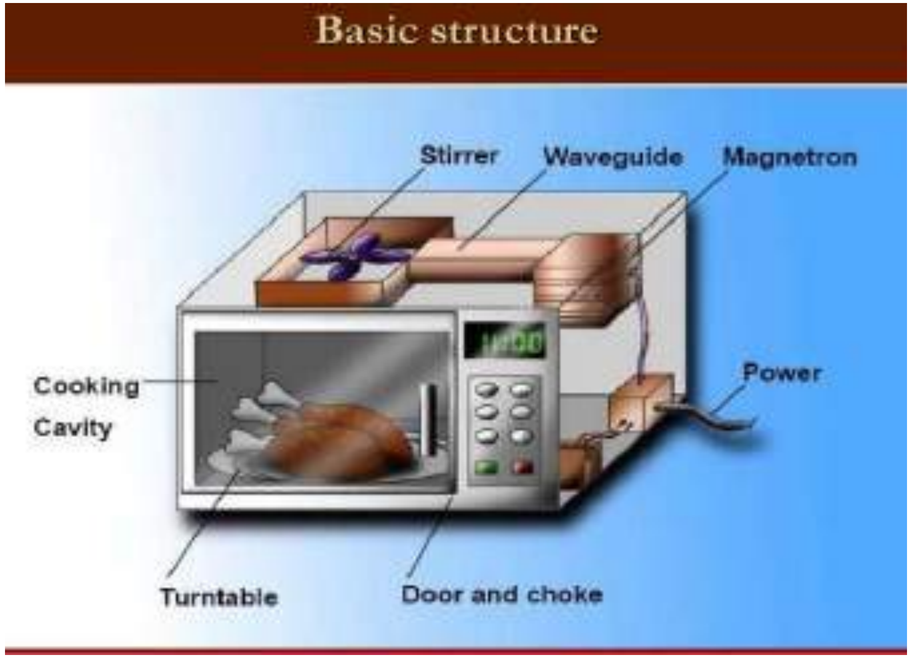


Continued…

- Working principle :

Microwave Oven generates electromagnetic waves(called microwaves), which makes water move.
•Microwave causes molecules to vibrate. •Vibration creates friction.
•Friction produces the heat that cook the food.

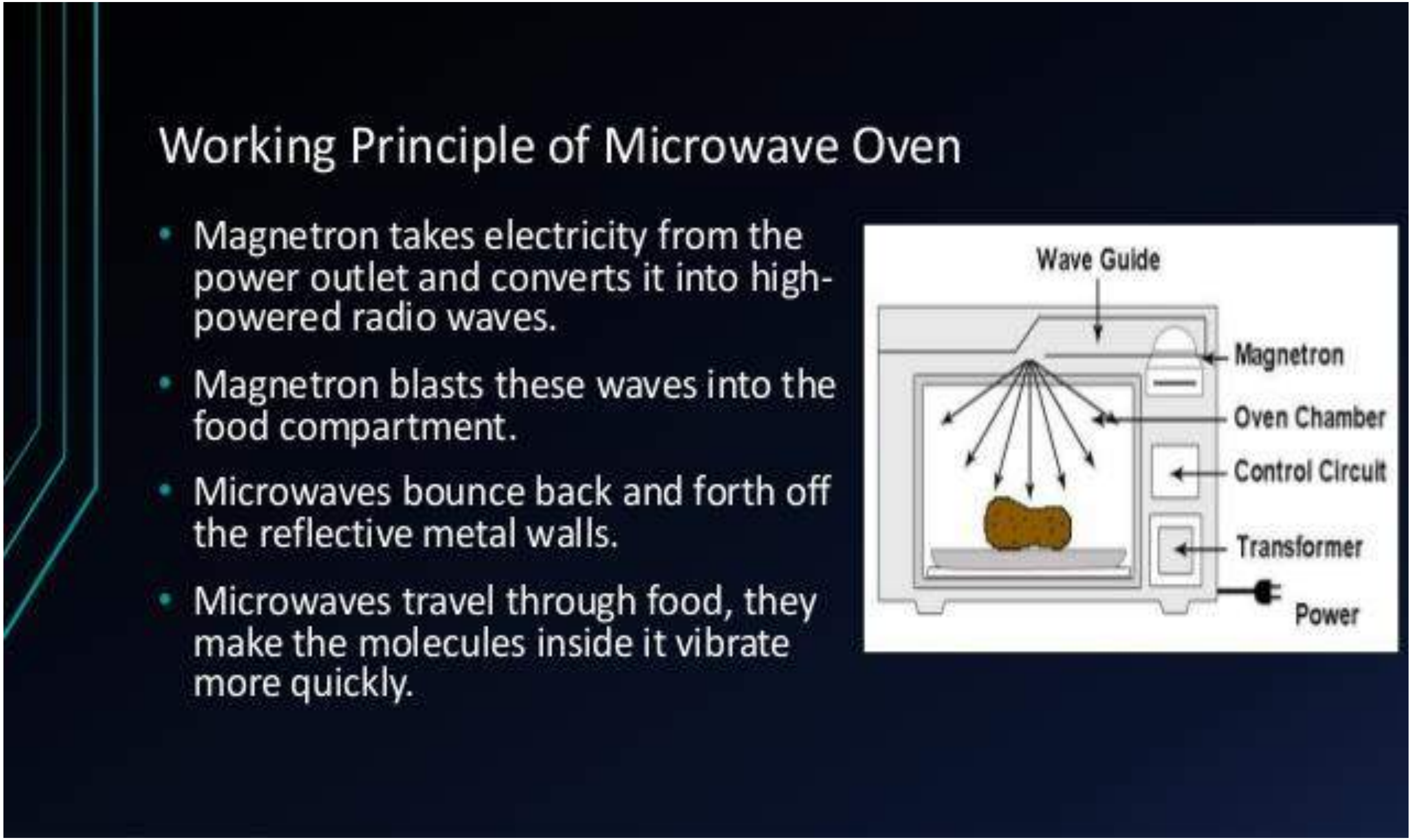
Heating Effect •Microwave heating is more efficient on liquid water.
•Much less so on fats & sugars(which have less molecular dipole moment). •And frozen water (where the molecules are not free to rotate).



Advantages

1. It saves time and energy.
2. It is safer than general fuel stoves.
3. Taste of the foods remain same.
4. If properly used, microwave cooking does not affect the nutrient content of foods.
5. Reduces the consumption of oil.

Continued…



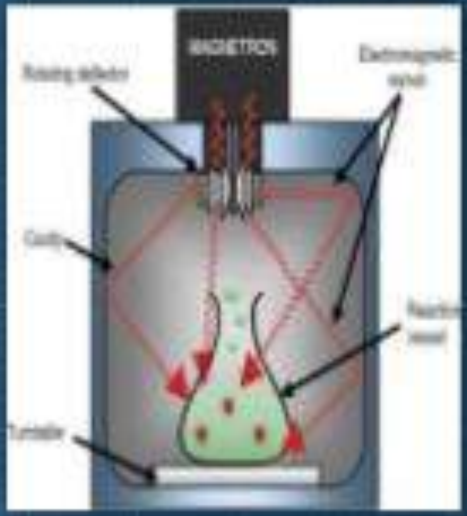
Working Principle of Microwave Oven

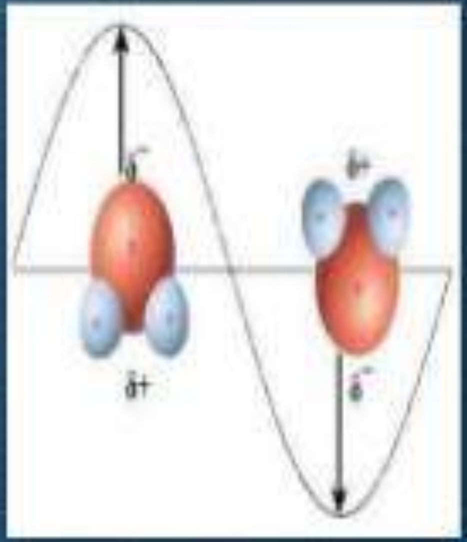
- Magnetron takes electricity from the power outlet and converts it into high-powered radio waves.
- Magnetron blasts these waves into the food compartment.
- Microwaves bounce back and forth off the reflective metal walls.
- Microwaves travel through food, they make the molecules inside it vibrate more quickly.

➤ Working Principles

- Microwave oven works by passing non-ionizing microwave radiation , usually at a frequency 2.45 GHz(a wavelength of 12.24 cm), through the food…water, fat & other substances in the food absorb energy from the microwaves in a process called dielectric heating .

- Many molecules (water) are electric dipoles, meaning that they have “+”charge at one end & “-” charge at other end therefore rotate as they try to align themselves & this rotation put them into motion which creates heat.





Containers used in MW Oven.

- According to the World Health Organization (WHO), microwaving **food** is generally **safe**. However, microwaving in **plastic containers** is associated with increased leaching — the transfer or leaking of chemicals into **food**. Note that even if a **plastic container** is labeled "**microwave safe**," that simply means it won't melt.

Glass and **ceramic** containers, along with plastic utensils that are labeled "microwave safe" are good choices. Do not use **glass** or **ceramic** that contains a metal . Polymer like Teflon and polystyrene can be used.

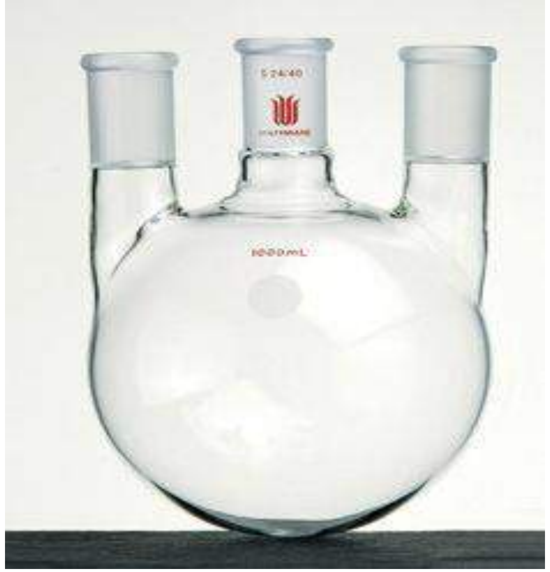
Tall containers are used in oven - round bottom flasks, conical flasks made up of standard Borosil, J-sil glass.

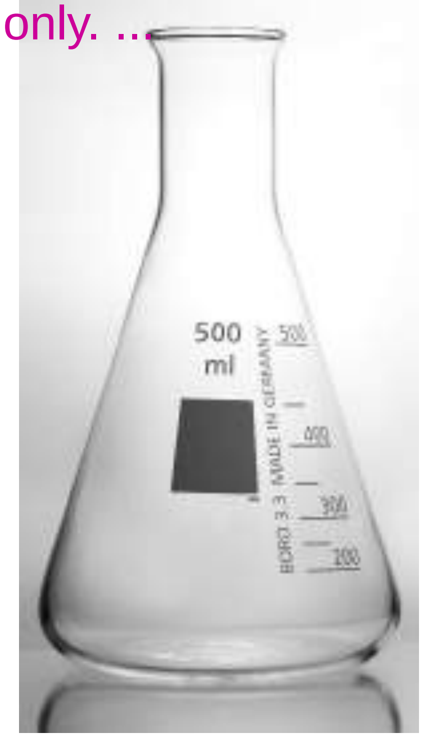
Use **containers** that are round or oval in **shape** which can help to heat food more evenly. With **square** or **rectangular shaped containers**, the corners tend to receive more energy, which can cause the food to overcook in these areas

Containers used for MW reactions.

- Microwave cookwares :
  - Aluminium foil: Shielding only. ...
  - Dinnerware: **microwave-safe** only. ...
  - Glass jars: always remove the lid. ...
  - Glassware: heat-resistant, **oven** glassware only. ...
  - **Oven** cooking bags: follow manufacturer's instructions. ...
  - Plastic: **microwave-safe** only. ...
  - Plastic wrap: **microwave-safe** only. ...

Glass and ceramic containers, along with plastic utensils that are labeled "microwave safe" are good choices. Do not use glass or ceramic that contains a metal rim.





Microwave Cookware

- **Glass and ceramic-**
  - Must be oven-proof
- **Stoneware, china, pottery-** no metal trim or metallic glaze
- **Plastic-** only microwave safe
- **Paper-** do not use recycled paper (may contain chemicals or metal fragments)

Precautions using Microwave oven :

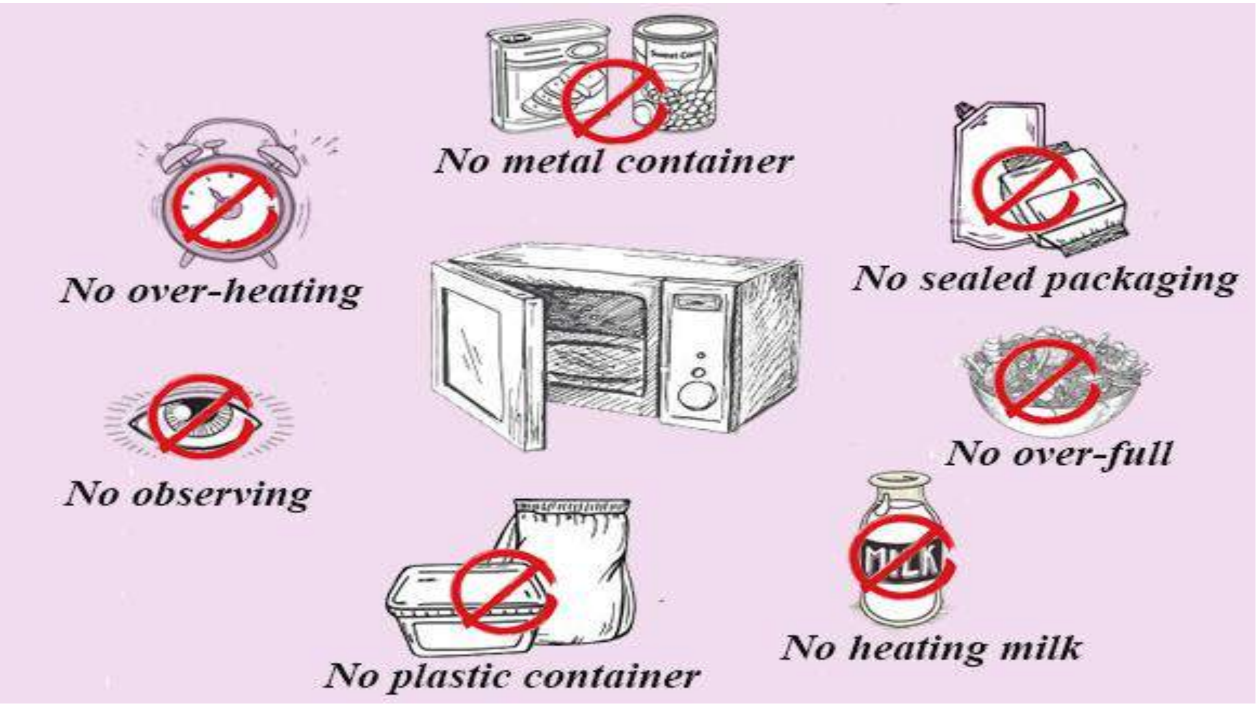
MICROWAVE RULES

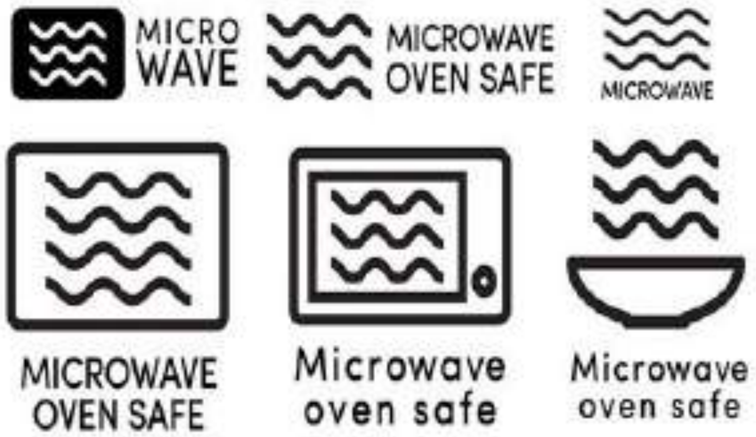
✓ **DO:**

- Cover items while cooking
- Clean up spills & splatters
- Reset the microwave controls when finished

☒ **DON'T:**

- Leave items unattended
- Interrupt the cooking of other people's food
- Put metal items in microwave such as tin foil





DO NOT PUT METAL OR FOIL IN THIS OVEN

Continued..

Microwave Oven Do's and Don'ts

Do's

- ✓ Clean up any messes or spills
- ✓ Reset the microwave controls when finished
- ✓ Cover all items in microwave
- ✓ Remove any metal/foil packaging

Don'ts

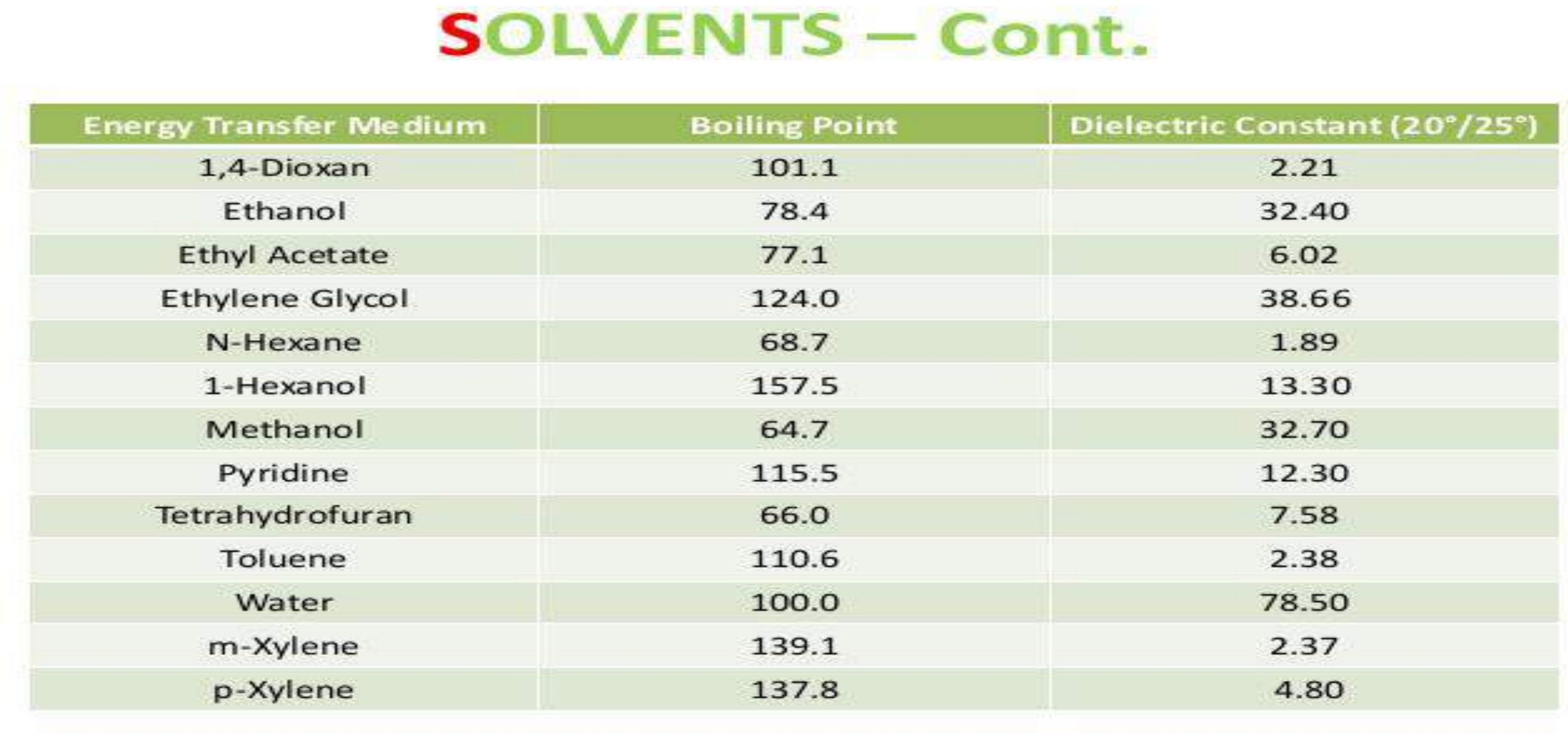
- ✗ Don't take someone else's food out of the microwave while cooking
- ✗ Don't leave your food unattended while it is in the microwave
- ✗ Don't fail to let the appropriate person know if the microwave is broken or faulty

MICROWAVE OVEN SAFETY

- Do not look closely into oven when it is switched on.
- People with heart pacemakers must not use this oven.
- Metal containers such as tin foil must not be placed in this oven.

Solvents used in Microwave reactions

- Polar **solvents having high dielectric constants are used** .
- (e.g. DMF, NMP, DMSO, methanol, ethanol, and acetic acid) work well with **microwaves** due to their polarity, you can be sure that the temperature will rise substantially with



SOLVENTS – Cont.

Energy Transfer Medium	Boiling Point	Dielectric Constant (20°/25°)
1,4-Dioxan	101.1	2.21
Ethanol	78.4	32.40
Ethyl Acetate	77.1	6.02
Ethylene Glycol	124.0	38.66
N-Hexane	68.7	1.89
1-Hexanol	157.5	13.30
Methanol	64.7	32.70
Pyridine	115.5	12.30
Tetrahydrofuran	66.0	7.58
Toluene	110.6	2.38
Water	100.0	78.50
m-Xylene	139.1	2.37
p-Xylene	137.8	4.80

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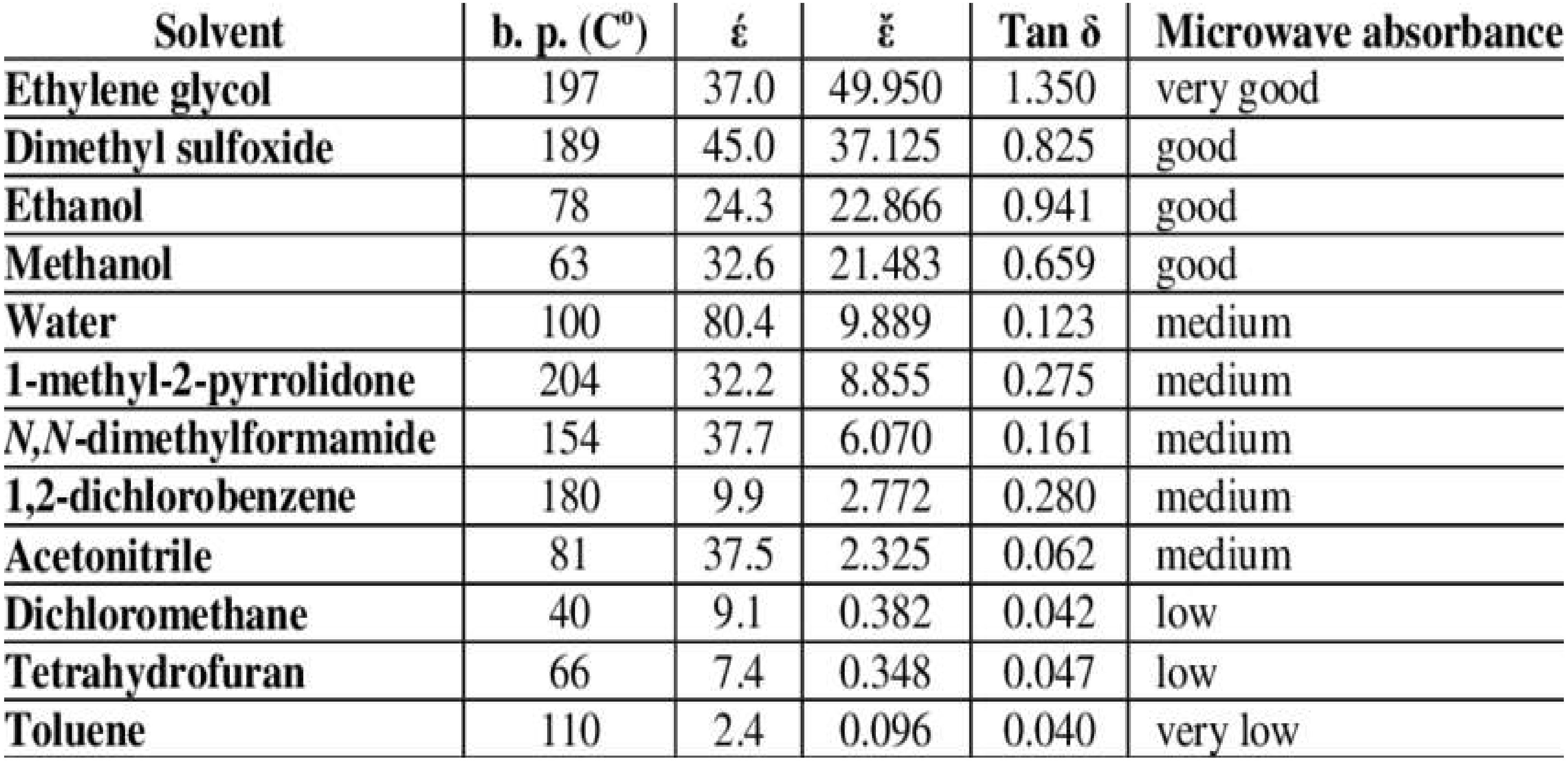
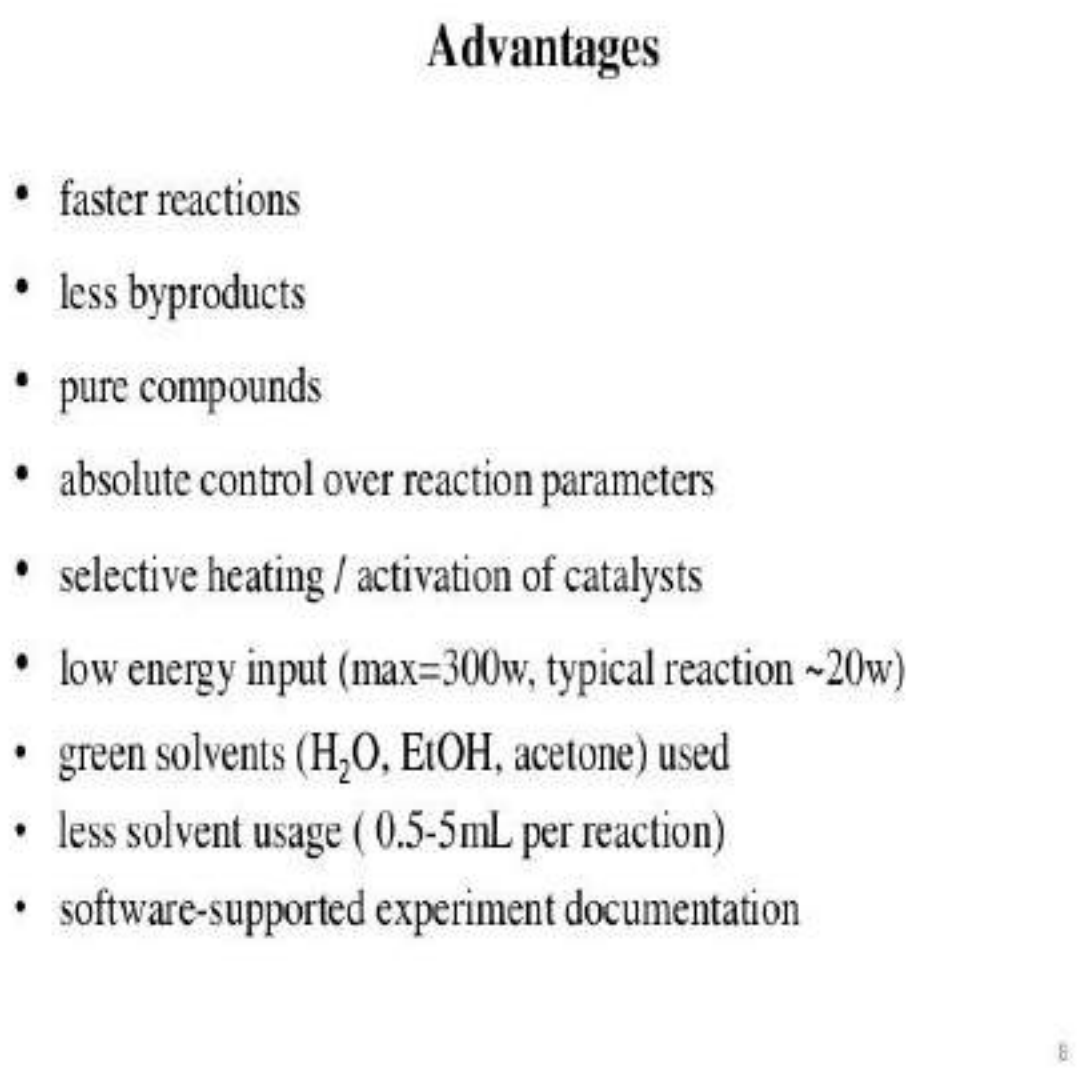


Solvent	b. p. (C°)	έ	ε̆	Tan δ	Microwave absorbance
Ethylene glycol	197	37.0	49.950	1.350	very good
Dimethyl sulfoxide	189	45.0	37.125	0.825	good
Ethanol	78	24.3	22.866	0.941	good
Methanol	63	32.6	21.483	0.659	good
Water	100	80.4	9.889	0.123	medium
1-methyl-2-pyrrolidone	204	32.2	8.855	0.275	medium
***N,N*-dimethylformamide**	154	37.7	6.070	0.161	medium
1,2-dichlorobenzene	180	9.9	2.772	0.280	medium
Acetonitrile	81	37.5	2.325	0.062	medium
Dichloromethane	40	9.1	0.382	0.042	low
Tetrahydrofuran	66	7.4	0.348	0.047	low
Toluene	110	2.4	0.096	0.040	very low

Advantages :



Advantages

- faster reactions
- less byproducts
- pure compounds
- absolute control over reaction parameters
- selective heating / activation of catalysts
- low energy input (max=300w, typical reaction ~20w)
- green solvents (H_2O, EtOH, acetone) used
- less solvent usage (0.5-5mL per reaction)
- software-supported experiment documentation

MERITS:

- ✓ Higher temperatures
- ✓ Faster reactions, lesser by products, pure compounds.
- ✓ Absolute control over reaction parameters
- ✓ Selective heating
- ✓ Energy efficient,rapid energy transfer
- ✓ Easy access to high pressure performance
- ✓ Does things that can't be done conventionally.
- ✓ Rapid synthesis results in lesser evaporation of solvents

Applications of Microwave Oven

APPLICATION

3. Commercial and industrial applications:

- Microwave oven
- Drying machines - textile, food and paper industry for drying clothes, potato chips, printed matters etc.
- Food process industry - Precooling / cooking, pasteurization / sterility, hat frozen / refrigerated precooled meats, roasting of food grains / beans.
- Biomedical Applications (diagnostic / therapeutic) - diathermy for localized superficial heating, deep electromagnetic heating for treatment of cancer, hyperthermia (local, regional or whole body for cancer therapy).

Industrial /Chemical / Applications of Microwave Heating

Food Processing

- + Defrosting
- + Drying / roasting / baking
- + Pasteurization

Drying Industry

- + Wood, fibers, textiles
- + Pharmaceuticals
- + Brick / concrete walls

Polymer Chemistry

- + Rubber curing, vulcanization
- + Polymerization

Ceramics/Materials

- + Alumina sintering
- + Welding, smelting, gluing

Plasma

- + Semiconductors

Waste Remediation

- + Sewage treatment

Analytical Chemistry

- + Digestion
- + Extraction
- + Ashing

Biochemistry / Pathology

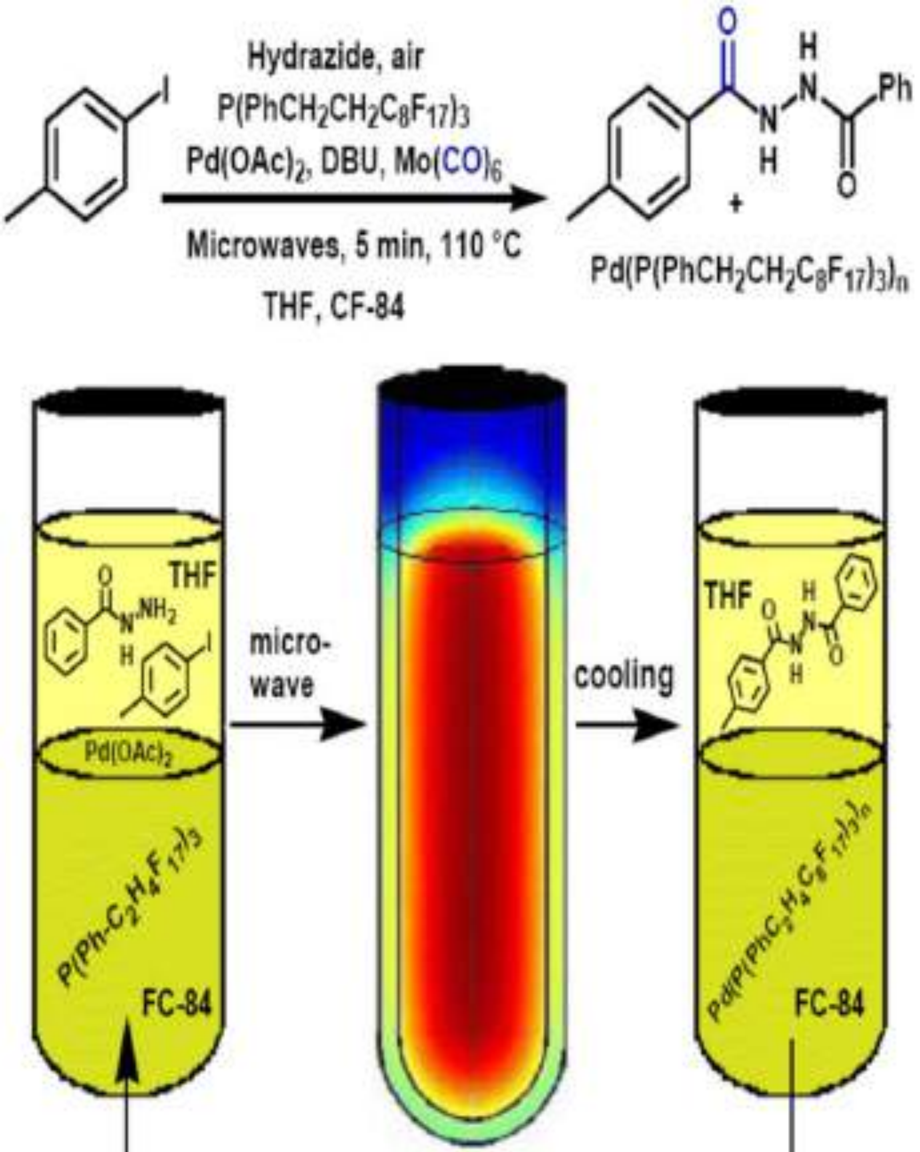
- + Protein hydrolysis
- + PCR, proteomics
- + Tissue fixation
- + Histoprocessing

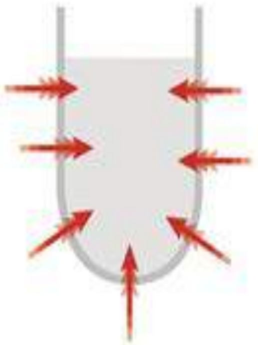
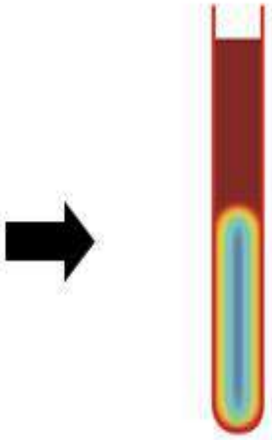
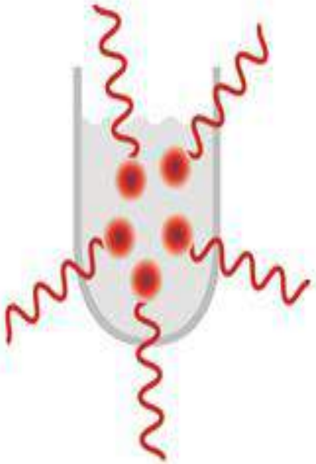
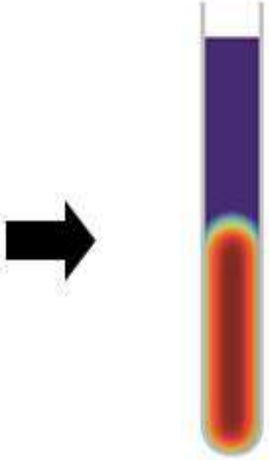
Medical

- + Diathermy, tumor detection
- + Blood warming
- + Sterilization (Anthrax)
- + Drying of catheters

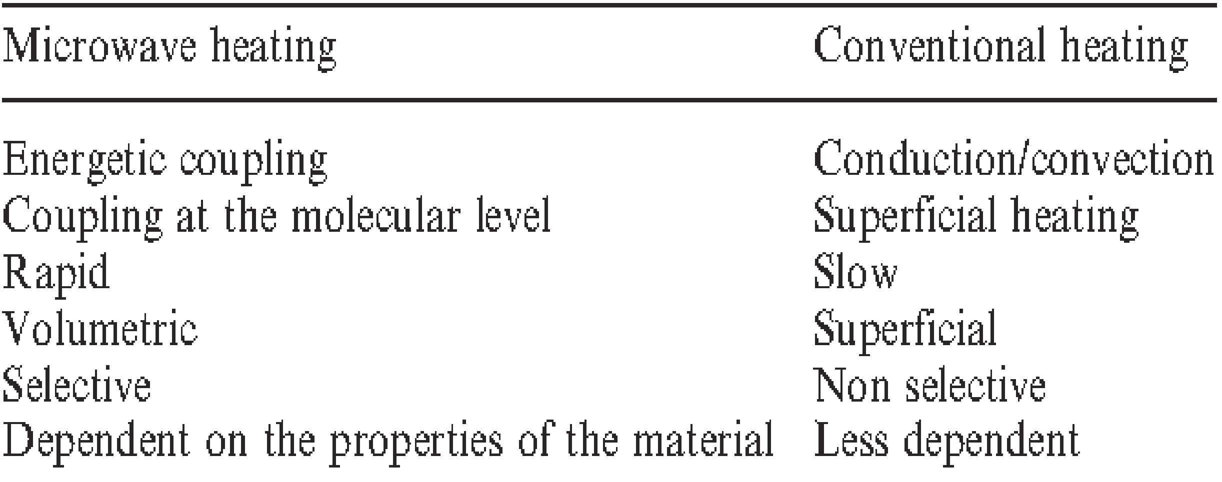
Dunărea de Jos University Galaţi

Mechanism of microwave heating :

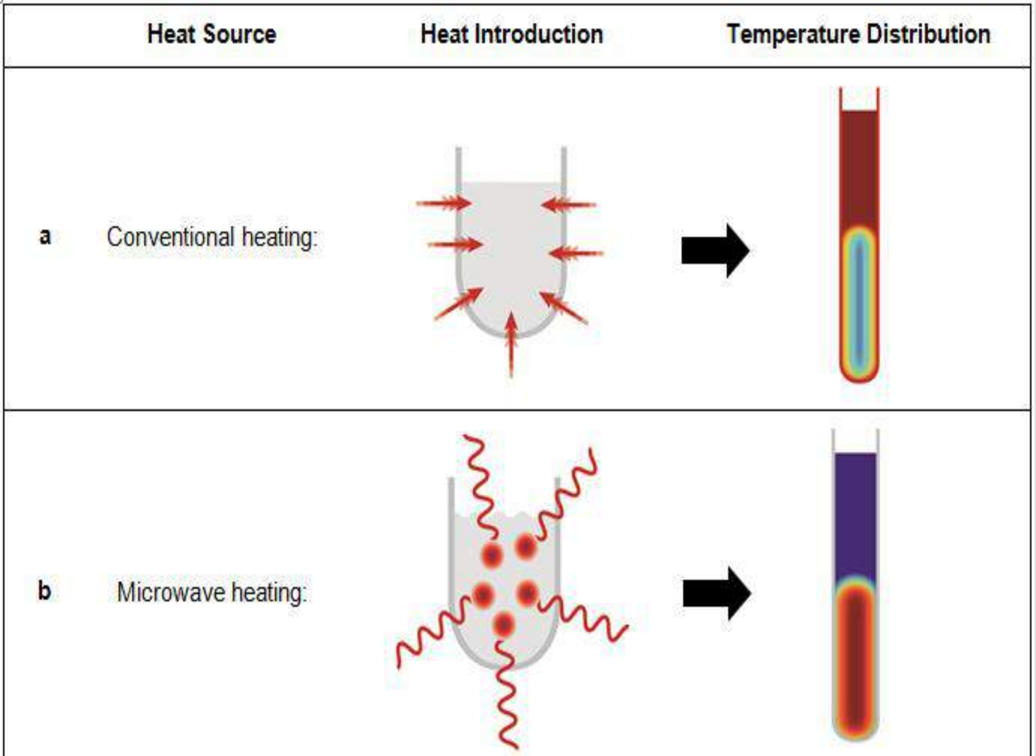


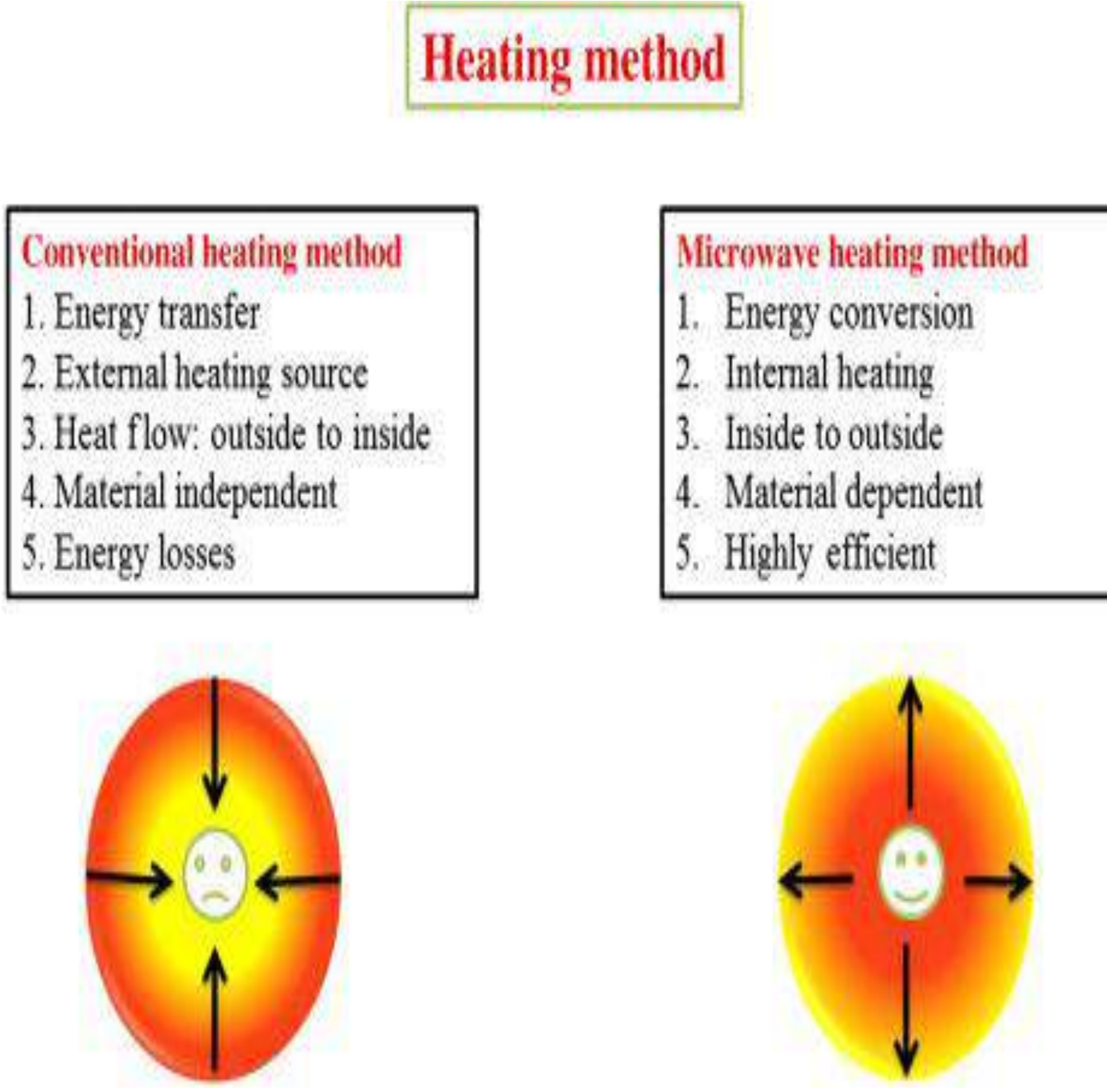
	Heat Source	Heat Introduction	Temperature Distribution
a	Conventional heating:		
b	Microwave heating:		

Difference between MW heating and Conventional heating



Microwave heating	Conventional heating
Energetic coupling	Conduction/convection
Coupling at the molecular level	Superficial heating
Rapid	Slow
Volumetric	Superficial
Selective	Non selective
Dependent on the properties of the material	Less dependent



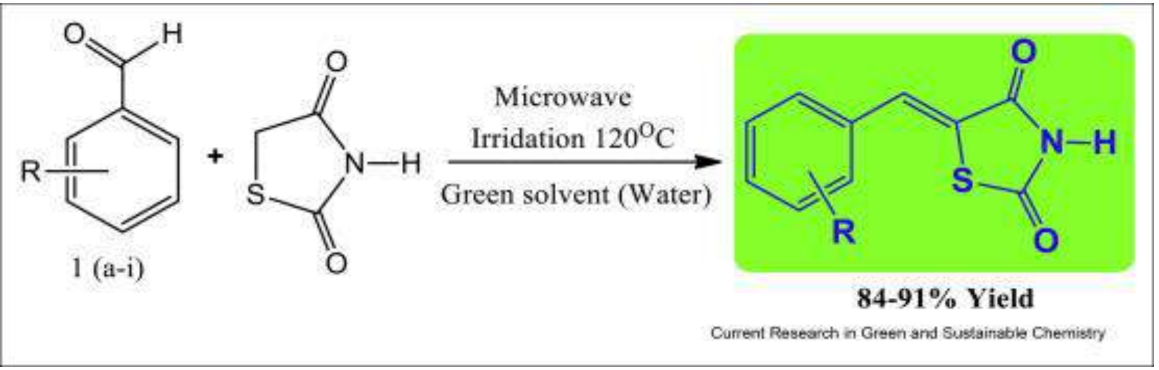


Heating method

Conventional heating method
1. Energy transfer
2. External heating source
3. Heat flow: outside to inside
4. Material independent
5. Energy losses

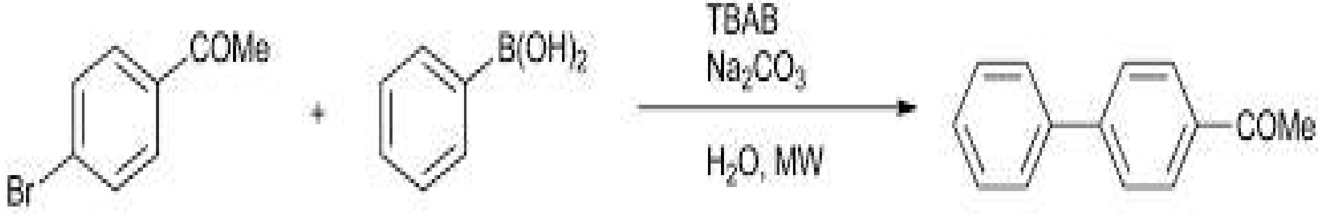
Microwave heating method
1. Energy conversion
2. Internal heating
3. Inside to outside
4. Material dependent
5. Highly efficient

1.Microwave assisted reactions in aqueous medium :

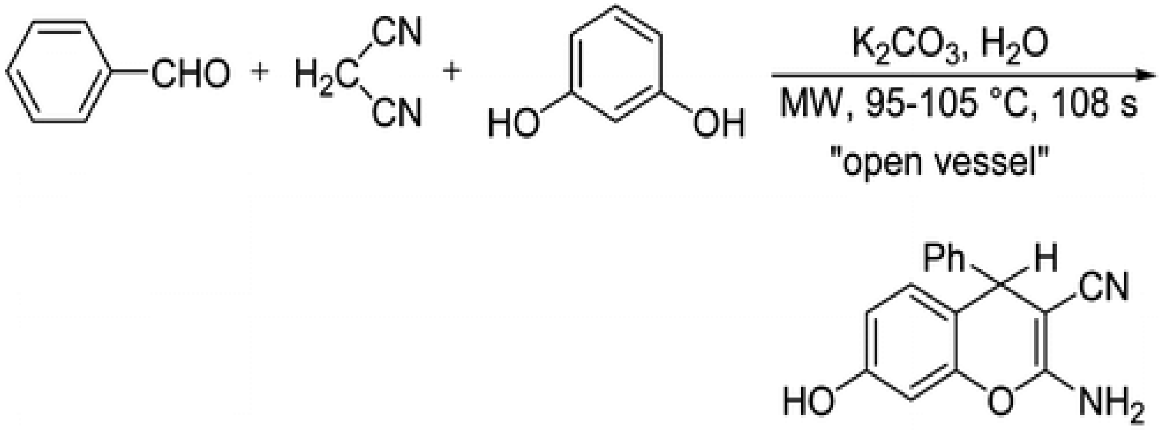


84-91% Yield

Current Research in Green and Sustainable Chemistry

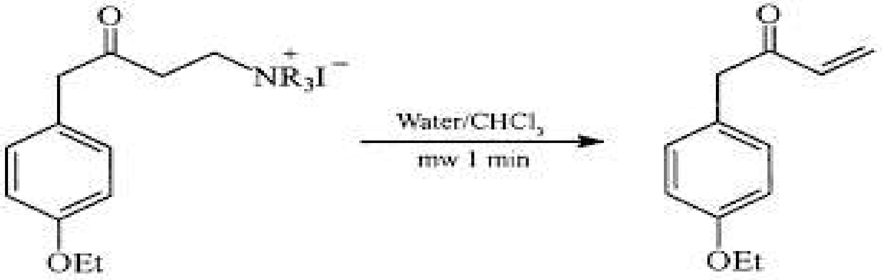


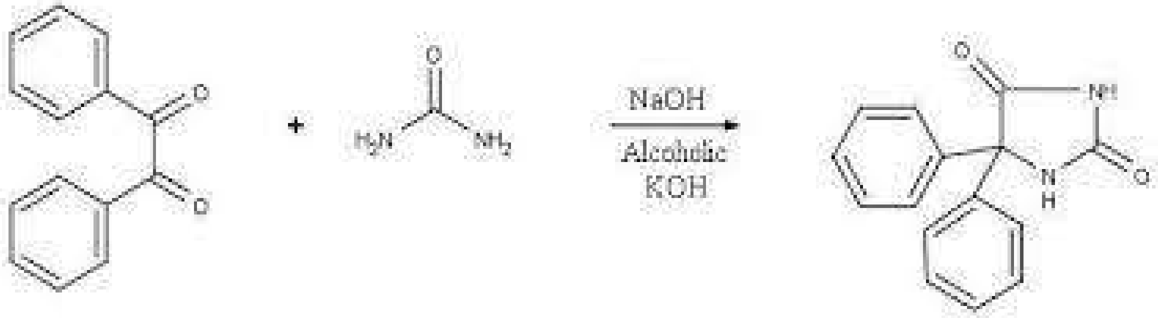
MW, 100 W, 150°C, 5 min 100%
CH, 150°C, 120 min 94%



71 (91%)

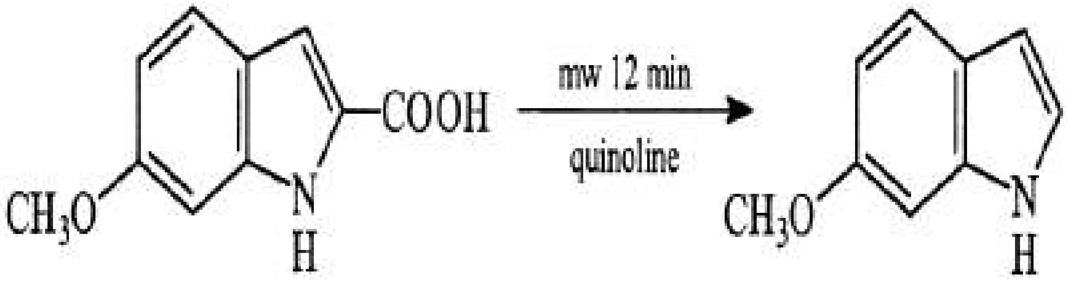
+ 7 related examples (87-93%)





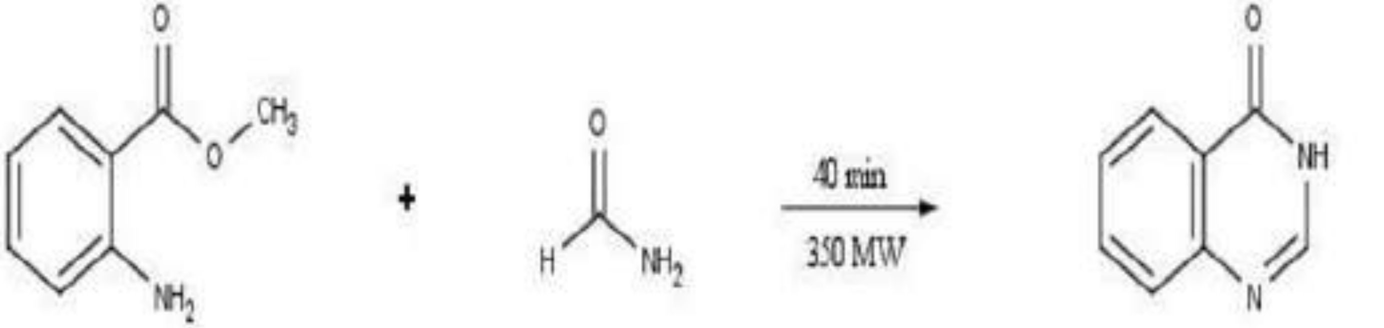
Benzil Urea 5,5 - diphenyl hydantoin

2. Microwave reactions in Organic medium :



6-Methoxy indole-2-carboxylic acid

6-Methoxyindole
99%

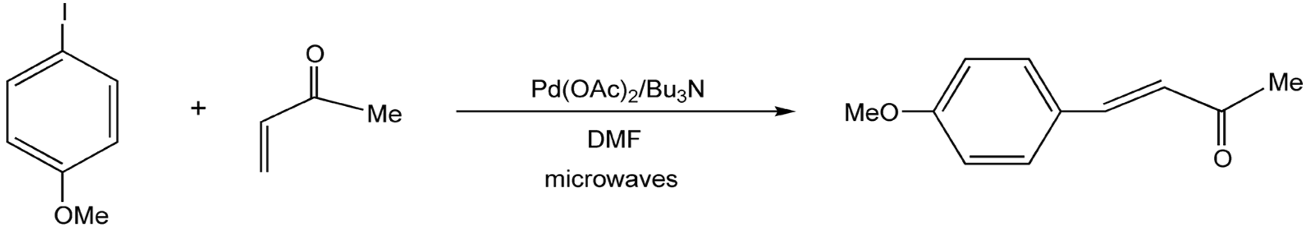


Methyl anthranilate

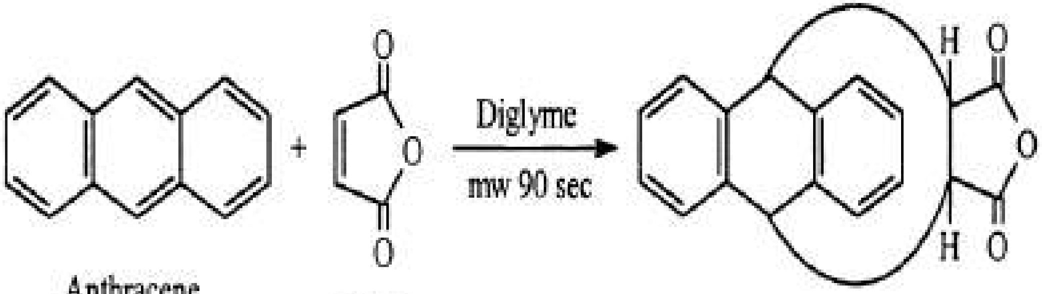
Formamide

3H- quinazoline - 4 - one

Scheme-V



Scheme 1

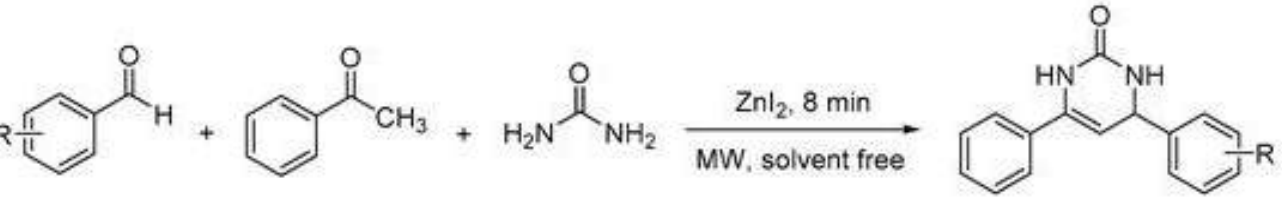


Anthracene

Maleic anhydride

Adduct
80%

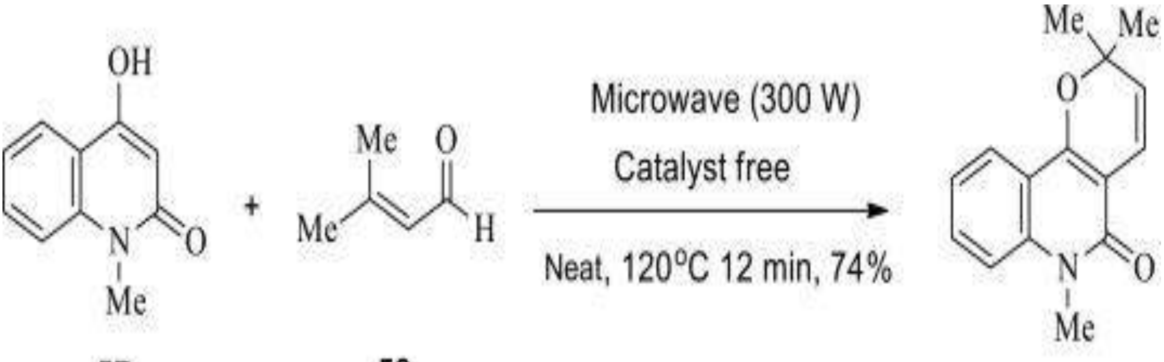
3.Solvent free reactions :



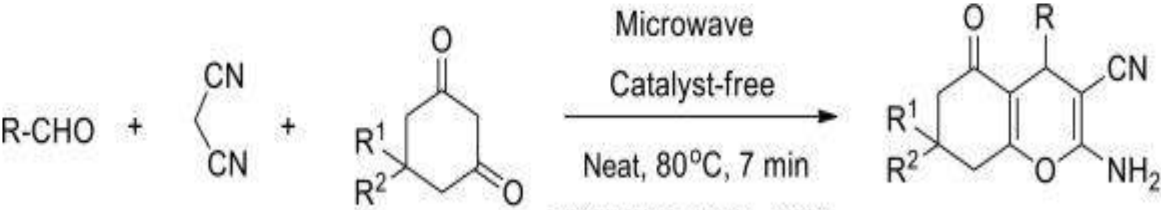
176 177 178 179

71%-96%

R = H, 2-MeO, 3-MeO, 4-MeO, 4-Cl, 2,6-Cl$_2$, 2,4-Cl$_2$, 4-OH, 4-*t*-Bu, 3-MeO-4-OH, 3-Br, 3,5-Br$_2$-4-OH, 4-Me, 3,4-(MeO)$_2$, 2-Cl, 4-CHO



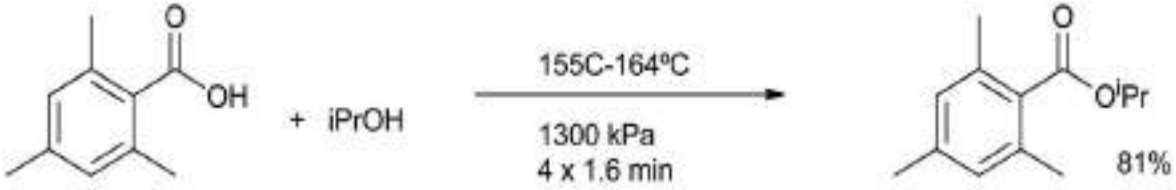
57 58 59

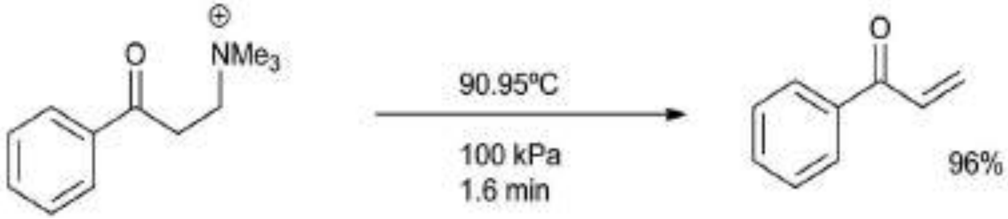


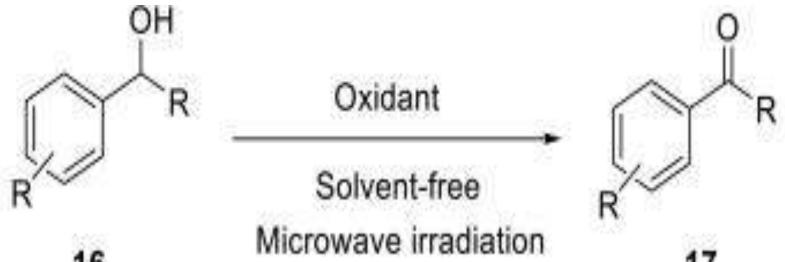
1 49 50 51

R^1/R^2 = H, Me

R = C$_6$H$_5$, 4-MeC$_6$H$_4$, 4-ClC$_6$H$_4$, 4-NO$_2$C$_6$H$_4$, 4-OMeC$_6$H$_4$, 3-OHC$_6$H$_4$, 4-OH-3-OMeC$_6$H$_3$, 3,4-OCH$_2$O-C$_6$H$_3$, 4-BrC$_6$H$_4$, 2-furyl, cyclohexyl







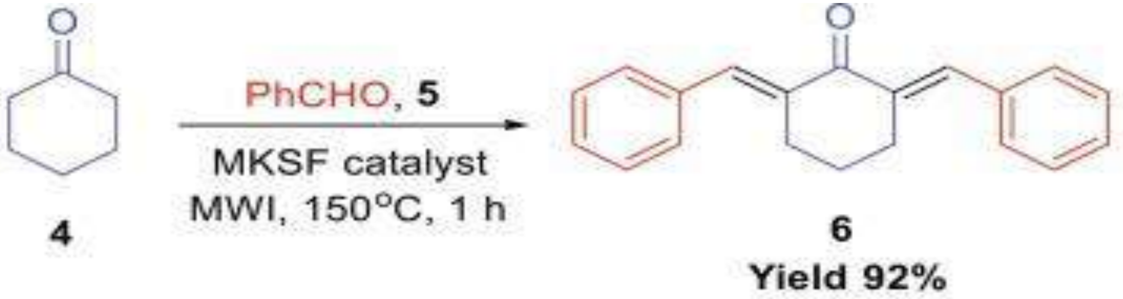
16 17

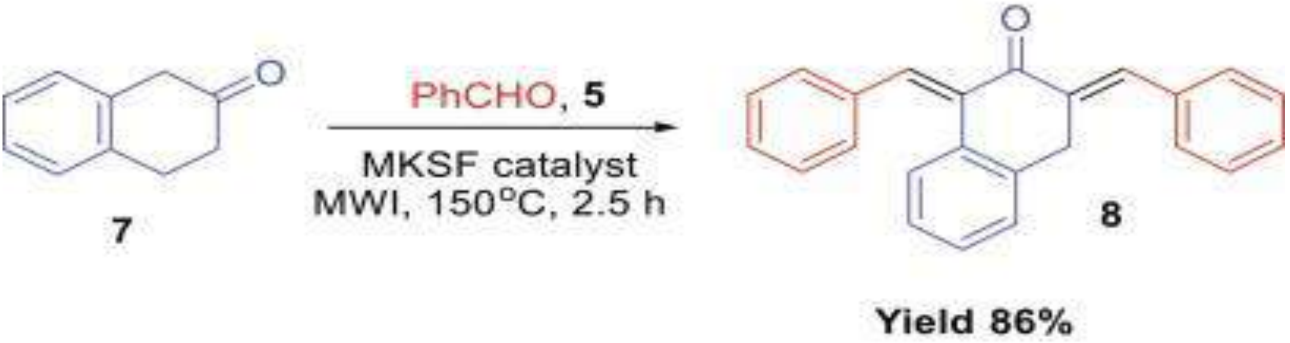
R = H, Aryl

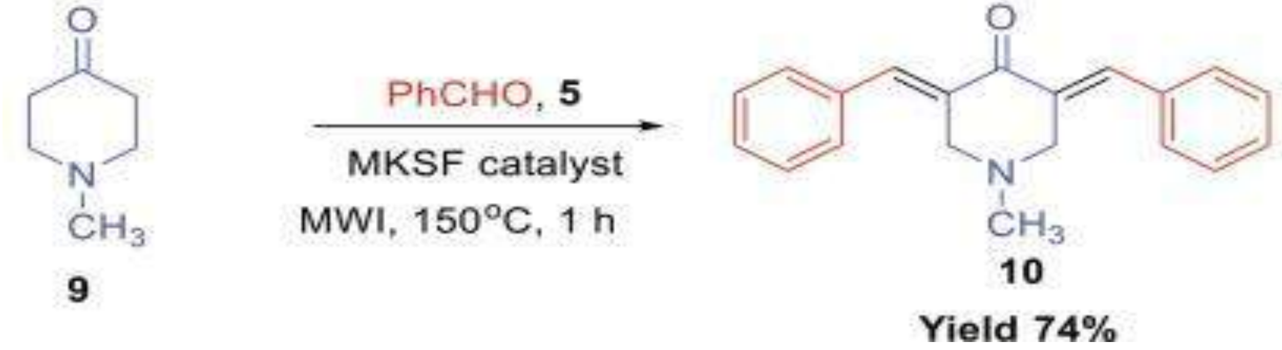
Magtrieve: 10–30 min: **41%–98%**
MnO$_2$: 3 h: **32.8%–37.7%** (conversion)
HIO$_3$/K-10 clay or silica gel: 50–120 s: **87%–94%** (K10-clay) and **70%–89%** (silica gel)
KIO$_4$, Et$_4$NBr: 1–8 min: **15%–98%**

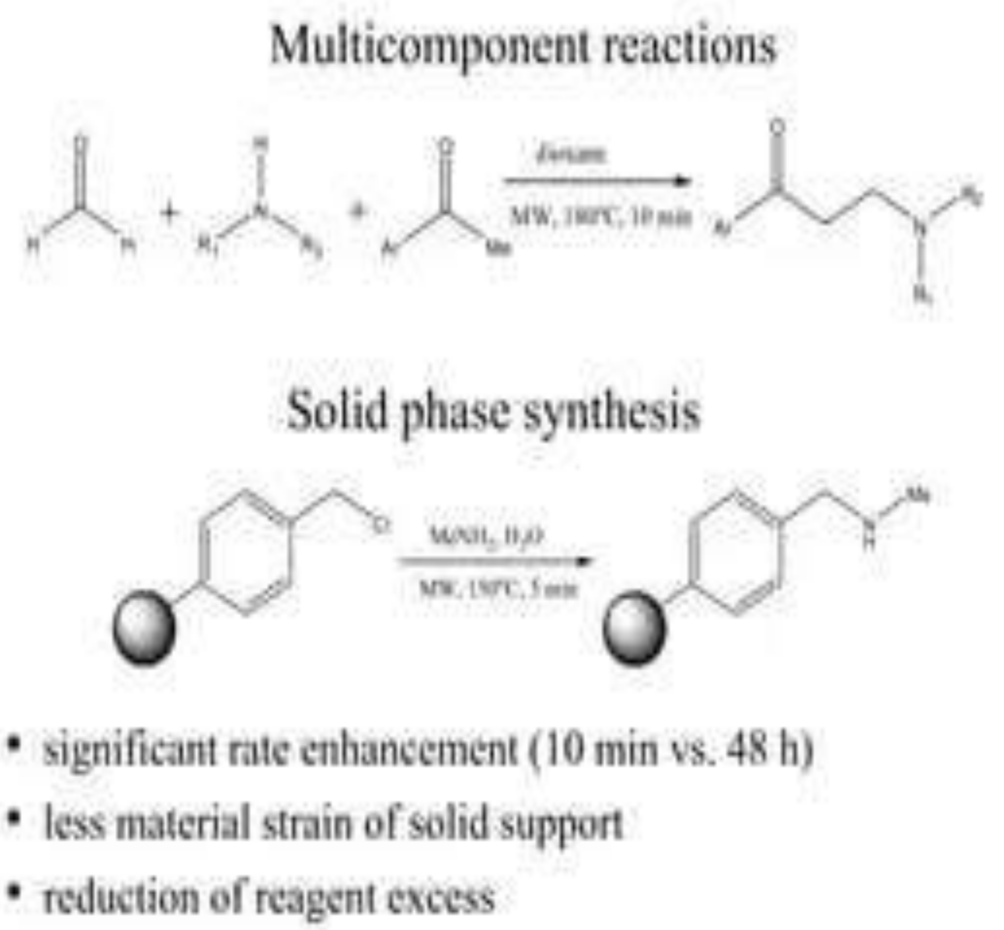
4. Microwave assisted reactions with solid support :

- Examples







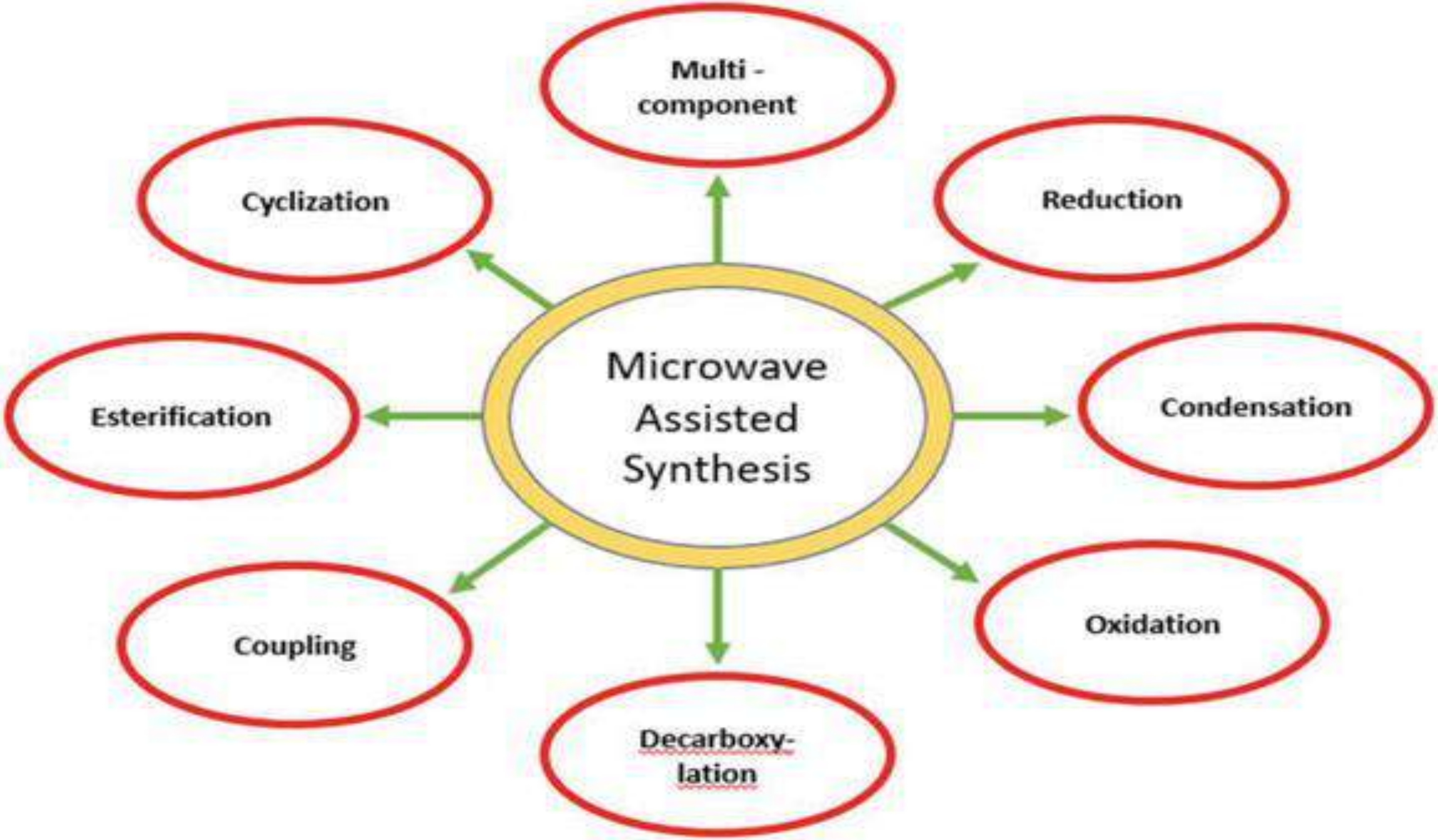


Multicomponent reactions

Solid phase synthesis

- significant rate enhancement (10 min vs. 48 h)
- less material strain of solid support
- reduction of reagent excess

Use of Microwaves in Organic Synthesis :



Diazonium Salts

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What are Diazonium salts ?

Diazonium - di' refers to 'two', azo is indicative of 'nitrogen' and ium implies that it is cationic in nature. Hence, they have two nitrogen atoms with one being charged. **Benzenediazonium chloride ($C_6H_5N_2^+Cl^-$), benzene diazonium hydrogen sulfate ($C_6H_5N_2^+HSO_4^-$)**, etc. are some of the examples of the diazonium salt.

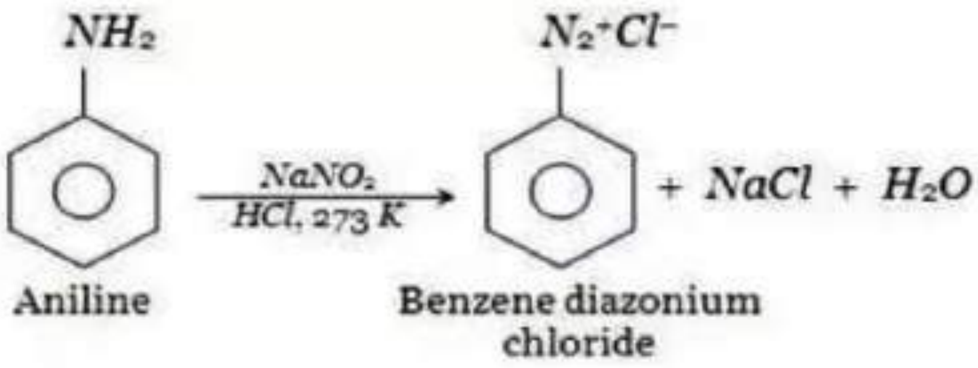
Diazonium salts are **a group of organic compounds that share one common R-NH_2+X^- group of functions**. R is an organic group, in R-NH_2+X^-. For example, the group alkyl or aryl. And azo compounds may also be formed by reacting with other aromatic compounds by diazonium salts.

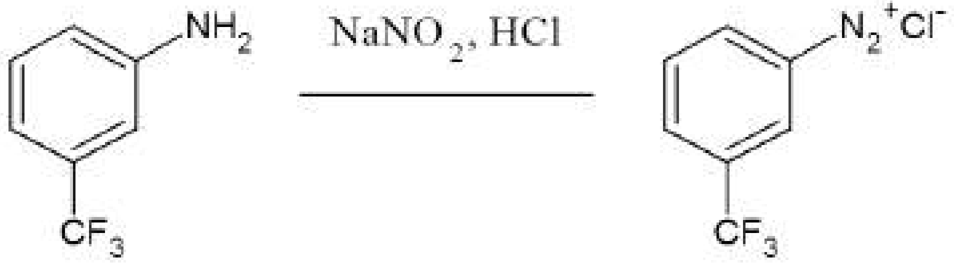
The process of producing diazonium salts or diazonium compounds is called diazotization or diazoniation or diazotation. It was 1st given by Peter Griess. Thus, diazotization is the process used in the formation of diazonium salts through aromatic amines. Examples of mineral acids are **HCl , H2SO4, HBF4 etc.**

One of the most common methods of preparation of diazonium salt is by the **reaction of nitrous acid with aromatic amines**. The reaction of aniline (aromatic amine) with nitrous acid results in

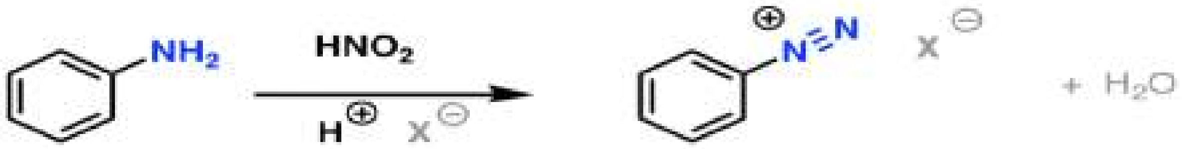
Preparation :

- One of the most common methods of preparation of diazonium salt is by the **reaction of nitrous acid with aromatic amines**. The reaction of aniline (aromatic amine) with nitrous acid results in the formation of the diazonium salt. This salt is the benzene diazonium chloride.



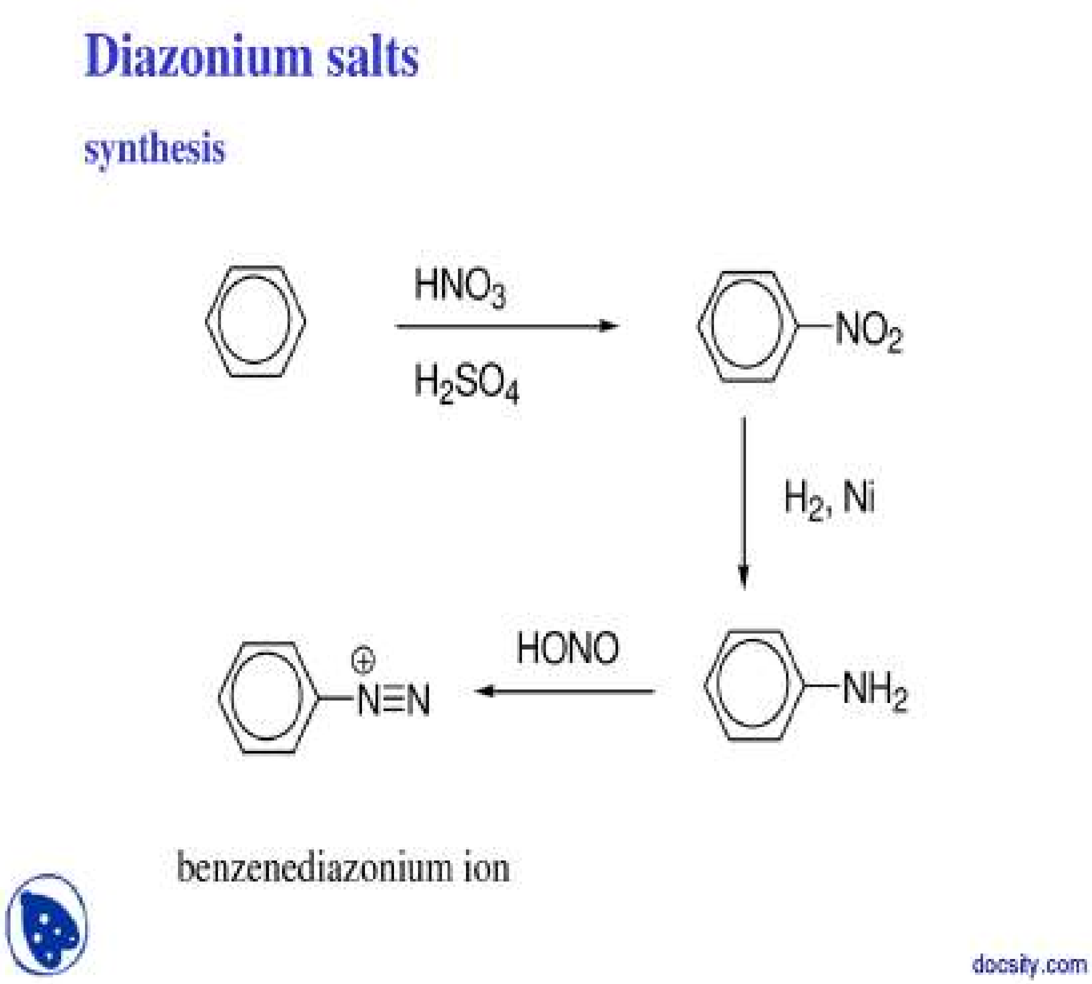


Formation of Diazonium Salts From Aromatic Amines



- N_2 is an excellent leaving group;
- Aryl diazonium salts are moderately stable, because aryl cations are slow to form *(alkyl diazonium salts are generally too unstable for practical use)*

Preparation from Benzene, by nitration and reduction



Diazonium salts

synthesis

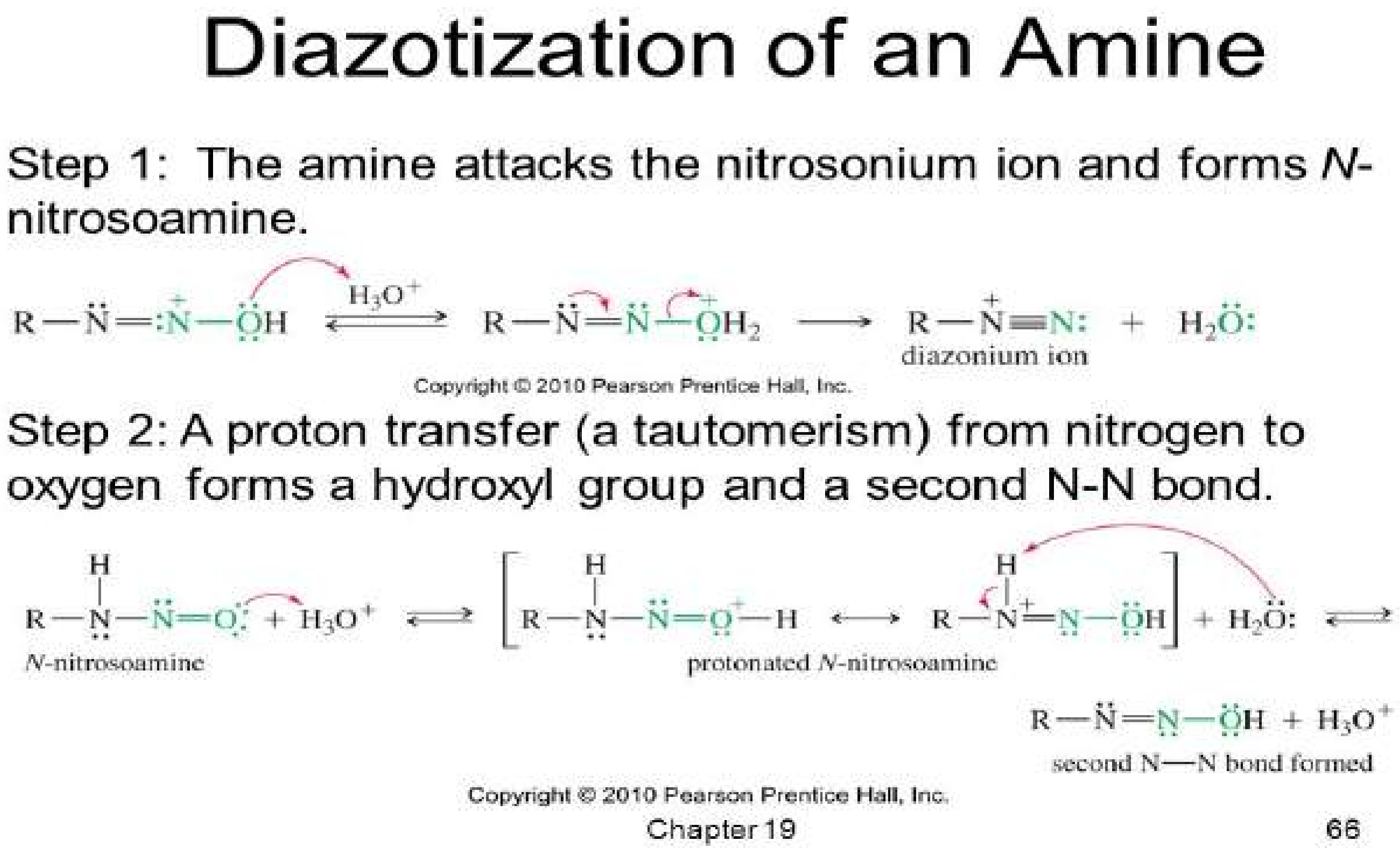
benzenediazonium ion

docsity.com

Diazotization is usually carried out at low temperatures between 0 – 5 °C. We have to maintain low temperatures because if the temperature is above 5 °C, diazonium salts which are in aqueous solution tend to decompose explosively.

During diazotization and coupling reactions we have to maintain a low temperature because at high temperature diazonium salts forms other by products and give phenol by reacting with water at high temperature which would lead to a large error in your experiments.

Reaction Mechanism :



Diazotization of an Amine

Step 1: The amine attacks the nitrosonium ion and forms *N*-nitrosoamine.

$$R-\ddot{N}=\overset{+}{:N}-\ddot{O}H \xrightleftharpoons{H_3O^+} R-\ddot{N}=\ddot{N}-\overset{+}{O}H_2 \longrightarrow R-\overset{+}{N}\equiv N: + H_2\ddot{O}:$$

diazonium ion

Step 2: A proton transfer (a tautomerism) from nitrogen to oxygen forms a hydroxyl group and a second N-N bond.

$$\underset{N\text{-nitrosoamine}}{R-\overset{H}{\underset{..}{N}}-\ddot{N}=\ddot{O}:} + H_3O^+ \rightleftharpoons \underset{\text{protonated } N\text{-nitrosoamine}}{\left[R-\overset{H}{\underset{..}{N}}-\ddot{N}=\overset{+}{O}-H \longleftrightarrow R-\overset{H}{\overset{+}{N}}=N-\ddot{O}H\right]} + H_2\ddot{O}: \rightleftharpoons$$

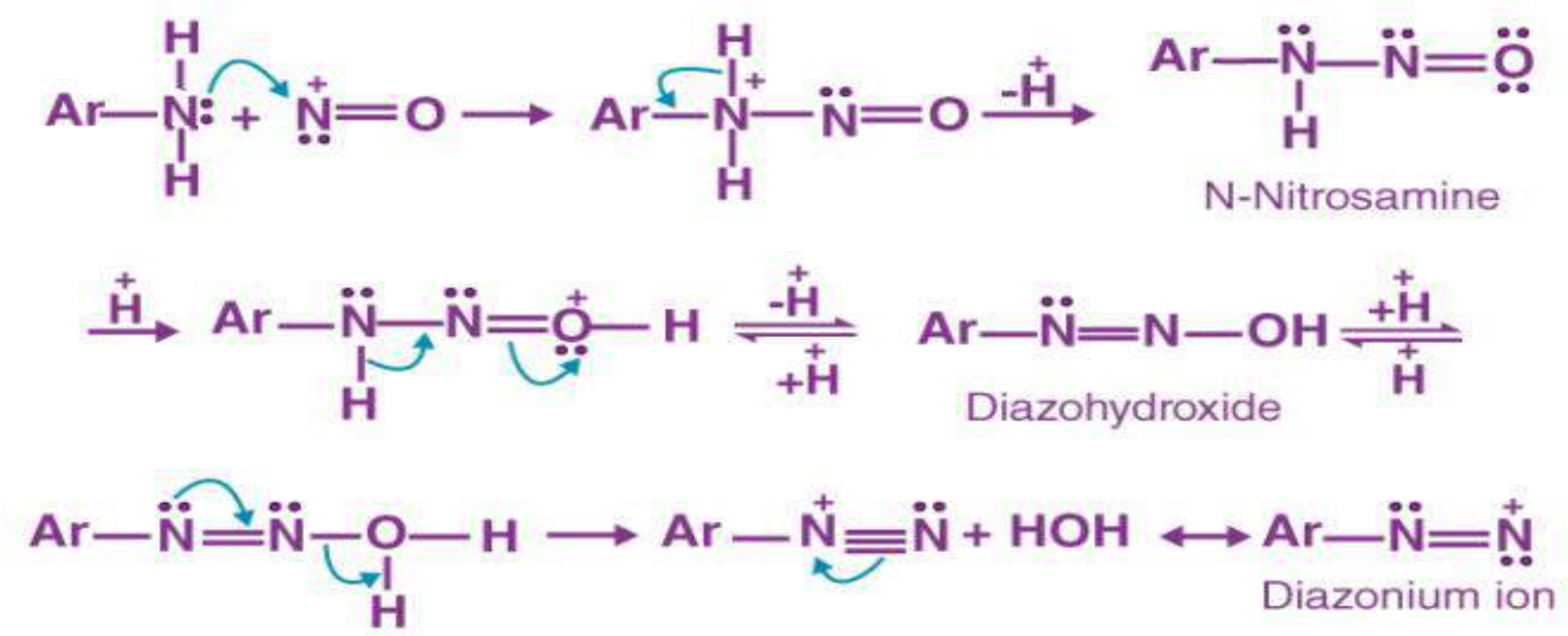
$$R-\ddot{N}=N-\ddot{O}H + H_3O^+$$

second N—N bond formed

Reaction Mechanism :

The first step is formation of a new N–N bond, which occurs through attack of the nitrosonium ion by the aromatic amine (Step 1). This is followed by two proton transfers from nitrogen to oxygen (Steps 2 and 3) accompanied by reorganization of the pi bonding framework [forming N–N (pi), breaking N–O (pi)]. The final step is formation of the nitrogen-nitrogen triple bond accompanied by expulsion of water (Step 4).

Mechanism for formation of diazonium ions from aromatic amines giving diazonium salt



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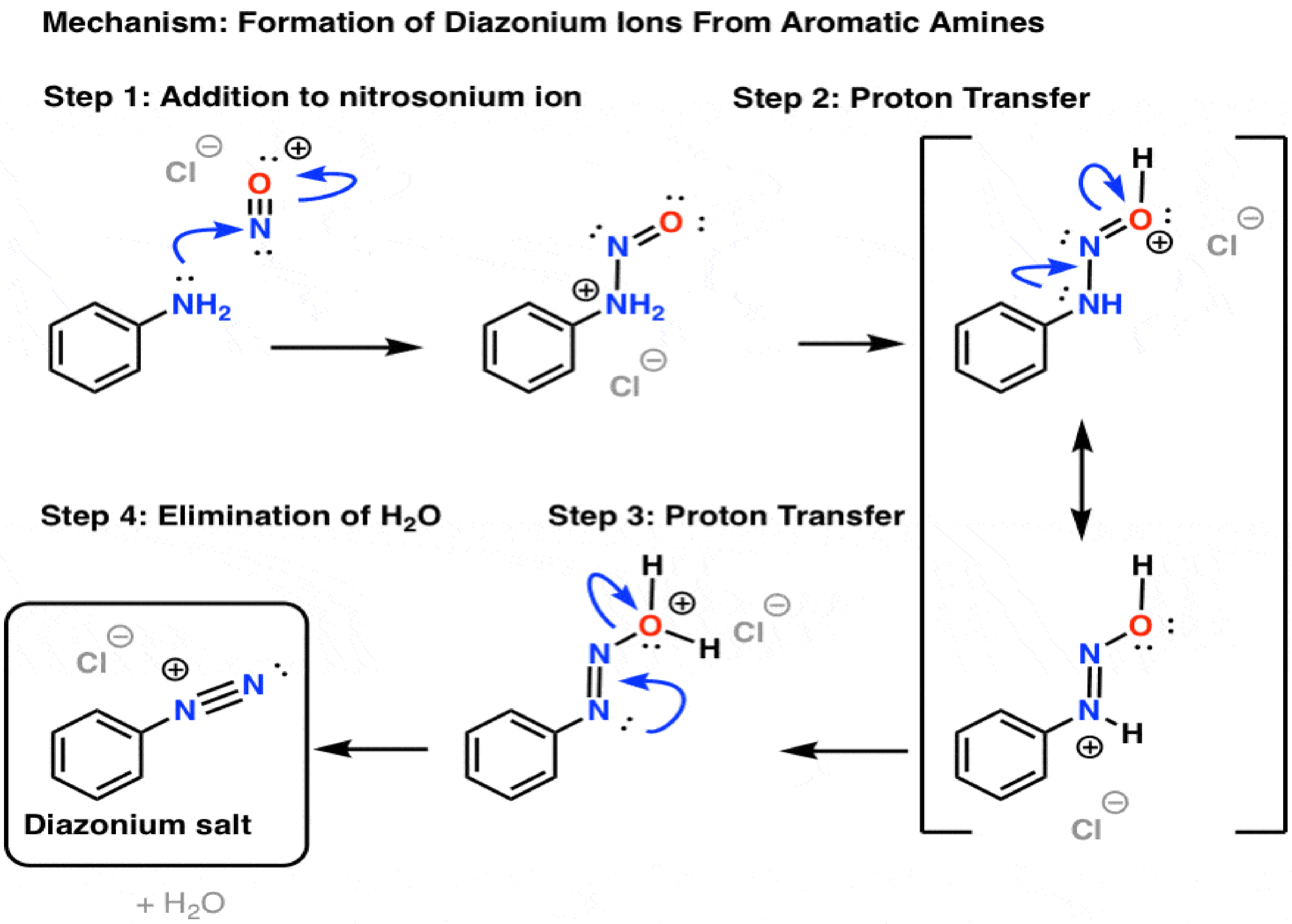
Mechanism: Formation of Diazonium Ions From Aromatic Amines
Step 1: Addition to nitrosonium ion
Step 2: Proton Transfer
Step 3: Proton Transfer
Step 4: Elimination of H_2O
Diazonium salt
+ H_2O
Cl
O
N
NH_2
NH
H

Continued…

The Sandmeyer reaction is a chemical reaction used to synthesize aryl halides from aryl diazonium salts using copper salts as reagents or catalysts. It is an example of a radical-nucleophilic aromatic substitution.

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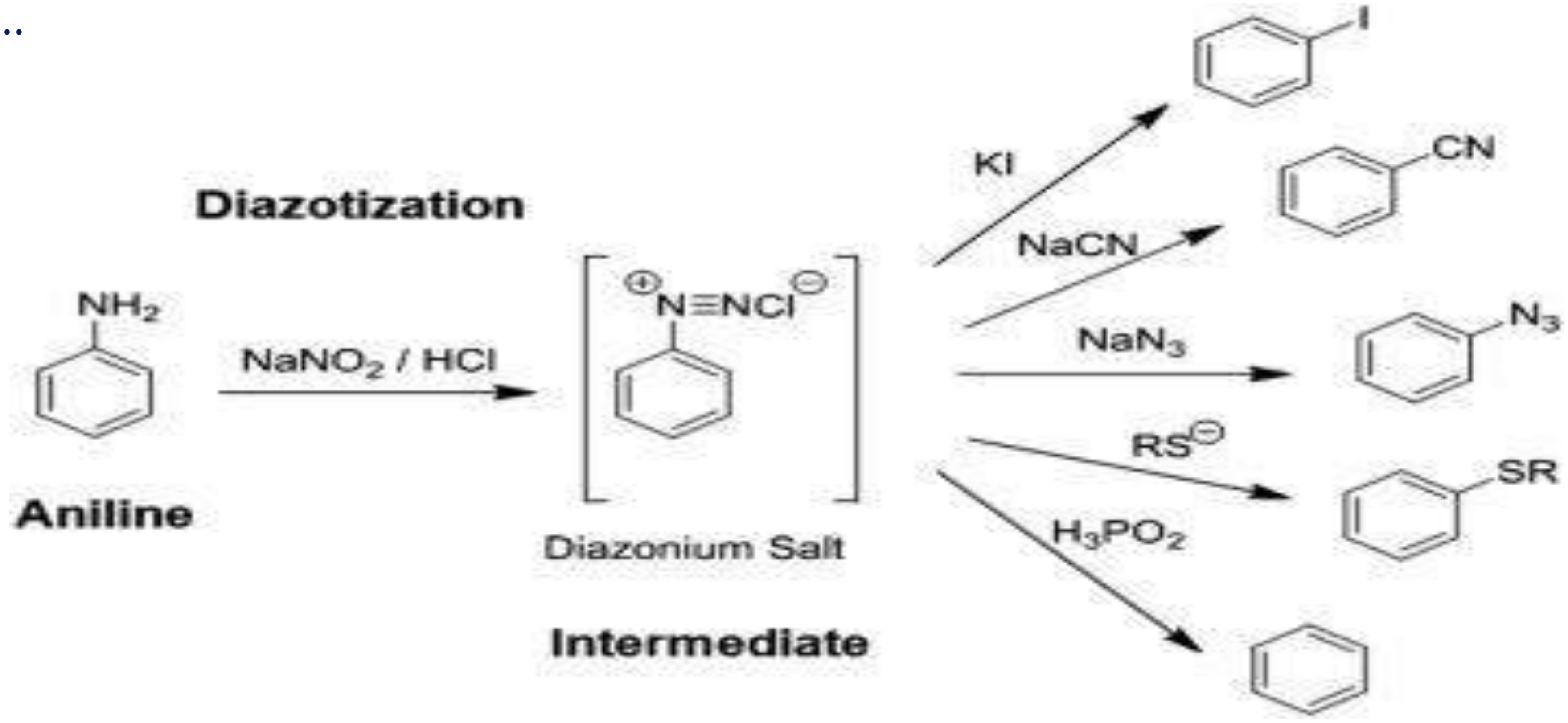


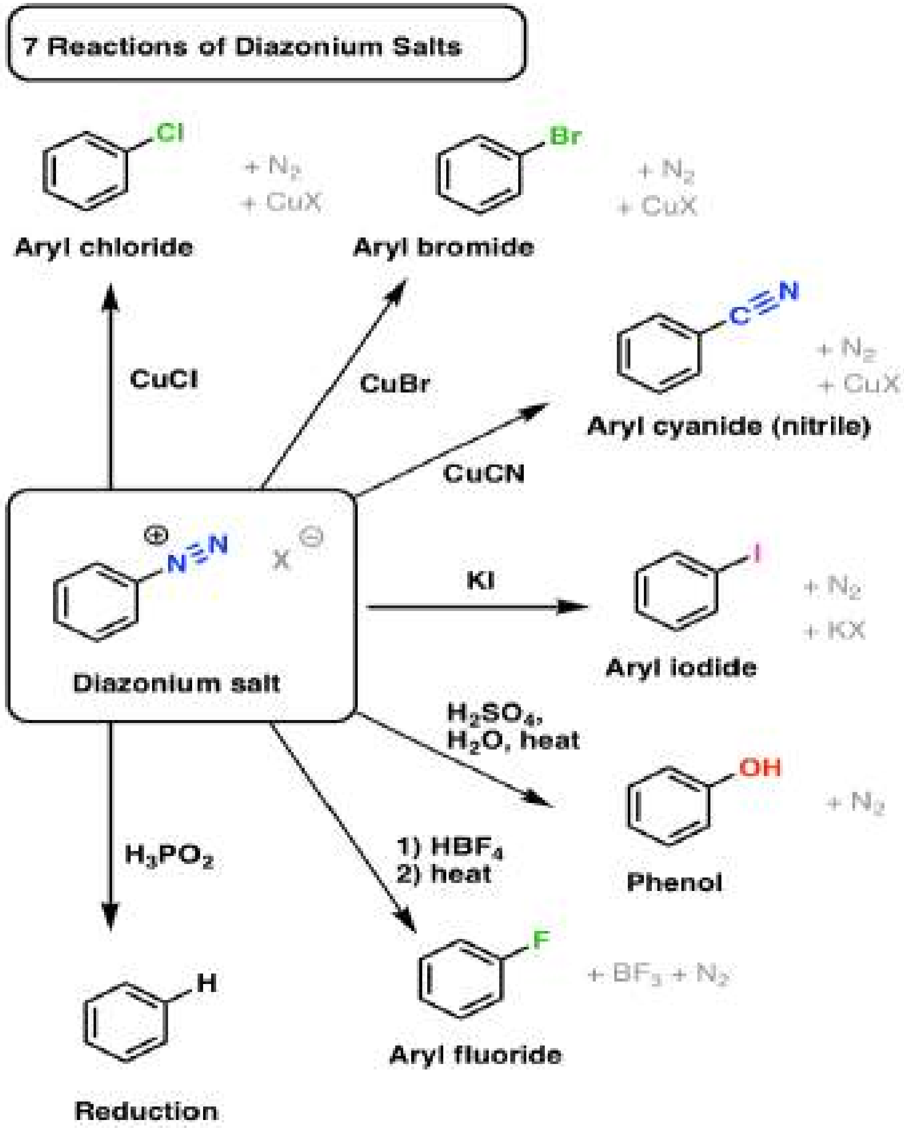
Sandmeyer's reaction

Sandmeyer Reactions

One way to transform diazonium salts is by treating them with various compounds of copper. These are known as Sandmeyer reactions, after Traugott Sandmeyer who first discovered the reaction in 1884 (with copper acetylide!).

Three key examples are:

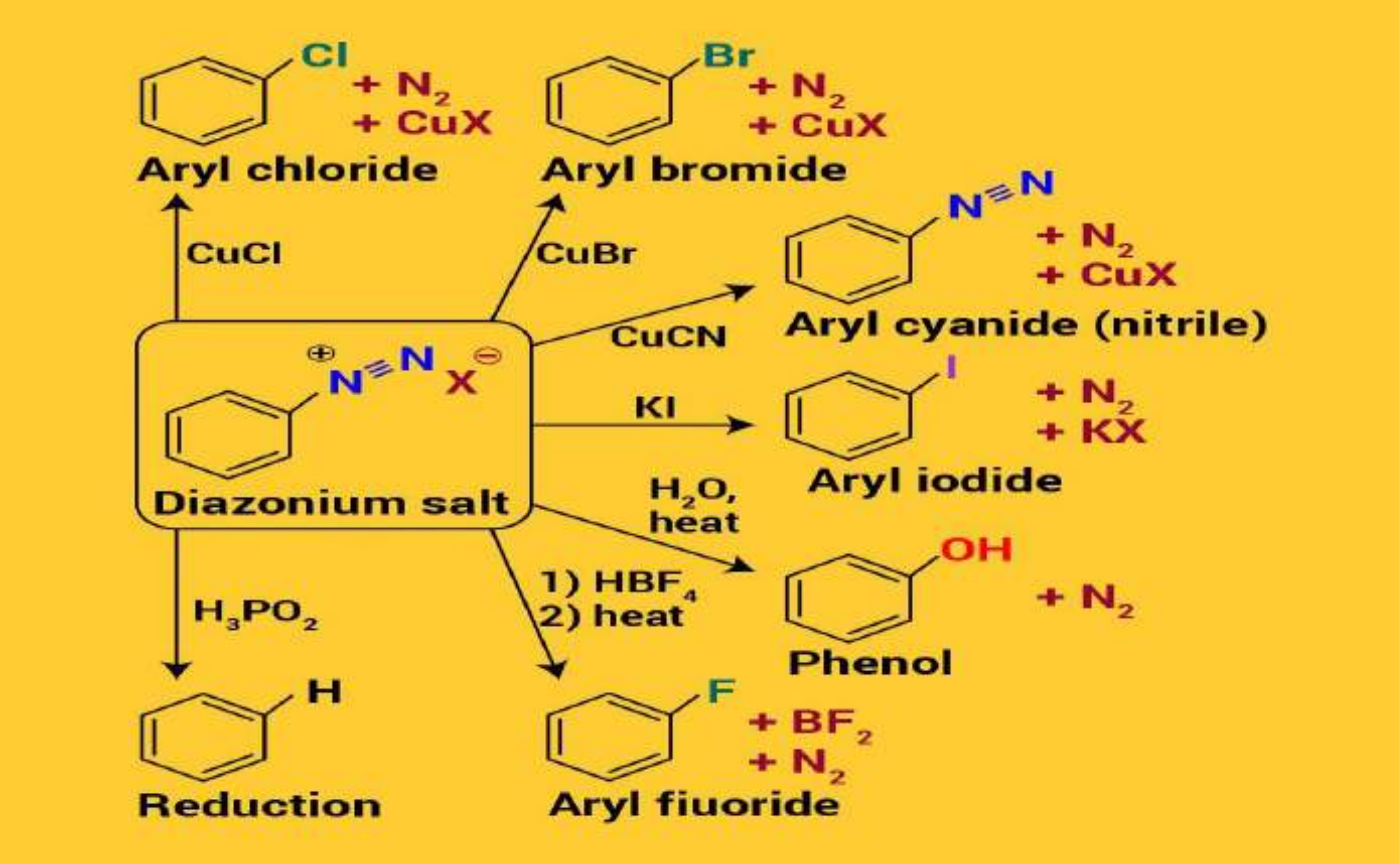
CuCl transforms aryl diazonium salts into aryl chlorides
CuBr transforms aryl diazonium salts into aryl bromides
CuCN transforms aryl diazonium salts into aryl cyanides (nitriles).
The mechanism, which you can read about elsewhere, likely proceeds through an aryl radical, which is oxidized to an aryl cation and then attacked by a nucleophile.



Continued…

- Other Reactions
- Copper isn’t necessary for substitution to occur if a strong enough nucleophile is present, or if the mixture is heated enough:
- Aryl iodides can also be obtained from aryl diazonium salts, through treatment with potassium iodide (KI).
- Hydroxyl groups (OH) can be installed on an aryl diazonium salt through heating with water and acid. (we’ve previously seen one example in John Roberts’ work on arynes, which we covered here.)
- Aryl fluorides can be installed through a two step process. The first involves exchanging the counterion (X–) on the aryl diazonium salt with the tetrafluoroborate (BF4–) ion by treating the diazonium salt with HBF4. Then, when heated, fluorine can act as a nucleophile, displacing N2 and releasing BF3 as a byproduct.
- The diazonium salt can also be reduced to C–H, by treating the aryl diazonium salt with hypophosphorous acid (H3PO2).

Reactions of Diazonium salt



Preparation of Azo Dyes :

- Preparation

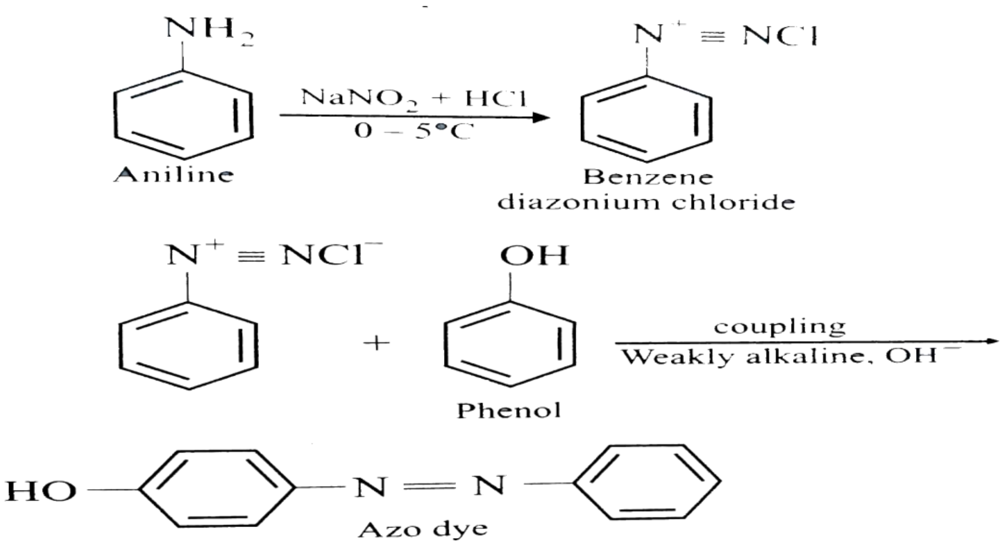
Aniline reacts with sodium nitrite in the presence of hydrochloric acid forms benzene diazonium chloride. Further benzene diazonium chloride reacts with 2-naphthol forms a bright orange colour 2-naphthol aniline dye. **Azo compounds** are prepared by the reaction of diazonium salts with phenol under alkaline conditions.

Generally, azo dyes are prepared **by diazotization of a primary aromatic amine, then followed by coupling with one or more than one electron-rich nucleophile**. Examples of electron-rich nucleophiles include- amino and hydroxyl group.

Azo dyes are coloured **because they contain alternating single and double bonds**, known as a conjugated system. This creates and areas of delocalization above and below the plane of the molecule

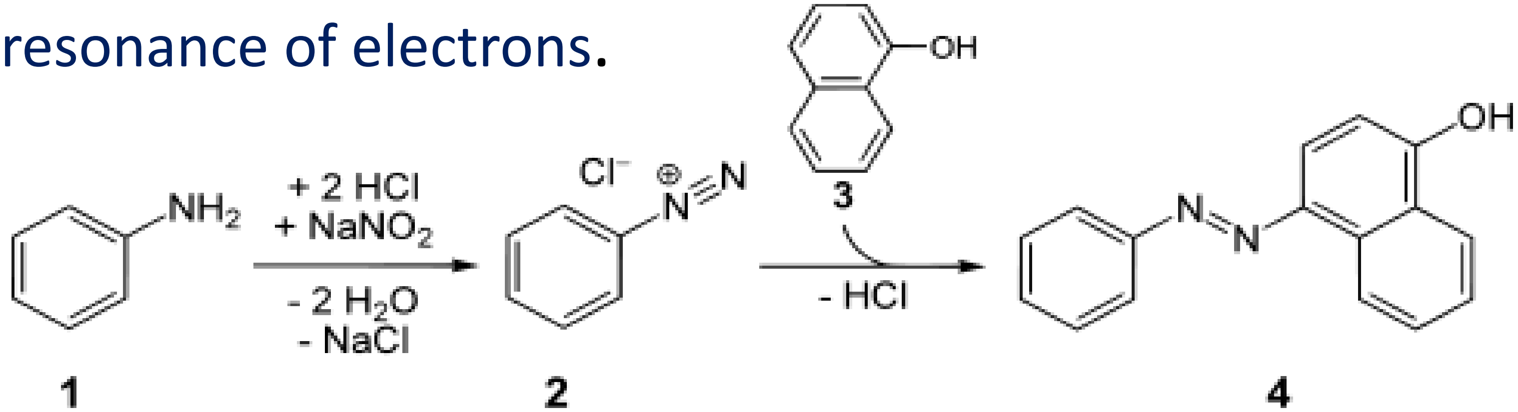
Continued…

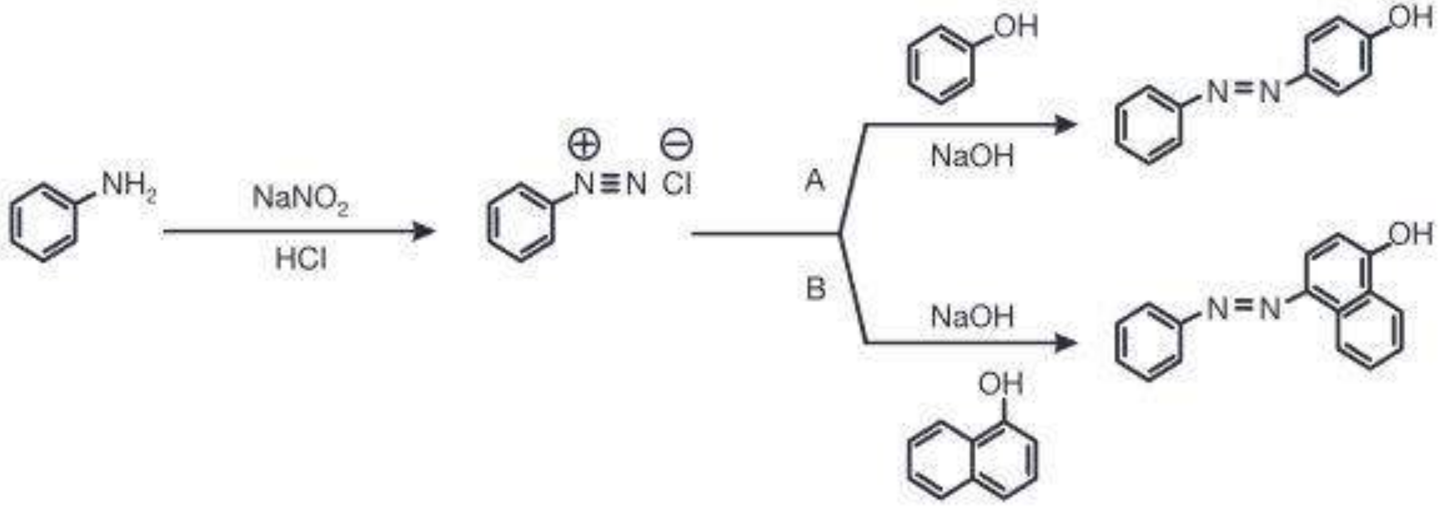
- Phenol reacts with benzene diazonium chloride to give a yellow-orange azo compound. The reaction is base-catalysed. Similarly β-naphthol couples with phenyl diazonium electrophile to produce an intense orange-red dye.
- The deep colors of the dyes **reflects their extended conjugation**. For example, the dye called aniline yellow is produced by mixing aniline and cold solution of diazonium salt and then shaking it vigorously.
- Azo dyes are also prepared by **the condensation of nitroaromatics with anilines followed by reduction of the resulting azoxy intermediates**



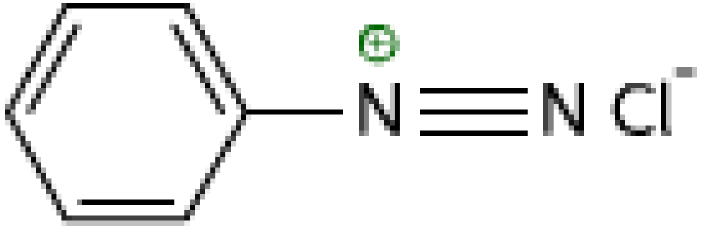
Preparation of Dye :

- Unlike most organic compounds, dyes possess colour because they 1) absorb light in the visible spectrum (400–700 nm), 2) have at least one chromophore (colour-bearing group), 3) have a conjugated system, i.e. a structure with alternating double and single bonds, and 4) exhibit resonance of electrons.

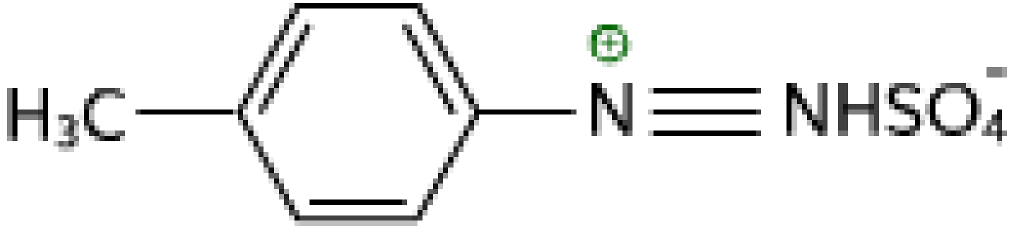




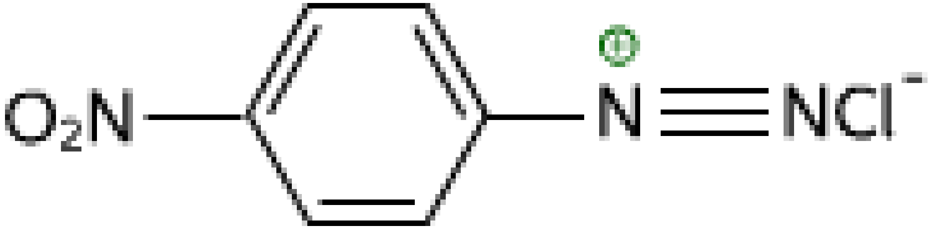
Other Examples :



Benzene
diazonium chloride



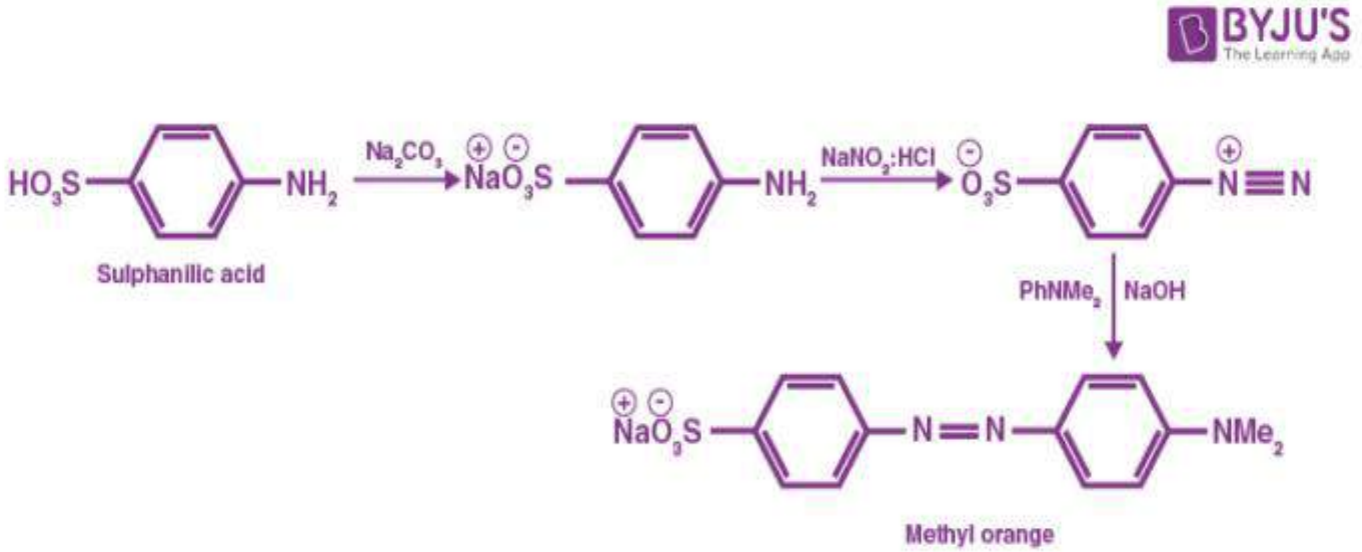
p-toluene-diazonium
hydrogen sulfate

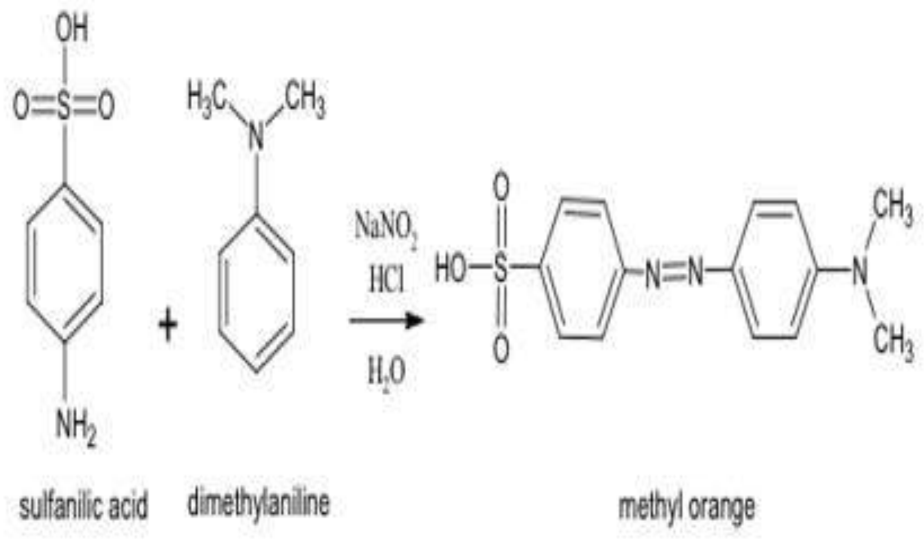


p-nitrobenzene diazonium chloride

Preparation of Methyl orange

- Methyl orange is made by adding sodium nitrite to sulfanilic acid in solution, this produces a diazonium salt.
- A diazonium coupling reaction was used to produce methyl orange from **sulfanilic acid and N, N-dimethylaniline**, which is a typical reaction for treating an aliphatic amine to yield a carbocation. A primary aliphatic amine reacts with nitrous acid to form an unstable diazonium salt that loses N2 to form a carbocation.





Uses of Methyl Orange :

- A dye is a colored organic compound that is used to impart color to an object or a fabric. Methyl orange is a very common acid-base indicator, red in solutions that have pH values less than 3.2 and yellow in solutions with pH greater than 4.4

Because of its simple and distinct colour shift, methyl orange is a commonly **used pH indicator in titrations**. It's commonly used in acid titrations because it changes colour at the pH of a midi-strength acid. In an acidic medium, methyl orange turns red, while in a basic medium, it turns yellow.

Methyl orange is a pH indicator frequently used in titration because of its clear and distinct color variance at different pH values.

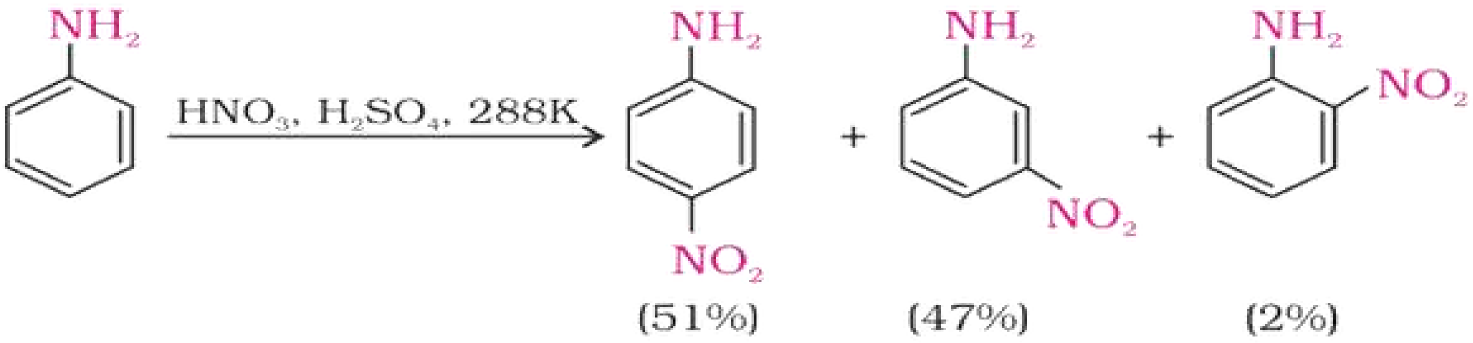
Electrophilic Substitution Reactions of Aniline

- 1. Nitration of Aniline
- **Electrophilic substitution reaction** refers to the

reaction in which an electrophile substitutes another electrophile in an organic compound. Anilines undergo the usual electrophilic reactions such as halogenation, nitration and sulphonation.

A mixture **of concentrated sulphuric and nitric acids**, used to introduce a nitro group (–NO_2) into an organic compound.

Nitration is **a process in which there is the replacement of a hydrogen atom (organic compound) with one or more nitro groups (single bond NO_2)**. The reaction usually occurs with high temperatures or we can say that the reaction is exothermic.



B. Sc. III – Unit- 5

A] Pharmaceuticals B] Green Chemistry

A) Pharmaceuticals – Introduction , importance, qualities of good drug, meaning of the terms - analgesic, antipyretic, anaesthetics , antibiotics, anti-inflammatory, tranquilizer, antiallergic, cardiovascular, anti-hypertensive, antineoplastic, sedative and hypnotics.

Synthesis and Uses - Isoniazid, benzocaine, ethambutol , phenobarbitone , chloramphenicol and paludrine.

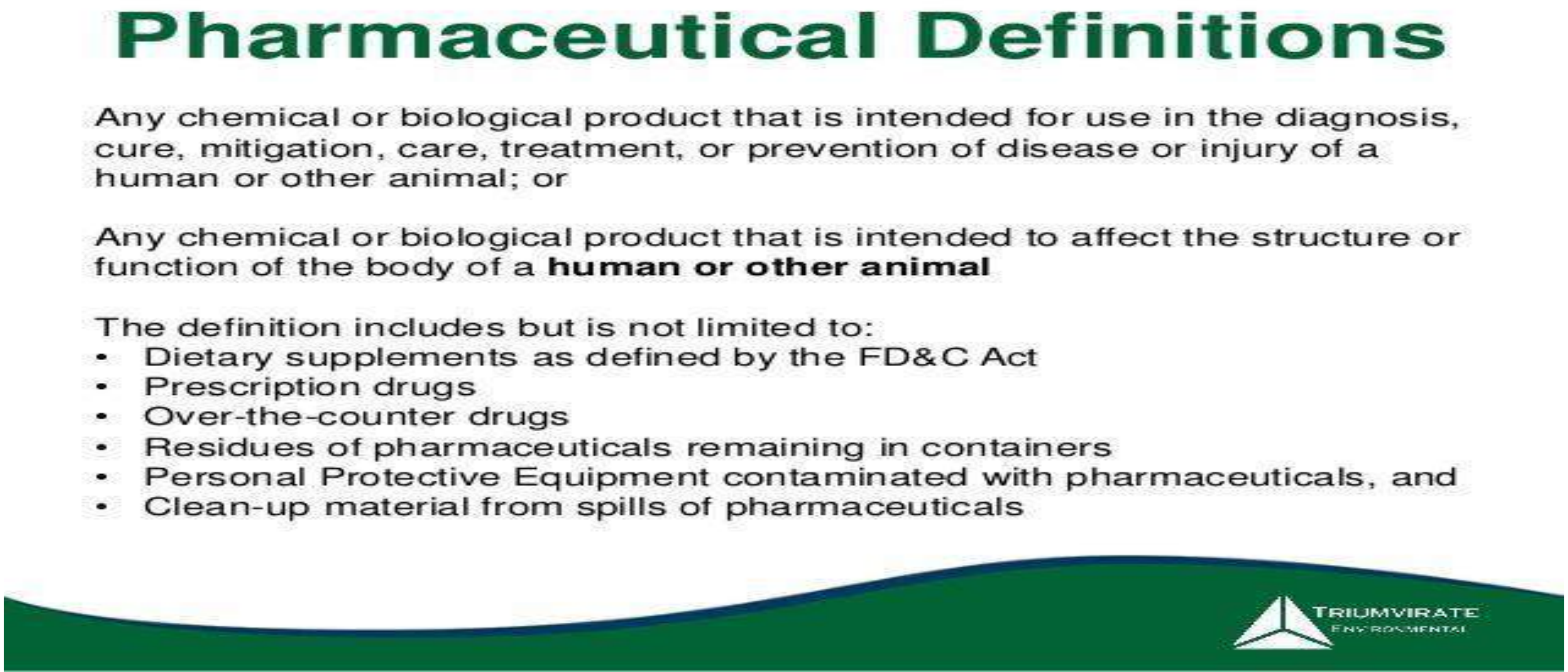
B) Green Chemistry – Introduction, Principles and Significance of Green Chemistry, Applications of microwaves and Ionic Liquids in chemical reactions.

Pharmaceuticals :

A pharmaceutical is a chemical substance which is used in healthcare.
The company makes antibiotics and other pharmaceuticals .
Pharmaceuticals are drug-containing products in dosage forms.

Definition :

- A pharmaceutical drug, also called a medication or medicine, is a **chemical substance used to treat, cure, prevent, or diagnose a disease or to promote well-being**.



Pharmaceutical Definitions

Any chemical or biological product that is intended for use in the diagnosis, cure, mitigation, care, treatment, or prevention of disease or injury of a human or other animal; or

Any chemical or biological product that is intended to affect the structure or function of the body of a **human or other animal**

The definition includes but is not limited to:

- Dietary supplements as defined by the FD&C Act
- Prescription drugs
- Over-the-counter drugs
- Residues of pharmaceuticals remaining in containers
- Personal Protective Equipment contaminated with pharmaceuticals, and
- Clean-up material from spills of pharmaceuticals

What is Drug ?

- A medicine or other substance which has a physiological effect when ingested or otherwise introduced into the body.
- A **chemical substance**, **especially one prescribed by a medical provider**, that is **used in the diagnosis**, **treatment**, or **prevention of a pathological condition or disease**.
- **A therapeutic agent; any substance, other than food, used in the prevention, diag nosis, alleviation, treatment, or cure of disease.**
- General term for any substance stimulating or depressing various physiological functions like blood circulation, blood filtration, respiration, digestion, nervous system, growth etc. , that can be habituating or addictive, especially a narcotic.
- Any substance that affects the normal body functions.

It's known as a Drug.

Importance of Drug :

- Pharmaceutical substance used in the diagnosis , treatment , or prevention of disease and for restoring, correcting, or modifying organic functions. (*Seealso* pharmaceutical industry.) is known as Drug.
- Pharmaceuticals are generally classified by chemical group, by the way they work in the body (pharmacological effect), and by therapeutic use. Alkaloids were the first pure pharmaceuticals derived from natural substances (plants); they include quinine, nicotine, cocaine, atropine, and morphine. Drugs of animal origin include glandular extracts containing hormones, such as insulin for use in treating diabetes.
- Antibiotics, vaccines, human blood-plasma fractions, and steroid hormones are other important pharmaceuticals manufactured from natural substances.
- Vitamins which were formerly obtained from natural sources, are now often made in the laboratory.

continued…

- Drug used can have a wide range of short- and long-term, direct and indirect effects. These effects often depend on the specific drug or drugs used, how they are taken, how much is taken, the person's health, and other factors.
- Short-term effects can range from changes in apetite. A drug is any substance that causes a change in an organism's physiology or psychology when consumed.

- Drugs are typically distinguished from food and substances that provide nutritional support. Consumption of drugs can be via inhalation, injection, smoking, ingestion, absorption via a patch on the skin, suppository, or dissolution under the tongue, wakefulness, heart rate, blood pressure,

continued :

- A drug is a chemical that interacts with proteins in the body to affect a physiological function. This is the general idea behind all medicines.

- Once these chemicals are absorbed into the systemic circulation they bind with certain proteins and changes the functioning of the cell slightly. For example, anticancer drugs bind to proteins on the surface of cancer cells this stimulates the cells to die. In this case cell death is the physiological action of the drug.

Properties or Qualities of Ideal drug :

- It should be non-toxic, bio-compatible, biodegradable and physicochemically stable in-vivo and in-vitro .

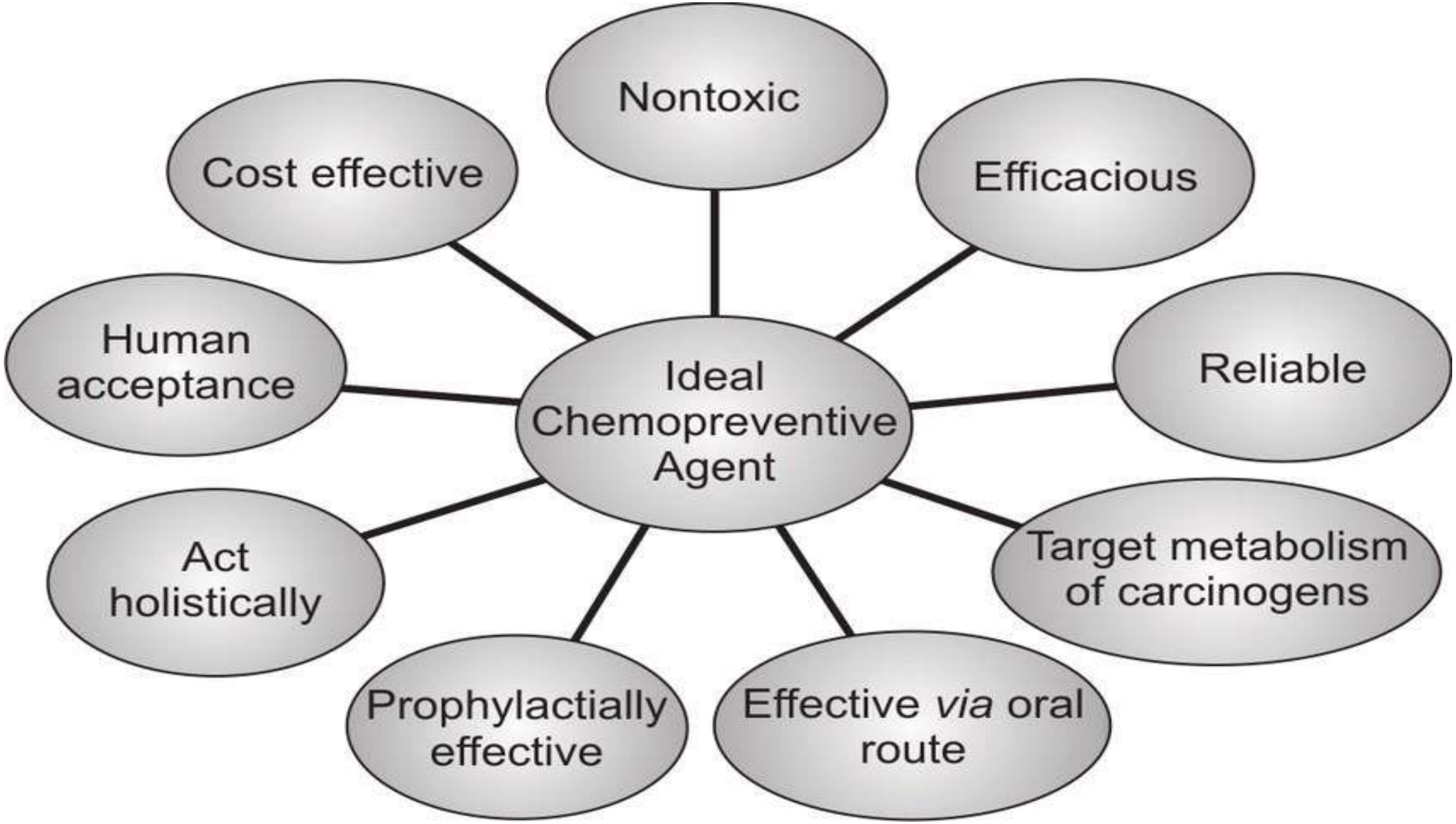
Drug distribution should be to target cells or tissues or organs and there should have uniform capillary distribution.

- Drug release should not affect the drug action.
- It should be safe, efficient and cost effective.
- Its antimicrobial action should be selective, and effective.
- It should be bactericidal rather than bacteriostatic.
- It should not induce resistance. It should be safe for the receipiant even if consumed for longer period and at higher dose .
- It should not retain in the body for a longer period than required.
- It should be stable enough to allow attainment of optimum concentration in the body.

TABLE 12.1 Characteristics of the Ideal Antimicrobial Drug

- Selectively toxic to the microbe but nontoxic to host cells
- Microbicidal rather than microbistatic
- Relatively soluble; functions even when highly diluted in body fluids
- Remains potent long enough to act and is not broken down or excreted prematurely
- Doesn't lead to the development of antimicrobial resistance
- Complements or assists the activities of the host's defenses
- Remains active in tissues and body fluids
- Readily delivered to the site of infection
- Reasonably priced
- Does not disrupt the host's health by causing allergies or predisposing the host to other infections

continued …



Ideal Chemopreventive Agent

Nontoxic

Efficacious

Reliable

Target metabolism of carcinogens

Effective *via* oral route

Prophylactially effective

Act holistically

Human acceptance

Cost effective

Action of Drug :

- **The action of drugs on the human body is called pharmacodynamics, and what the body does with the drug is called pharmacokinetics. The drugs that enter the human tend to stimulate certain receptors, ion channels, act on enzymes or transporter proteins. As a result, they cause the human body to react in a specific way.**
- **Mechanism of Drug Action - All drugs bring about complex interactions with molecules of living systems. These actions, either physical or chemical, mainly act at four levels: Molecular – Receptor, ion channel, enzyme, carrier molecules.**

Actions of drugs are the **biochemical physiological mechanisms by which the chemical produces a response in living organisms**. The effect is the observable consequence of a drug action. For example, the action of penicillin is to interfere with cell wall synthesis in bacteria and the effect is the death of the bacteria.

Classification of Drugs :

A drug class is a term used to describe medications that are grouped together because of their similarity. There are three dominant methods of classifying these groups:[1]

- By their mechanism of action, meaning the specific biochemical reaction that occurs when you take a drug.
- By their physiologic effect, meaning the specific way in which the body responds to a drug
- By their chemical structure.

- A sampling of classes of medicine includes:
- **1.Antipyretics:** reduces fever (pyrexia/pyresis).Reduces body temperature in fever condition but not below the normal body temperature.
- **2.Analgesics:** reducing pain (painkillers).- Releives pains.
- **3.Antimalarials** : treating malaria.
- **4.Antibiotics**: inhibiting germ growth.
- **5.Antiseptics**: prevention of germ growth near burns, cuts and wounds.

continued …

- 6.Antihistamines : These are drugs which treat allergic rhinitis and other allergies. **Antihistamines** are a class of agents that block **histamine** release from **histamine**-1 receptors and are mostly used to treat allergies or cold and flu symptoms, although some first-generation **antihistamines** may also be used for other conditions..
- **7.Antiinflammatory drugs :** Nonsteroidal anti-inflammatory drugs are medications that relieve or reduce pain. The most popular examples of this group of drugs are **aspirin and ibuprofen**. Nonsteroidal anti-inflammatory drugs (NSAIDs) also come under the wider definition of non-opioid analgesics. These types of drugs (such as **diclofenac and ibuprofen)** are the most widely prescribed medication in the world.
- **8.Anaesthetics :** A local anaesthetic drug is injected at the site of the surgery to cause numbness. You will be awake but feel no pain. An obvious example of local anaesthesia is **numbing an area of skin before having a cut stitched**.

continued :

- **9.Anaesthetics continued…**

There is a temporary loss of sensation or awareness. They may be divided into two broad classes: general anesthetics, which result in a reversible loss of consciousness, and local anesthetics, which cause a reversible loss of sensation for a limited region of the body without necessarily affecting consciousness. **10.Tranquilizers:**

A tranquilizer refers to a drug which is designed for the treatment of anxiety, fear, tension, agitation, and disturbances of the mind, specifically to reduce states of anxiety and tension.

a depressant drug, as Valium or Librium, used as a calming agent in relieving and controlling various emotional disturbances, **anxiety neuroses**, **certain psychoses**, **etc**.

continued :

- 11.**Antihypertensive Drugs** : It is a class of drugs that are used to treat hypertension .The overall class of antihypertensive agents lowers blood pressure, although the mechanisms of action vary greatly.

  Antihypertensive therapy seeks to prevent the complications of high blood pressure, such as stroke and myocardial infarction. Evidence suggests that reduction of the blood pressure by 5 mmHg can decrease the risk of stroke by 34%, of ischaemic heart disease by 21%, and reduce the likelihood of dementia, heart failure, and mortality from cardiovascular disease.

- 12.**Antiallergic drug can be used to relieve fever and other allergic reactions**. Antiallergic drugs temporarily relieve the symptoms of allergic reactions. An antiallergic substance prevents or relieves allergies. COBUILD Key Words for the Pharmaceutical Industry.

  - Anti-allergic drugs - relieving, controlling, or preventing allergic symptoms.

continued :

- **13. Cardiovascular Drugs** : Some examples of the drugs used in cardiovascular medicine include: **Anticoagulants or blood thinners** - These agents prevent coagulation or clotting of the blood. Injectable forms of anticoagulants include dalteparin, enoxaparin, tinzaparin and heparin. Warfarin is a commonly used blood thinner that can be taken in the form of a tablet.Also include isosorbide, dinitrate and hydralazine. Digoxin - This agent is used to stimulate a heartbeat in some cases of heart failure. Statins - These agents reduce the synthesis of blood cholesterol in the liver. High blood cholesterol is one of the major causes of atherosclerosis.

- **14.Sedatives :**Sedatives are a type of prescription medication that slows down your

. brain activity. They're typically used to make you feel more relaxed. Doctors commonly prescribe sedatives to treat conditions like anxiety and sleep disorders.

tending to calm, moderate, or tranquilize nervousness or excitement.

Continued…

- **15. Antineoplastic agen**t. antineoplastic therapy a regimen that includes chemotherapy, aimed at **destruction of malignant cells** using a variety of agents that directly affect cellular growth and development. Chemotherapy is but one of a variety of methods available in the treatment of cancer.

Any of several drugs that control or kill neoplastic cells; used in chemotherapy to kill cancer cells; all have unpleasant side effects that may include nausea and vomiting and hair loss and suppression of bone marrow function.

List of hormonal cytostatic antineoplastic agents; Lonidamine; Losoxantrone; Low-dose chemotherapy; LS-1727; Lucanthone;
Lurbinectedin; Lurtotecan

continued :

- **Hypnotics** :Hypnotic (from Greek Hypnos, sleep), or soporific drugs, commonly known as sleeping pills, are a class of psychoactive drugs whose primary function is to induce sleep and for the treatment of insomnia (sleeplessness), or for surgical anesthesia.

This group is related to sedatives. Whereas the term sedative , g. escribes drugs that serve to calm or relieve anxiety, e.g. Zolpidem, Alprazolam, Benzodaizepine.

Sedative-Hypnotic Drugs

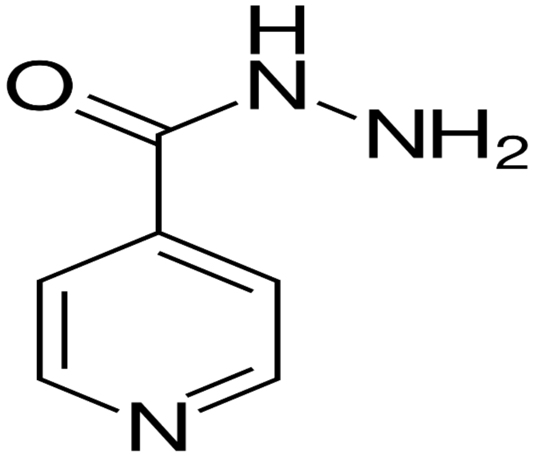
- **Sedative-hypnotic drugs** are central nervous system depressants that produce relaxing to sleep-inducing effects
- Three main types of sedative-hypnotic drugs:
  - Barbiturates
  - Nonbarbiturate sedatives
  - Minor tranquilizers

DRUG CLASSIFICATION AND END OF WORD CLUES

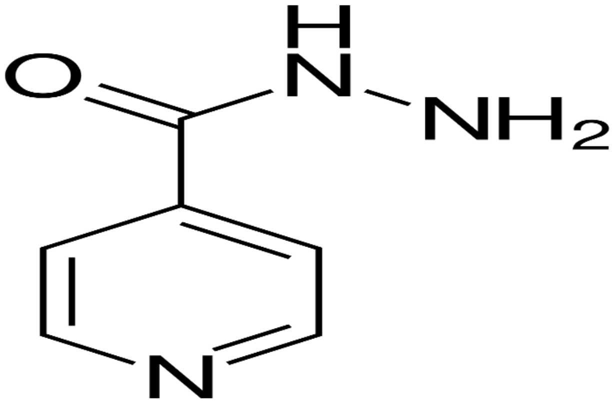
DRUG TYPE	SUFFIX	DRUG TYPE	SUFFIX
Antianxiety drugs	pam	Antivirals	vir, ine
Antibiotics	cycline, cillin, micin, mycin, xacin	Beta-adrenergic blocking agents	olol
Anticoagulants	parin, ase	Benzodiazepines	pam
Anticonvulsants	pam, toin	Bronchodilators	rol, ine
Antidepressants	ine, pram	Calcium channel blockers	ine
Antihistamines	ine	Corticosteroids	sone
Antihypertensive (ACE inhibitors)	pril	Diuretics	ide
Antihyper-lipidemics	statin	Local Anesthetics	caine
Antimigraine	ptan	Neuromuscular blockers	ium
Antipsychotics	zine, ine	Proton Pump	azole

Isoniazid

- Isoniazid inhibits synthesis of mycolic acids, which are essential components of mycobacterial cell walls.
- Isoniazid is a prodrug that is activated by KatG, the mycobacterial catalase-peroxidase.
- The activated form of isoniazid forms a covalent complex with an acyl carrier protein **(AcpM)** and a beta-ketoacyl carrier protein synthetase (**KasA)**, which blocks mycolic acid synthesis and kills the cell.



Synthesis of Isoniazid / Isonicotinic acid hydrazide :



Isoniazid, also known as isonicotinic acid hydrazide ,is an antibiotic used for the treatment of tuberculosis. For active tuberculosis it is often used together with rifampicin, pyrazinamide, and either streptomycin or ethambutol. It may also be used for a typical types of mycobacteria, such as M. avium, M. kansasii, and M. xenopi. It is usually taken by mouth but may be used by injection into muscle.. Methods of Synthesis :

- Synthesis -In case of synthesis of isoniazid, the ethyl or methyl ester of isonicotinic acid is **refluxed with hydrazine hydrate** .

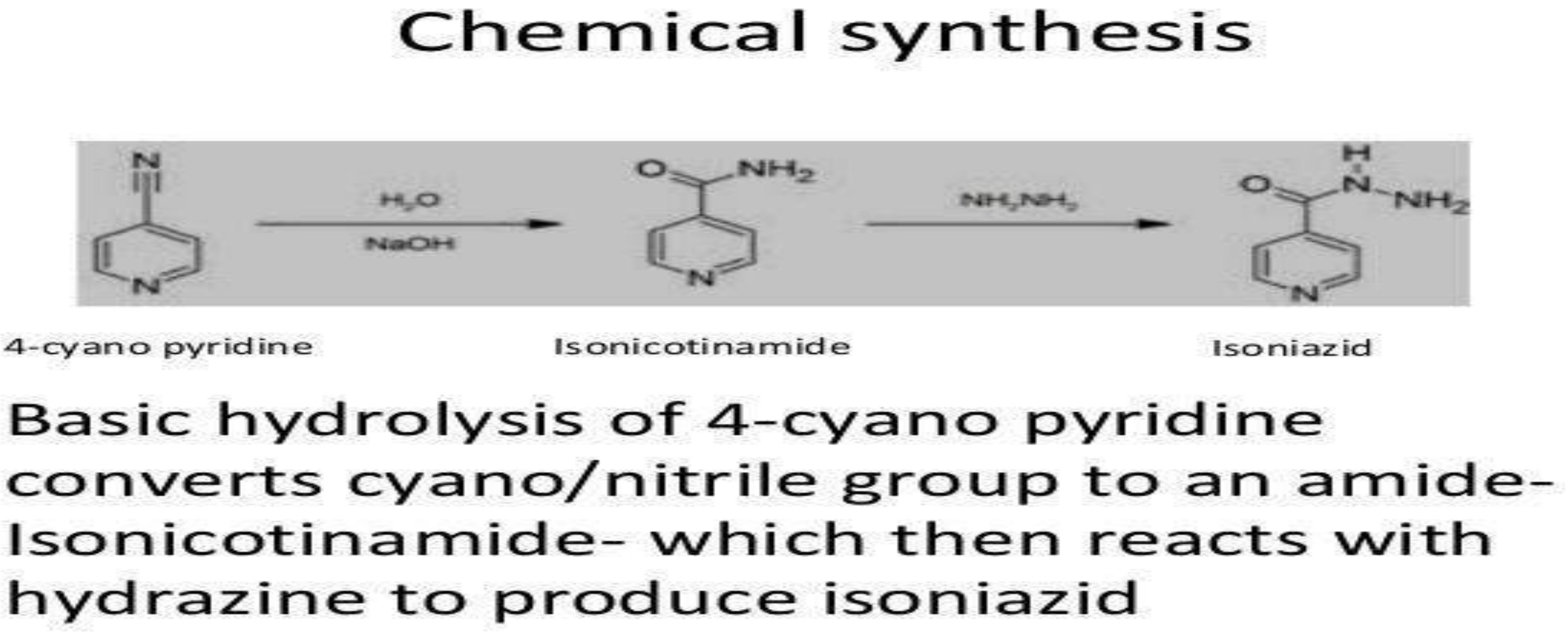
- Among the hydrazides , isonicotinic acid hydrazide or isoniazid can be synthesized by using **lipases**.

Synthesis of Isoniazid : First

It is an antibacterial drug which acts as bactericidal as well as bacteriostatic . It is known as

method

rimifon or isonicotinic acid hydrazide used to cure tuberculosis.



Chemical synthesis

4-cyano pyridine

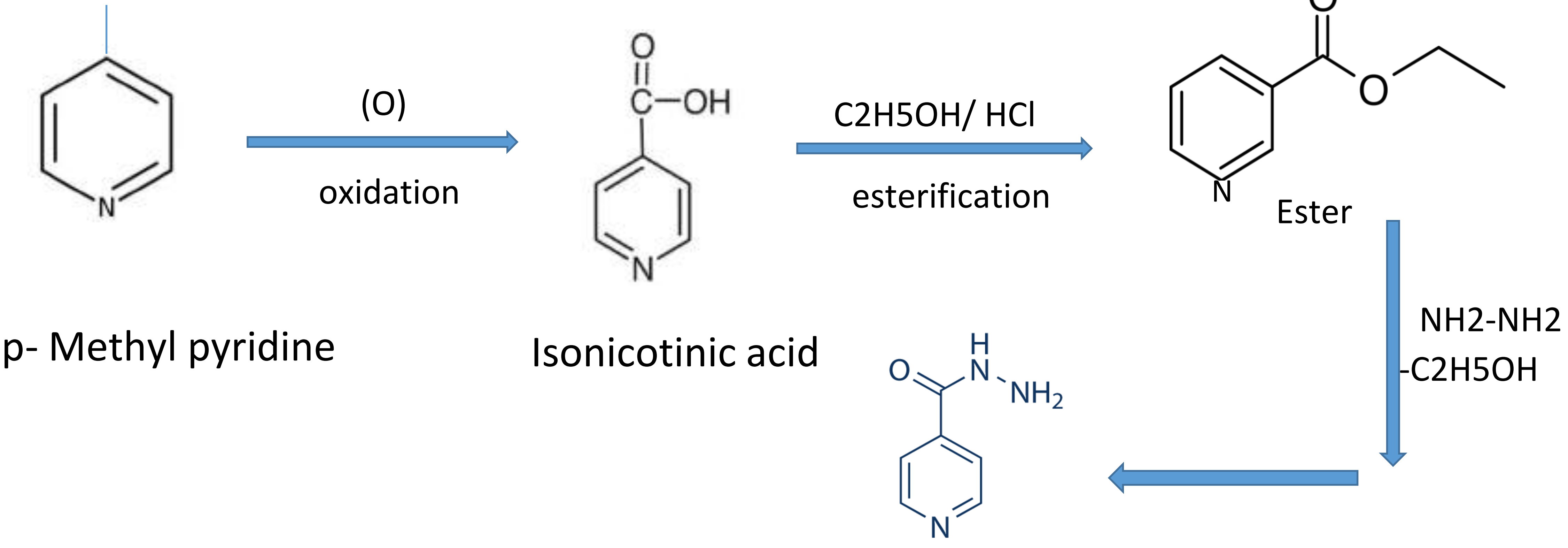
Isonicotinamide

Isoniazid

Basic hydrolysis of 4-cyano pyridine converts cyano/nitrile group to an amide- Isonicotinamide- which then reacts with hydrazine to produce isoniazid

II nd method

- It is synthesized from 4-methyl pyridine , on oxidation it forms isonicotinic acid . This is followed by esterification and treatment with hydrazine to give isoniazid.



p- Methyl pyridine

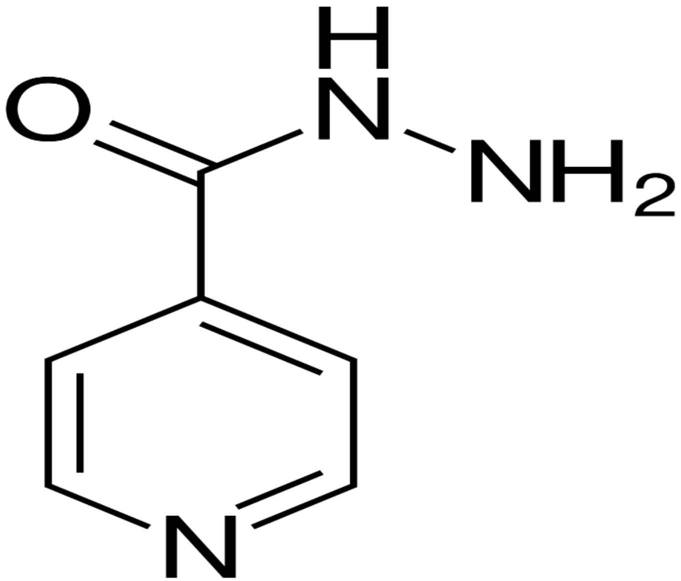
Isonicotinic acid

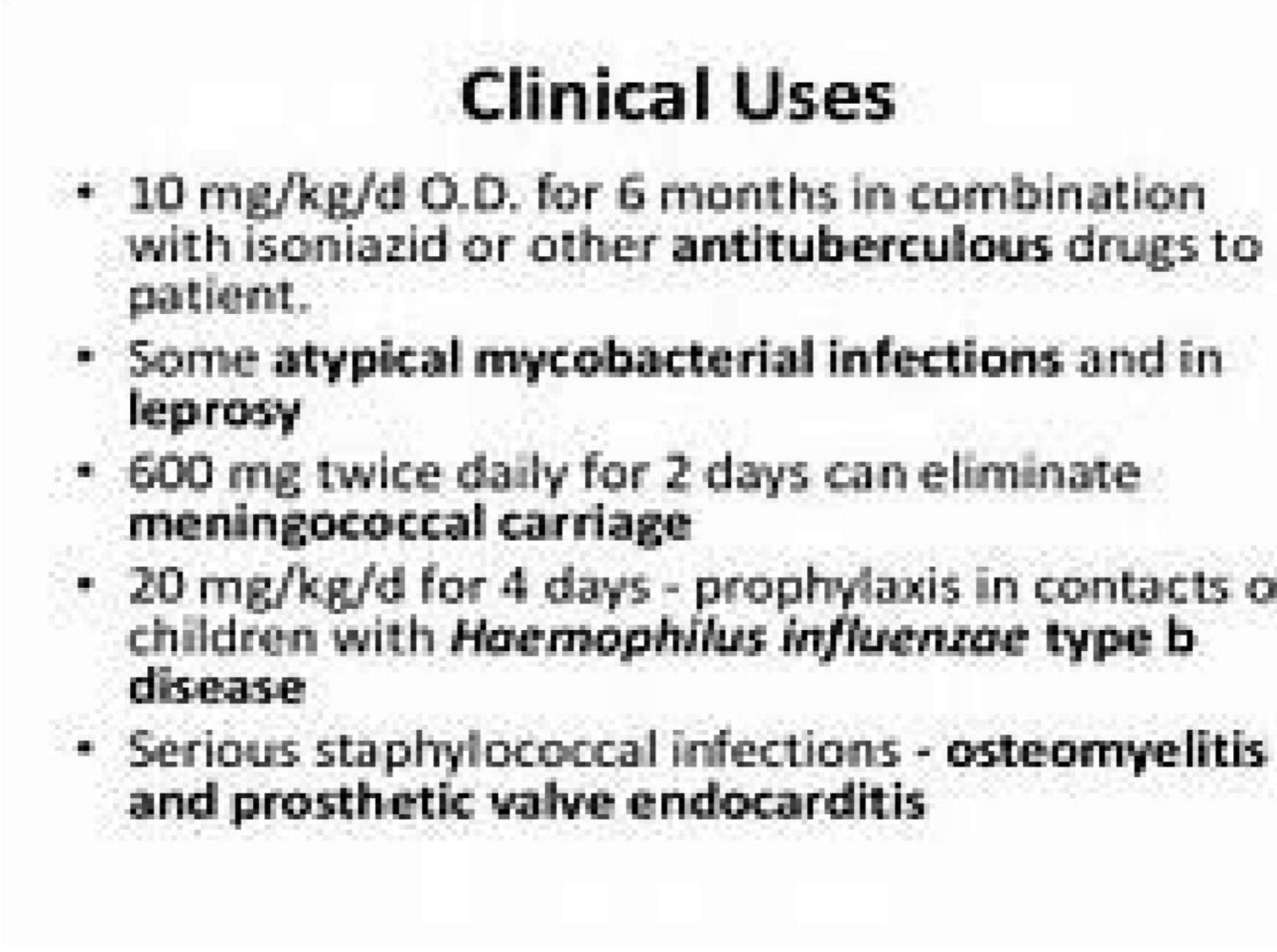
Ester

Isoniazid

Isoniazid

- first-line medication in prevention and treatment of Tuberculosis.
- Synthesized in the early 20th century.
- Isoniazid is available in tablet, syrup, and injectable forms (given intramuscularly or intravenously).
- Isoniazid is manufactured from isonicotinic acid, which is produced from 4-methylpyridine.





Clinical Uses

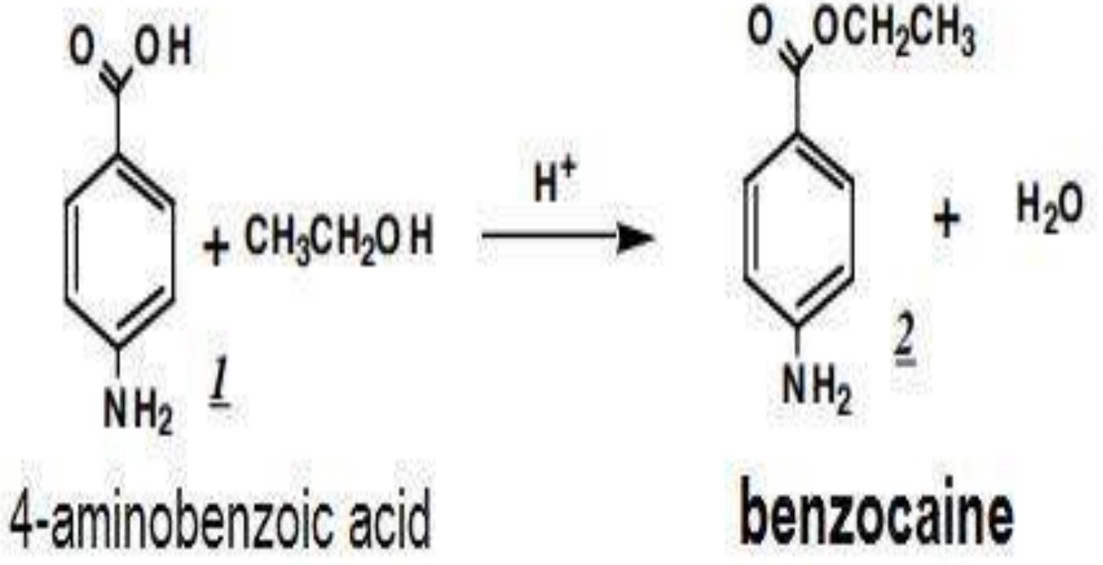
- 10 mg/kg/d O.D. for 6 months in combination with isoniazid or other **antituberculous** drugs to patient.
- Some **atypical mycobacterial infections** and in **leprosy**
- 600 mg twice daily for 2 days can eliminate **meningococcal carriage**
- 20 mg/kg/d for 4 days - prophylaxis in contacts o children with ***Haemophilus influenzae* type b disease**
- Serious staphylococcal infections - **osteomyelitis and prosthetic valve endocarditis**

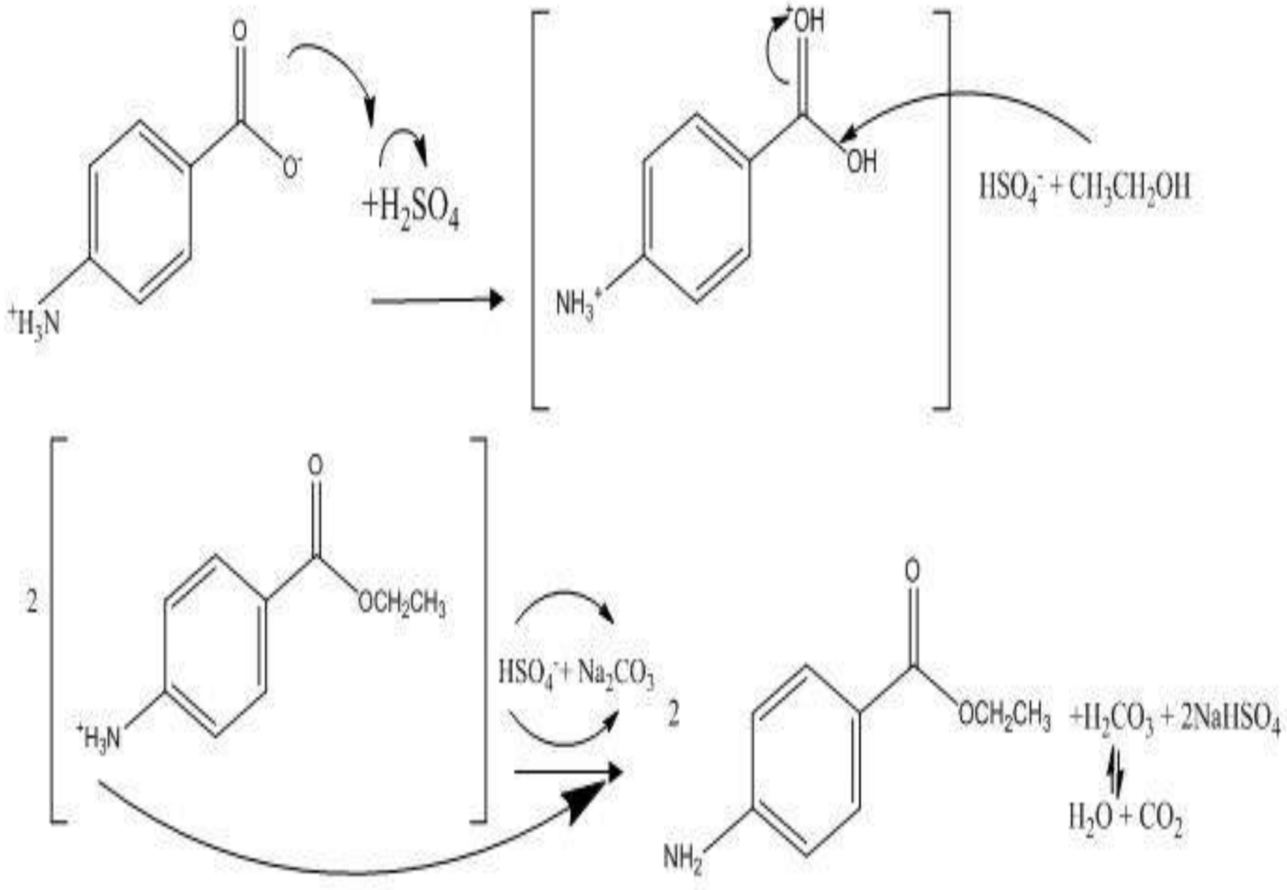
2. Benzocaine : Synthesis from PABA

- Benzocaine is synthesized by Fischer Esterification of p-aminobenzoic acid with ethanol in an acidic condition.

- The mechanism of this reaction involved several steps. First, the starting material p- aminobenzoic acid is activated by protonation of carbon which synthesize benzocaine i. e. an ester, from 4-aminobenzoic acid, by Fischer Esterification. The mechanism was to combine 4-aminobenzoic acid and ethanol in a reflux reaction with the addition of sulphuric acid as a catalyst to produce the product.
- Esters are important compounds in organic chemistry. The mechanism of the Fischer Esterification that was utilized to produce benzocaine is very straightforward carbonyl chemistry. The purpose of this lab is to synthesize benzocaine, an ester, from p-aminobenzoic acid, a carboxylic acid, by Fischer Esterification.

Fischer’s Esterification reaction and mechanism :





Common brand names: Benzodent, Americaine
This medication is used on the skin to stop itching and pain from certain skin conditions and to treat minor discomfort and itching caused by hemorrhoids and certain other problems of the genital/anal area.

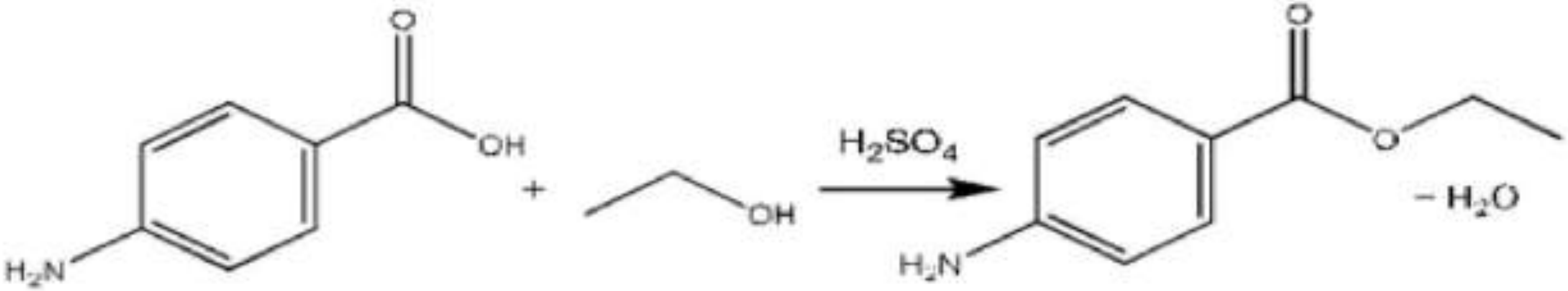
Synthesis of Benzocaine

A. Introduction/Aims:

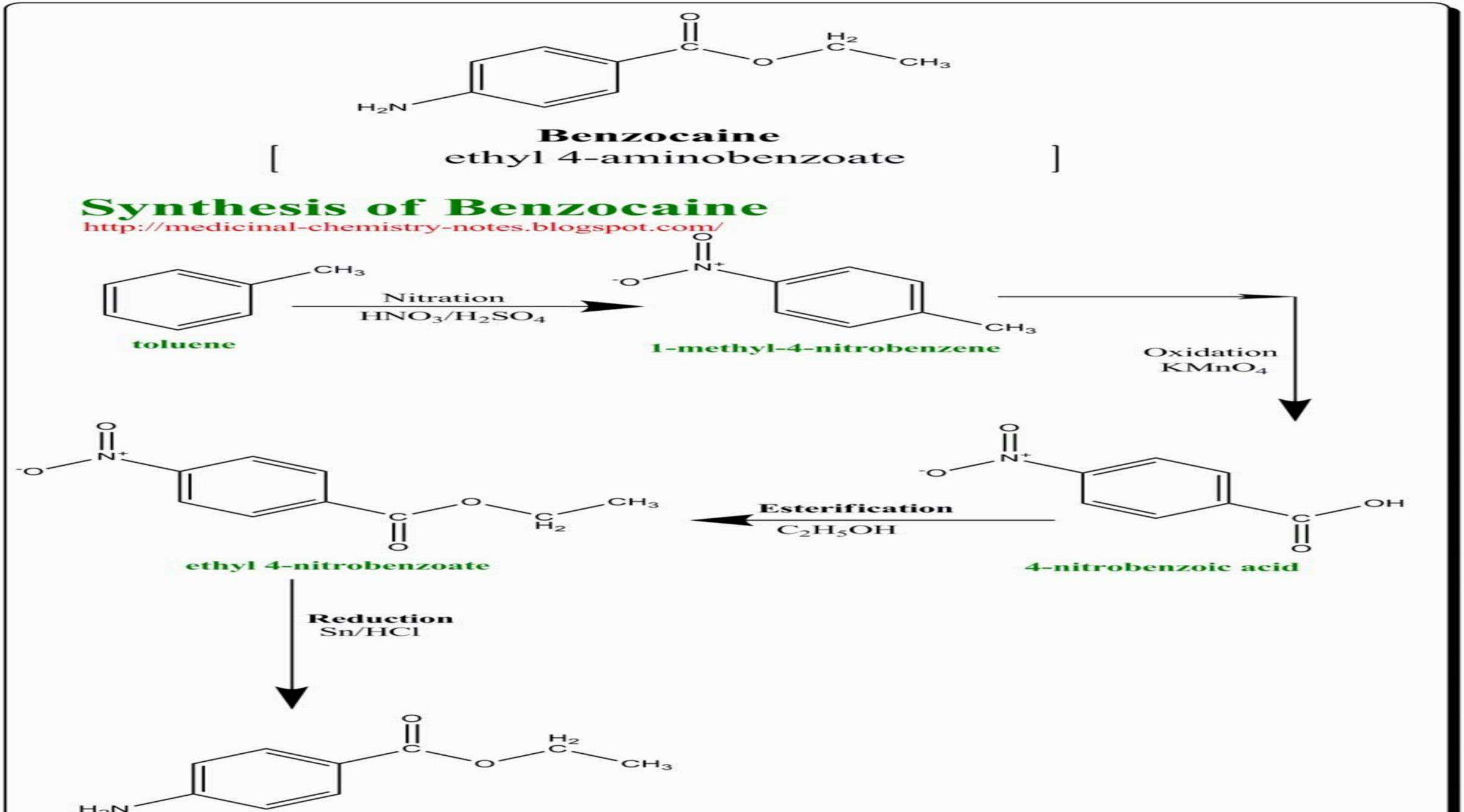
The aim of the current investigation is to investigate the acid-catalysed Fischer esterification mechanism underlying the synthesis of the anaesthetic benzocaine using p-aminobenzoic acid and ethanol in excess. The resulting synthesised compound was subject to IR and melting point analyses in order to determine the identity and indeed the purity of the obtained sample.

Benzocaine exhibits two main components common to the anaesthetic family: (1) an aromatic system usually having directly attached an ester and (2) a one to four unit hydrocarbon chain. The ester group is essential in body detoxification of this substance due to enzymatic cleavage of the ester linkage. Other anaesthetics may also contain a tertiary amine functional group which translates into the compound being soluble in the body.

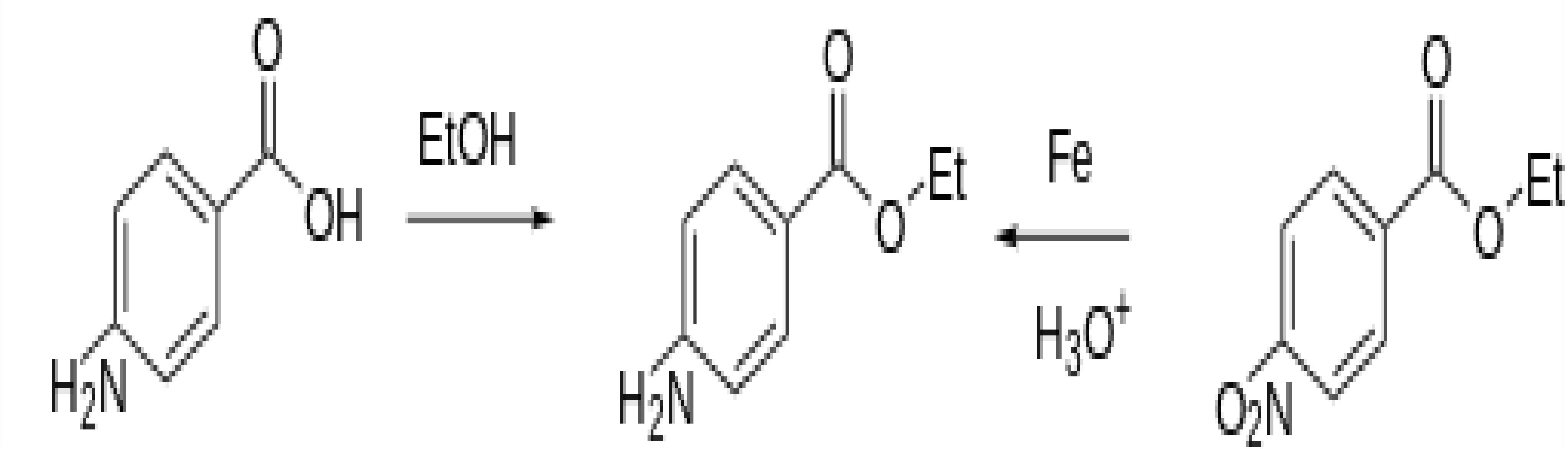
B. Stoichiometric Equations:



Synthesis of Benzocaine : III rd method



Ist and II nd method for synthesis of Benzocaine :



Uses of Benzocaine :

1. This medication is used on the skin to stop itching and pain from certain skin conditions and to treat minor discomfort and itching caused by hemorrhoids and certain other problems of the genital/anal area.

Benzocaine is a local anesthetic that’s applied to the skin, mouth or gums to numb nerve endings. It relieves pain and itching caused by conditions like insect bites, sore throats and toothaches. Board-certified physicians medically review of content to ensure its accuracy and quality.

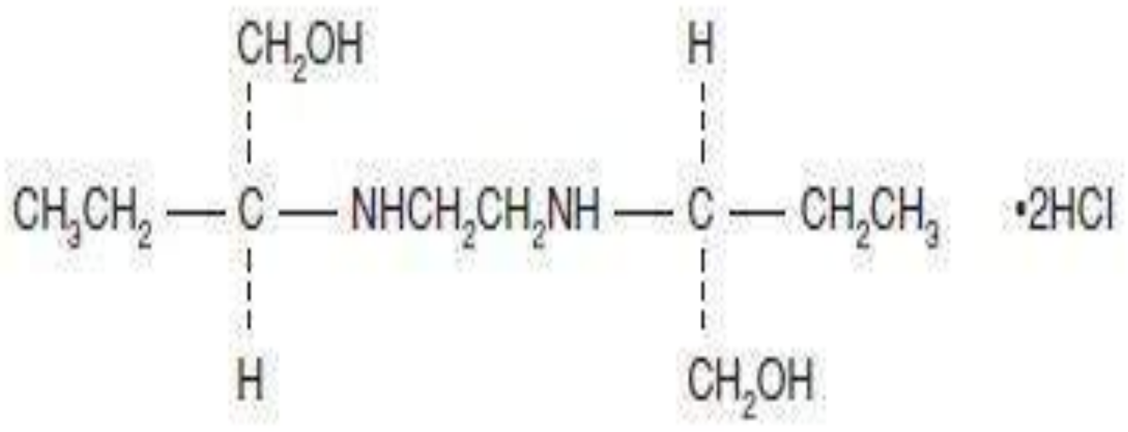
3. Synthesis and Uses of Ethambutol : Introduction

- **1.Ethambutol is one of the front-line agents recommended by the World Health Organization (WHO) for the treatment of tuberculosis. In an effort to develop more potent therapies to treat tuberculosis.**

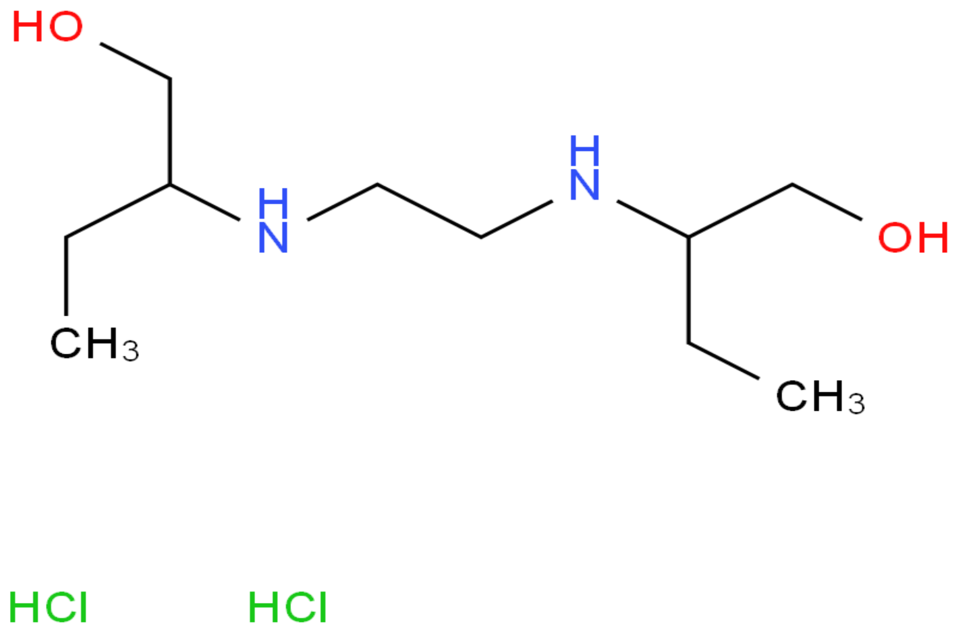
Ethambutol is a medication primarily used to treat tuberculosis. It is usually given in combination with other tuberculosis medications, such as isoniazid, rifampicin and pyrazinamide. It may also be used to treat Mycobacterium avium complex, and Mycobacterium kansasii. It is taken by mouth.

Ethambutol inhibits RNA **synthesis** and decreases tubercle bacilli replication. Nearly all strains of M. tuberculosis and M. kansasii as well as a number of strains of MAC are sensitive to **ethambutol**. **Ethambutol** is an antibiotic with bacteriostatic, antimicrobial and antitubercular properties.

Nomenclature of Ethambutol :



$$CH_3CH_2-\overset{CH_2OH}{\underset{H}{C}}-NHCH_2CH_2NH-\overset{H}{\underset{CH_2OH}{C}}-CH_2CH_3 \quad \cdot 2HCl$$



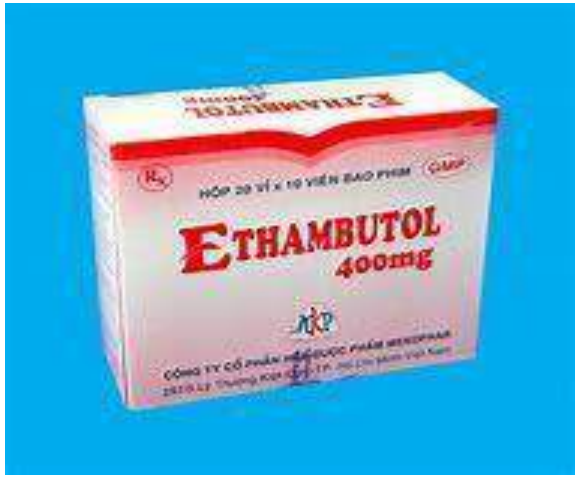
$C_{10}H_{24}N_2O_2 \cdot 2HCl$ M.W. 277.23

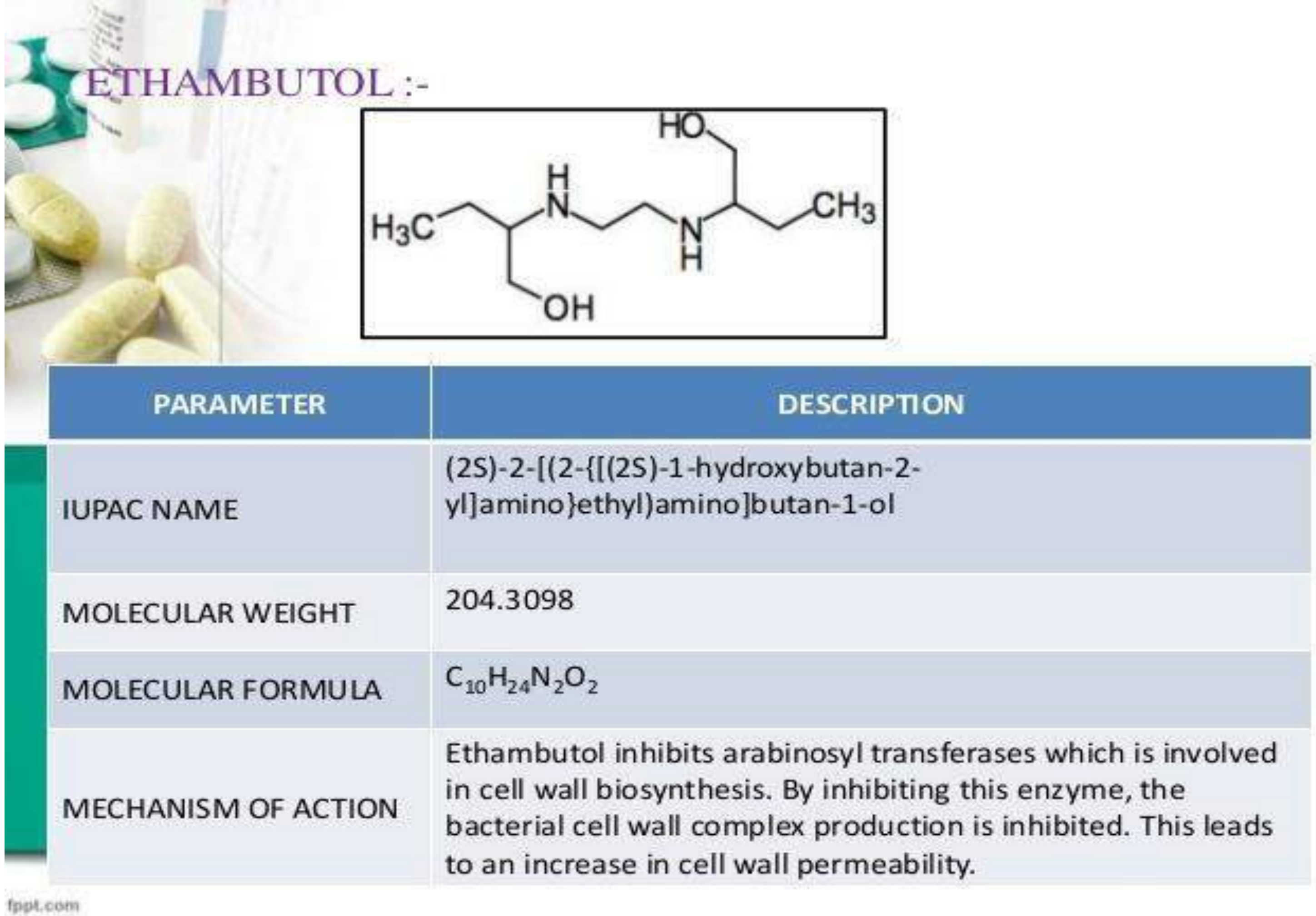
(+)-2,2' (Ethylenediimino)-di-1-butanol dihydrochloride

2.Ethambutol is bacteriostatic against actively growing TB bacilli. It works by obstructing the formation of cell wall. Mycolic acids attach to the 5'-hydroxyl groups of D-arabinose residues of arabinogalactan and form mycolyl-arabinogalactan-peptidoglycan complex in the cell wall. It

disrupts arabinogalactan synthesis by inhibiting the enzyme arabinosyl transferase. Disruption of the arabinogalactan synthesis inhibits the formation of this complex and leads to increased permeability of the cell wall.

Continued :





ETHAMBUTOL :-

PARAMETER	DESCRIPTION
IUPAC NAME	(2S)-2-[(2-{[(2S)-1-hydroxybutan-2-yl]amino}ethyl)amino]butan-1-ol
MOLECULAR WEIGHT	204.3098
MOLECULAR FORMULA	$C_{10}H_{24}N_2O_2$
MECHANISM OF ACTION	Ethambutol inhibits arabinosyl transferases which is involved in cell wall biosynthesis. By inhibiting this enzyme, the bacterial cell wall complex production is inhibited. This leads to an increase in cell wall permeability.

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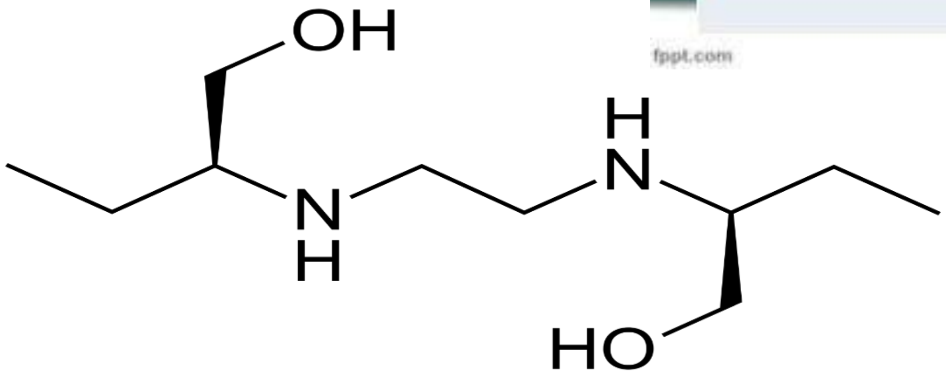
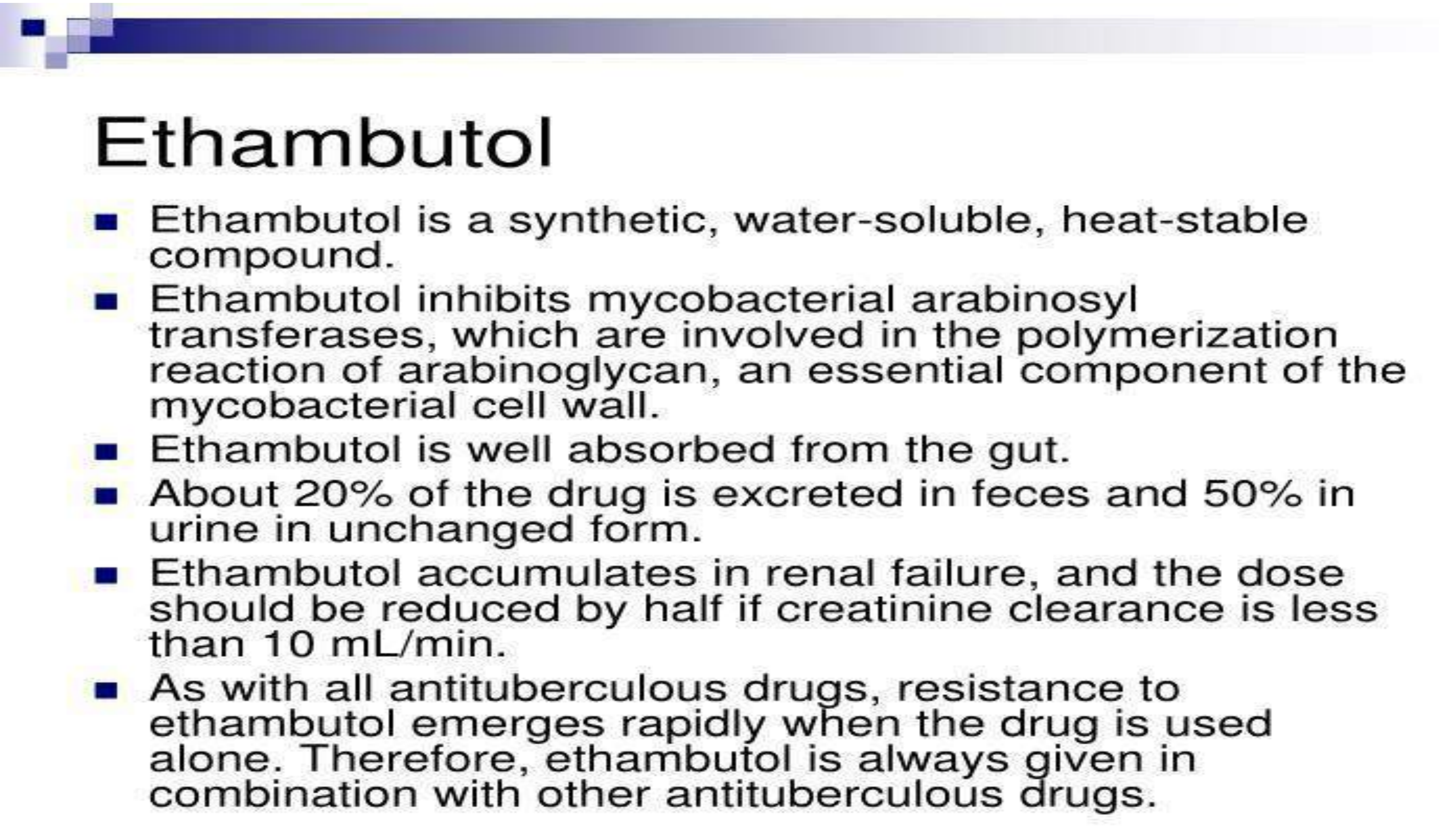




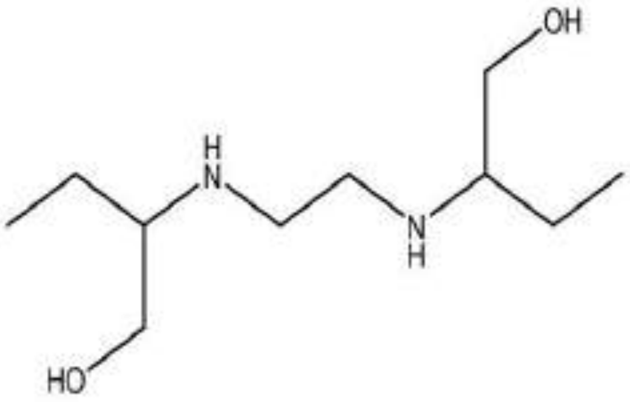
Ethambutol

- Ethambutol is a synthetic, water-soluble, heat-stable compound.
- Ethambutol inhibits mycobacterial arabinosyl transferases, which are involved in the polymerization reaction of arabinoglycan, an essential component of the mycobacterial cell wall.
- Ethambutol is well absorbed from the gut.
- About 20% of the drug is excreted in feces and 50% in urine in unchanged form.
- Ethambutol accumulates in renal failure, and the dose should be reduced by half if creatinine clearance is less than 10 mL/min.
- As with all antituberculous drugs, resistance to ethambutol emerges rapidly when the drug is used alone. Therefore, ethambutol is always given in combination with other antituberculous drugs.

Continued :

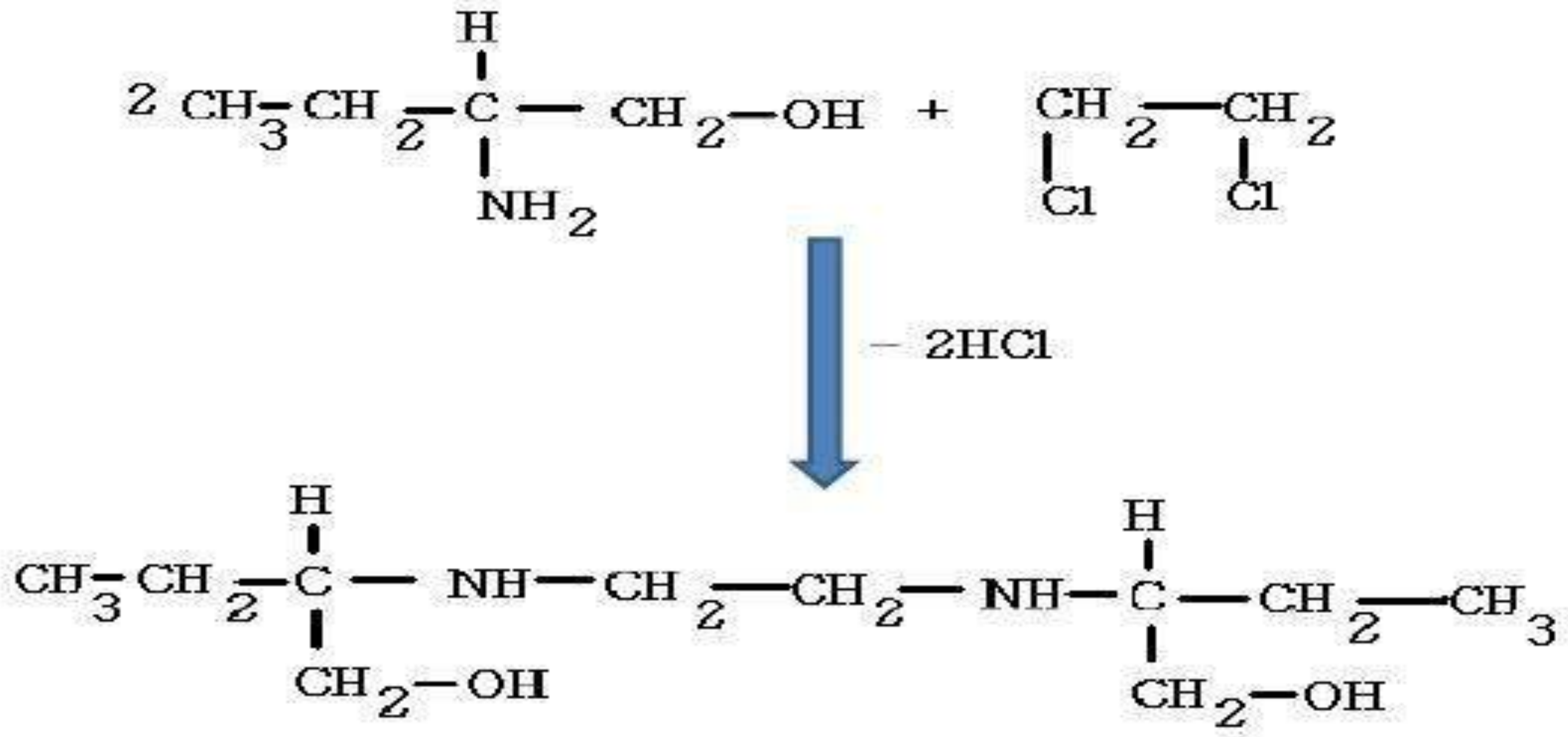
- **Ethambutol** is an ethylenediamine derivative that is ethane-1,2-diamine in which one hydrogen attached to each of the nitrogen is substituted by a 1hydroxybutan-2-yl group (S,S-configuration). It is a bacteriostatic antimycobacterial drug.

The literature methods for the synthesis of ethambutol involve direct **alkylation** (with 1,2-dibromoethane) or **reductive alkylation** (with glyoxal) of the amino group of (S)-**2amino-1-butanol**, which in turn is obtained by resolution of the corresponding racemic material.



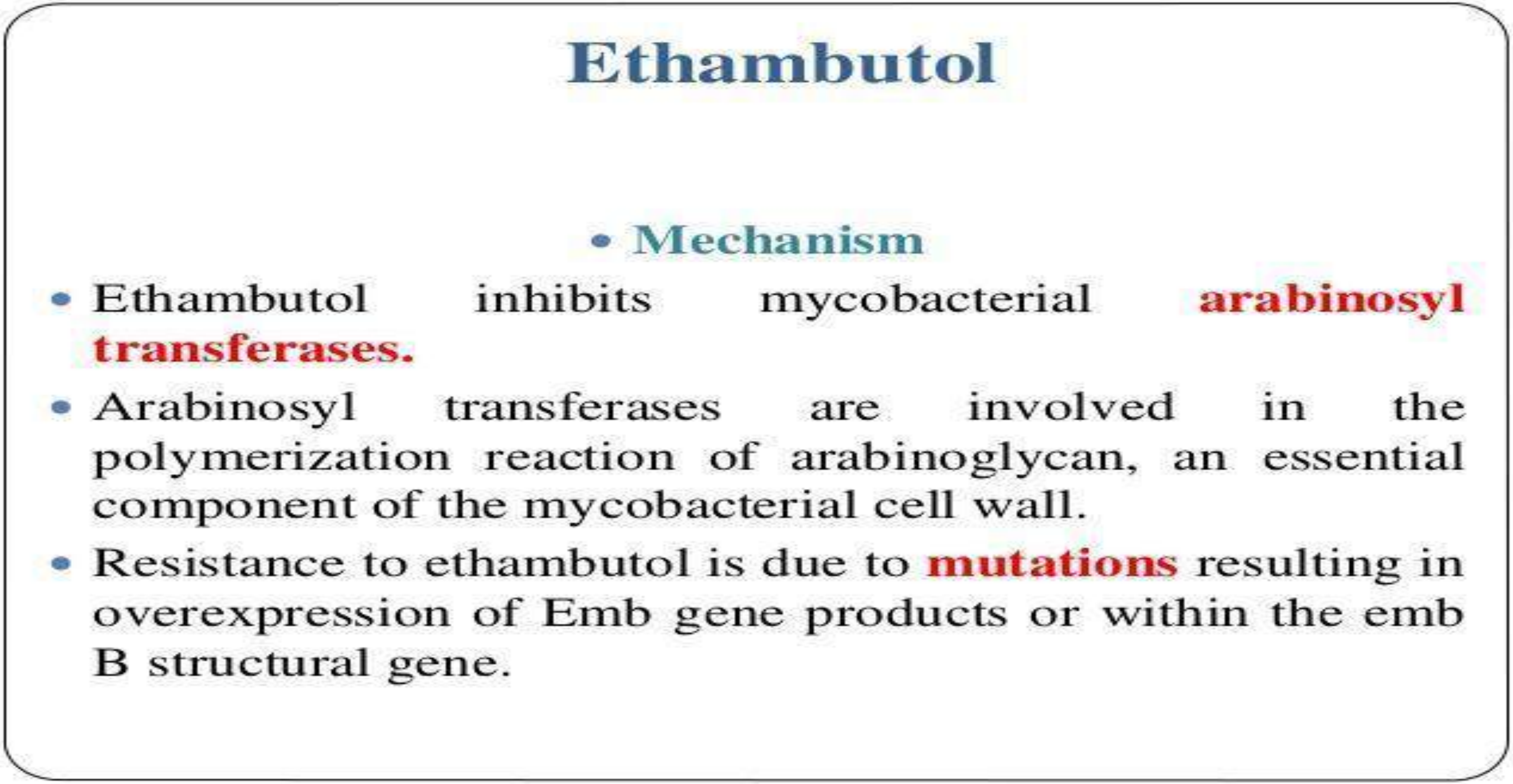
Synthesis of Ethambutol :

Chemical Synthesis



2-amino butanol reacts with 1, 2 dichloro ethane to produce ethambutol

Action of drug - Ethambutol :



Ethambutol

- **Mechanism**

- Ethambutol inhibits mycobacterial **arabinosyl transferases.**
- Arabinosyl transferases are involved in the polymerization reaction of arabinoglycan, an essential component of the mycobacterial cell wall.
- Resistance to ethambutol is due to **mutations** resulting in overexpression of Emb gene products or within the emb B structural gene.

Uses of Ethambutol :

- Ethambutol is a medication primarily used to treat tuberculosis. It is usually given in combination with other tuberculosis medications, such as isoniazid, rifampicin and pyrazinamide. It may also be used to treat Mycobacterium avium complex, and Mycobacterium kansasii. It is taken by mouth.
- **Side Effects :**
- Common side effects include problems with vision, joint pain, nausea, headaches, and feeling tired. Other side effects include liver problems and allergic reactions.

4. Phenobarbitone / Phenobarbital :

- Phenobarbital use originally was as a sedative. While it can be used **for short-term sedation**, **such as for emergency treatment**, **in surgery**, or **to calm someone have a psychiatric episode**,
- It is most famous as a long-term sedative for individuals in intensive care. This is because it is longer acting than many other tranquilizers available in the market, allowing caregivers .
- . Phenobarbital, also known as phenobarbitone or phenobarb, or by the trade name Luminal, is a medication of the barbiturate type. It is recommended by the World Health Organization (WHO) for the treatment of certain types of epilepsy in developing countries.
- Phenobarbital belongs to a class of **drugs** known as barbiturate anticonvulsants/hypnotics. It works by controlling the abnormal electrical activity in the brain that occurs during a seizure.

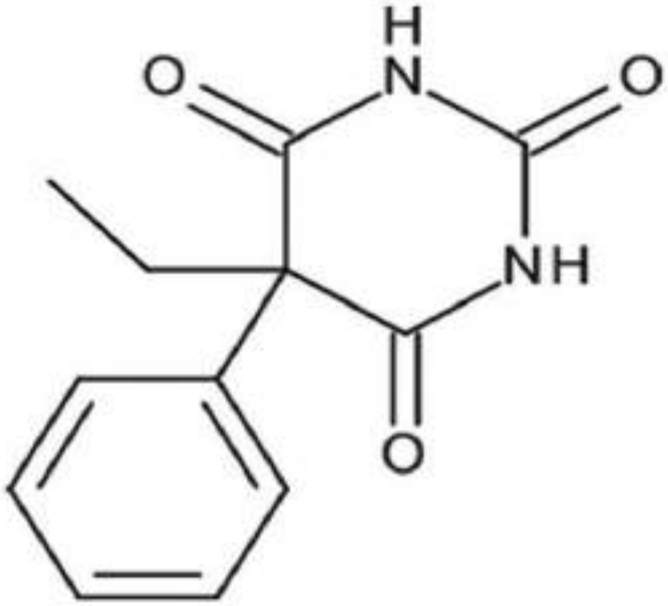
Phenobarbitone

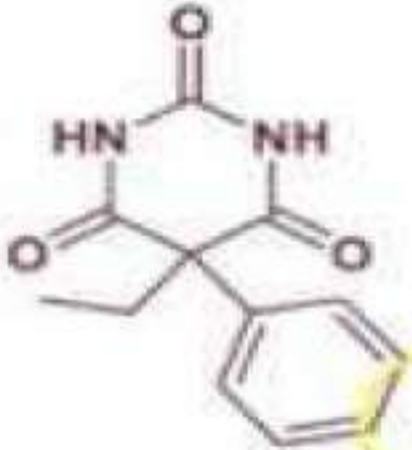
- **Discovery:**

  1912: First efficacious AED, it raised seizure threshold as well as limits spread, suppresses kindled seizures with wide spectrum, one of the safest drugs

- **Pharmacokinetics:**
  - Slow oral absorption, long plasma t1/2 (80-120 hours), 40-60% bound to plasma proteins
  - Metabolism: liver , excreted unchanged by kidney
- **Disadvantage:**
  - Sedation, nystagmus, ataxia, hyperactivity in children and confusion in the elderly
- **Dose:**

Adult: 60mg OD to tds, children: 3-6mg/kg/day





Phenobarbital

Chemical name :
5-ethyl-5-phenylpyrimidine-2,4,6(1H,3H,5H)-trione

Inactive metabolite :
5-ethyl-5-(4-hydroxyphenyl)pyrimidine-2,4,6 (1H,3H,5H)-trione

Physicochemical properties :
Polymorphism – seen in other barbiturates; up to 13 crystal modifications
the commercial preparations are usually made up largely of thermally stable modification II (174°C)

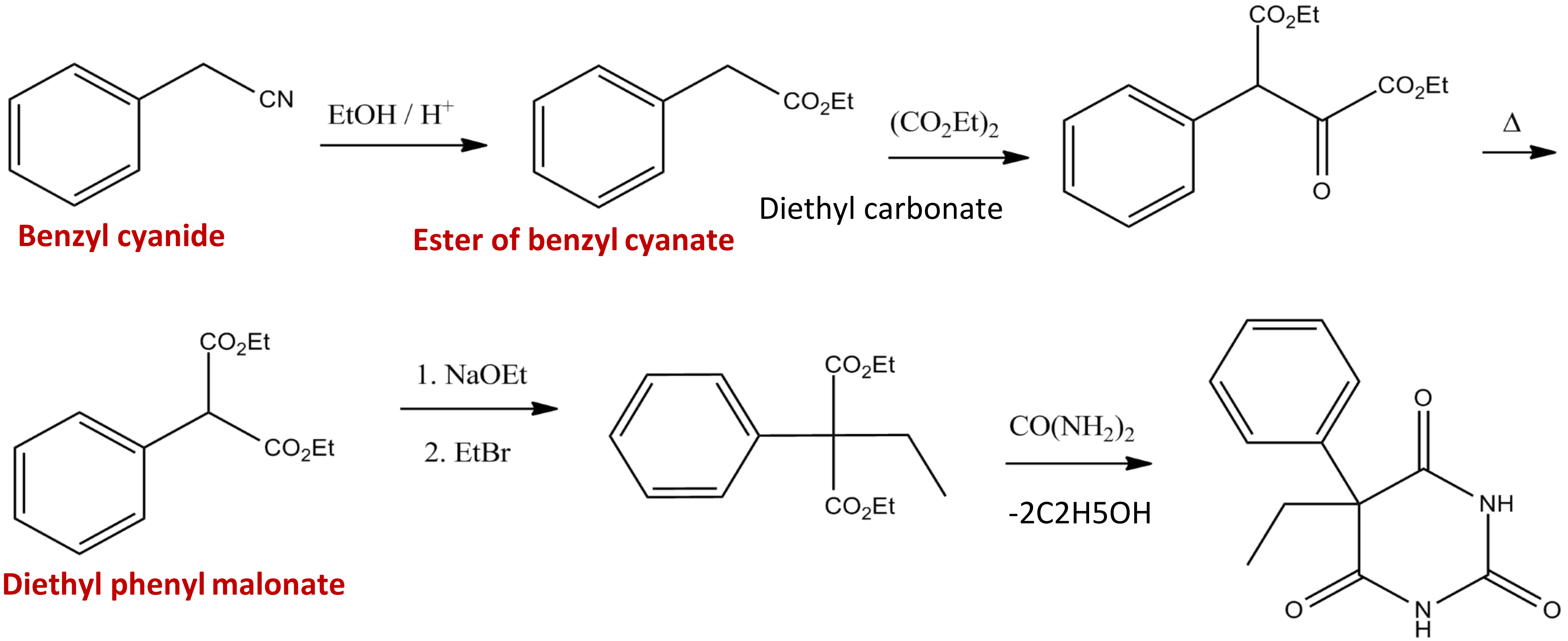
How is it synthesized ?

Barbiturate drugs are obtained via condensation reactions between a derivative of diethyl malonate and urea in the presence of a strong base. The synthesis of phenobarbital uses this common approach as well but differs in the way in which this malonate derivative is obtained. The reason for this difference is due to the fact that aryl halides do not typically undergo nucleophilic substitution in malonic ester.

- There are eight methods for the synthesis of phenobarbital. Here only two methods are investigated. The first method was based on the reaction of diethyl ethylphenylmalonate and urea in the presence of sodium ethoxide (by adding 1/2, 1/4, 1/8 and 1/8 portion of sodium ethoxide solution for first, second, third and fourth hour, respectively).

Synthesis of phenobarbitone / phenobarbital :

It is a CNS drug prepared by condensing benzyl cyanide and diethyl carbonate . The product obtained is hydrolysed and ethylated to give diethyl phenyl malonate . On treatment with sodium and ethyl bromide forms an ethyl derivative which on condensation with urea yields phenobarbital.

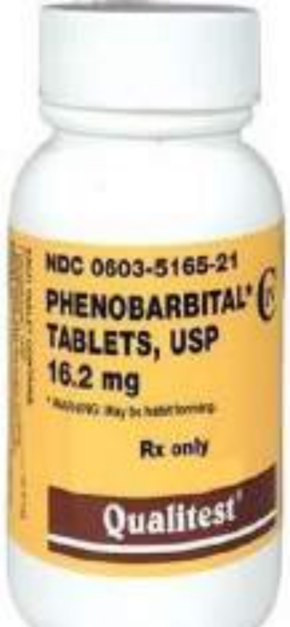


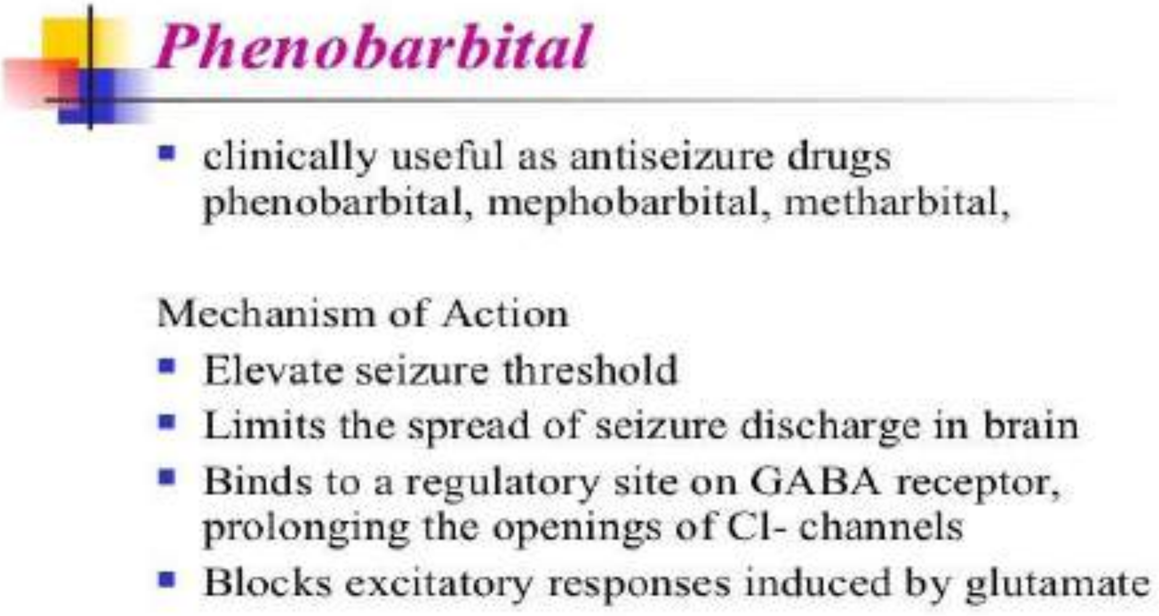
Phenobarbital

Phenobarbitone :

Mechanism of Action

Phenobarbital works on GABA receptors, increasing synaptic inhibition. This has the effect of elevating seizure threshold and reducing the spread of seizure activity from a seizure focus. Phenobarbital may also inhibit calcium channels, resulting in a decrease in excitatory transmitter release.





Phenobarbital

- clinically useful as antiseizure drugs phenobarbital, mephobarbital, metharbital,

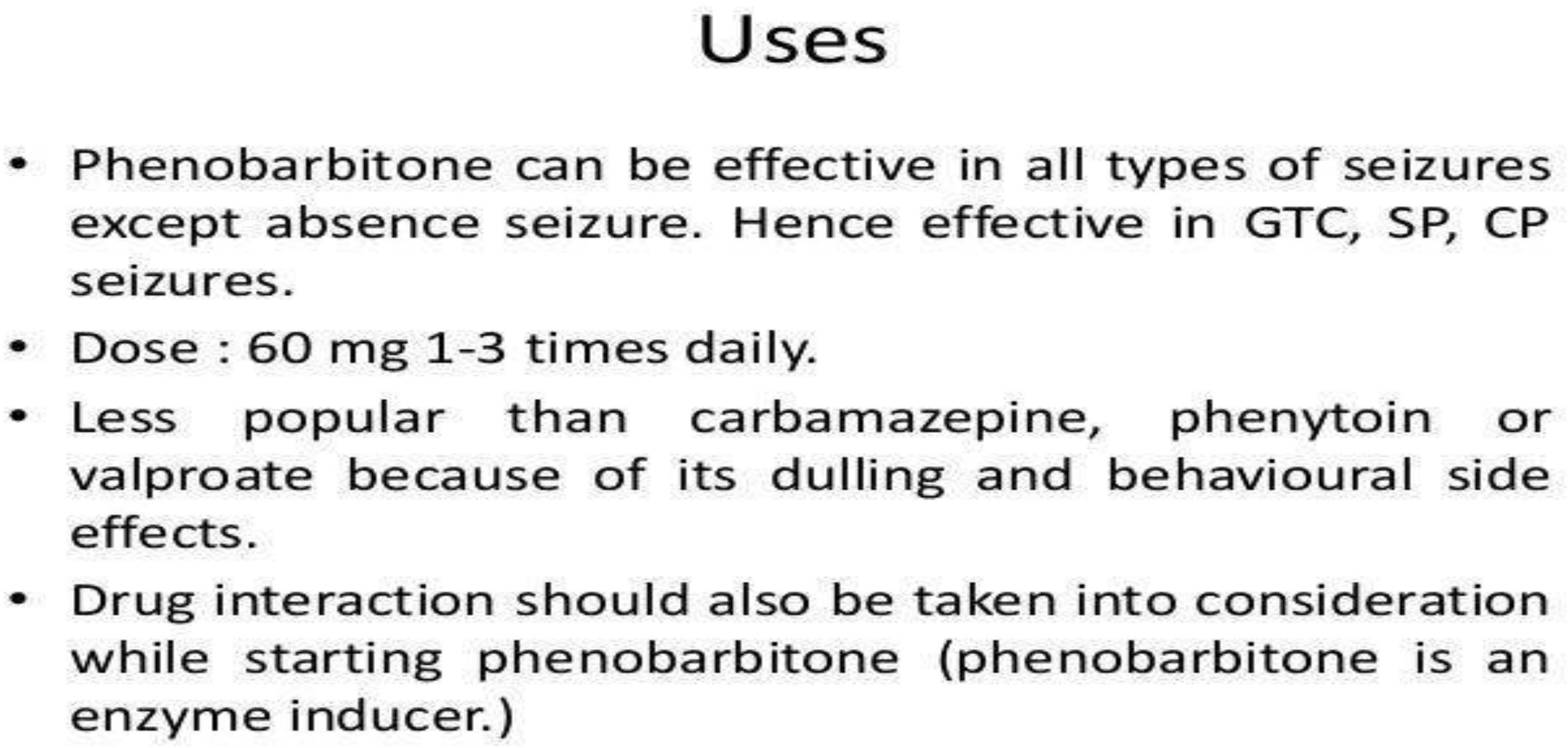
Mechanism of Action

- Elevate seizure threshold
- Limits the spread of seizure discharge in brain
- Binds to a regulatory site on GABA receptor, prolonging the openings of Cl- channels
- Blocks excitatory responses induced by glutamate

open which in turn depresses the central nervous system. This is done by acting on GABA-A receptor subunits.

Phenobarbital acts

Uses :



Uses

- Phenobarbitone can be effective in all types of seizures except absence seizure. Hence effective in GTC, SP, CP seizures.
- Dose : 60 mg 1-3 times daily.
- Less popular than carbamazepine, phenytoin or valproate because of its dulling and behavioural side effects.
- Drug interaction should also be taken into consideration while starting phenobarbitone (phenobarbitone is an enzyme inducer.)

Uses of phenobarbitone continued :

- It is a potent hypnotic but it’s onset of action is slow but duration of it’s action is long (10- 16 hrs.)It is also effective in the control of Epileptic seizures . So used in the treatment of general convulsions in children.
- Anticonvulsant action of barbiturates is a part of their hypnotic effect. Phenobarbitone is prescribed to control seizures or fits.
- Phenobarbitone belongs to barbiturate group of medicines. In exceptional circumstances, it is also used to treat seizures that sometimes accompany a high fever in children.
- **Side Effects** - It has also been known to cause complications when used with drugs like aceprometazine, adipilon, etc. Usage of Phenobarbitone can lead to temporary and common side effects like drowsiness, excitation, irritability, loss of balance or coordination, headache, loss of appetite, nausea, vomiting, constipation, etc.

Uses continued…

- Phenobarbital is used to control seizures. Phenobarbital is also used to relieve anxiety.
- It is also used to prevent withdrawal symptoms in people who are dependent ('addicted'; feel a need to continue taking the medication) on another barbiturate medication and are going to stop taking the medication.
- It works by controlling the abnormal electrical activity in the brain that occurs during a seizure. This medication is also used for a short time (usually no more than 2 weeks) to help calm you or help you sleep during periods of anxiety. It works by affecting certain parts of the brain to cause calming.

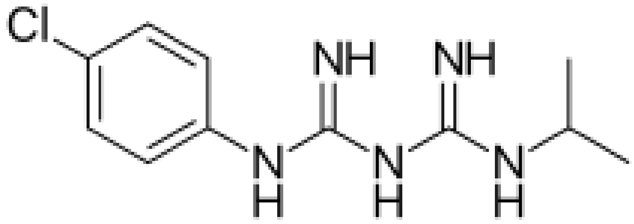
4. Paludrine / (Proguanil) : Antimalarial Drug

- Paludrine or Proguanil is used for the prevention and treatment of malaria in both adults and children, particularly in areas where chloroquine-resistant P. falciparum malaria has been reported. It is usually taken in combination with atovaquone, another antimalarial drug.

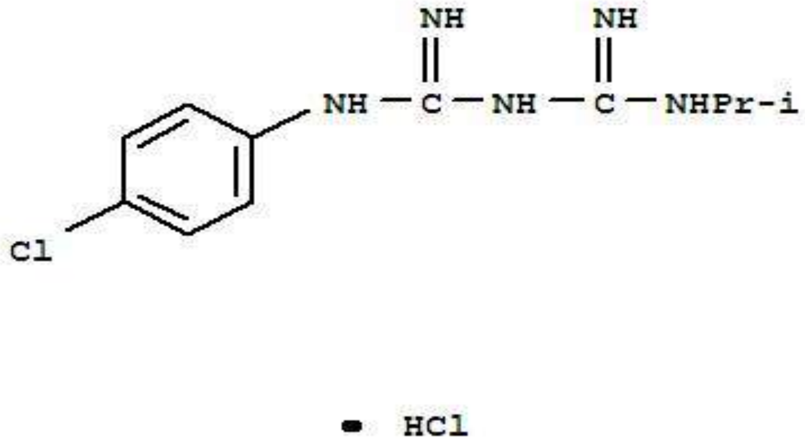
  It is also effective in the treatment of most other multi-drug resistant forms of P. falciparum.

- Paludrine Tablet contains Proguanil as an active ingredient. It works by stopping the growth of malaria parasite and Plasmodium vivax.,

  and success rate exceeds 93%.



Structure of Paludrine :



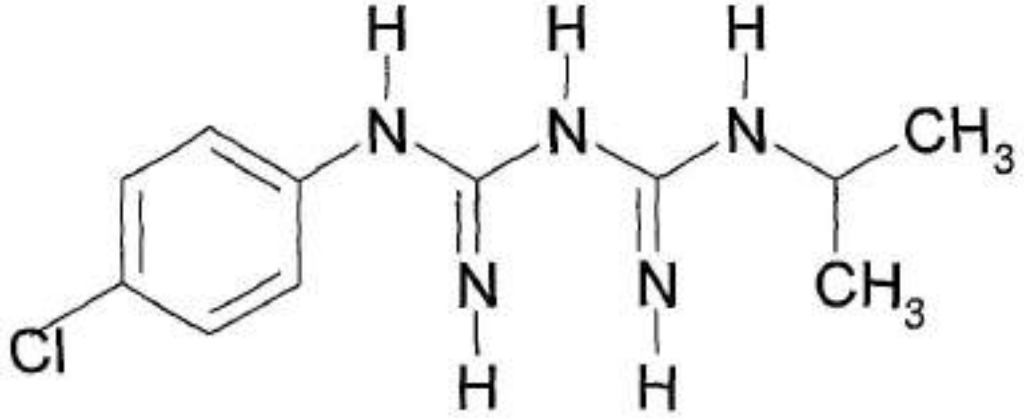
Anti malarial drugs

G.Vishnupriya pharma
MD

Proguanil, also known as chlorguanide and chloroguanide, is a medication used to treat and prevent malaria.

It is often used together with chloroquine or atovaquone.

When used with chloroquine the combination will treat mild chloroquine resistant malaria. It is taken by mouth.



N1-p-Chlorophenyl –N-5 isopropylguanide

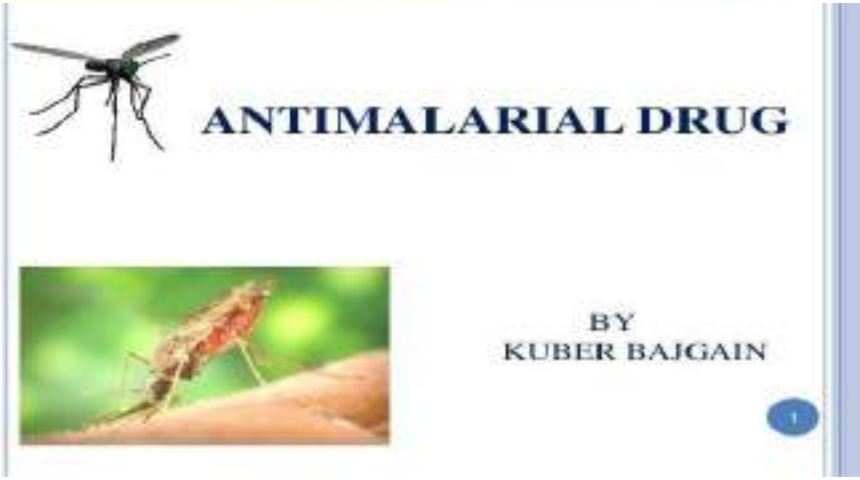
(paludrine)

History :

- **Paludrine tablets contain the active ingredient proguanil hydrochloride, which is an antimalarial medicine. It is used to prevent malaria caused due to various types of parasites known as Plasmodium.**
- **Malaria is a potentially fatal disease caused by various types of parasites known as Plasmodium, contain the active ingredient chloroquine phosphate.**
- **Malaria is a potentially fatal disease caused by he first pharmaceutical used to treat malaria, quinine, which was derived from the tree bark of Cinchona calisaya .**
- **Quinine synthesis was first attempted in 1856 by William Henry Perkins, but synthesis was not successful until 1944.various types of parasites known as Plasmodium.**

Antimalarial drugs

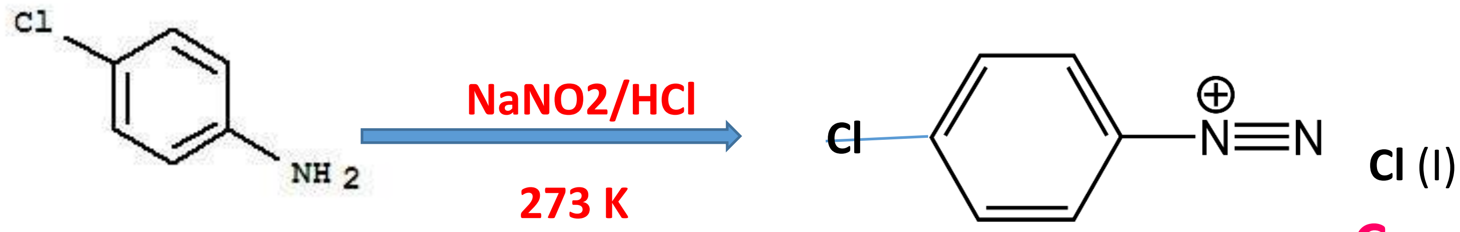
- Malaria is an acute infectious disease caused by five species of the protozoal genus Plasmodium
  - ***Plasmodium falciparum*** – Found in Africa, and it is most common parasite responsible for most malaria deaths worldwide. is the most dangerous species, causing an acute, rapidly fulminating disease that is characterized by persistent high fever, orthostatic hypotension, and massive erythrocytosis.
  - ***Plasmodium vivax*** – Mainly found in Asia and South America. Common in tropical countries.
  - ***Plasmodium ovale*** – Uncommon and found in West Africa.
  - ***Plasmodium malariae*** –Found in Africa, uncommon.
  - ***Plasmodium knowlesi*** –Very rare and found in parts of southeast Asia.


ANTIMALARIAL DRUG

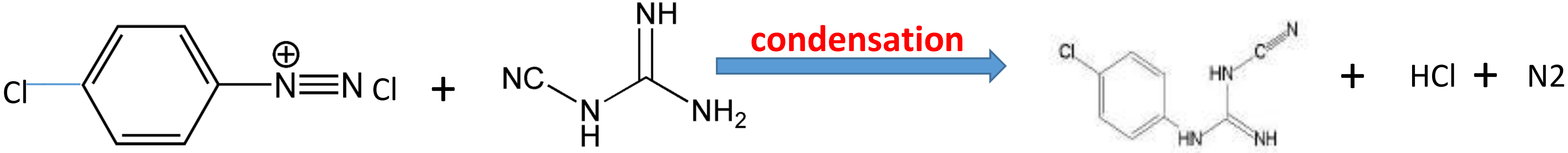
BY
KUBER BAJGAIN

Synthesis of Paludrine :

- Starting from p-chloroaniline it is prepared through following steps.
- **i) Diazotization of p- chloroanline to p- chlorobezene diazonium chloride salt (I).**



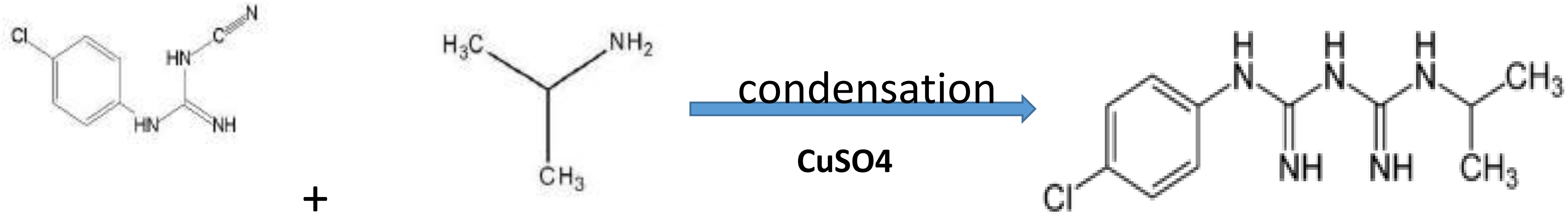
ii) Condensation of (I) with cyanoguanidine (II) to give product (III).



(I) (II) (III)

Synthesis continued…

- iii) Condensation of (III) with isopropyl amine (IV) in presence of copper sulphate to form paludrine .



(III)

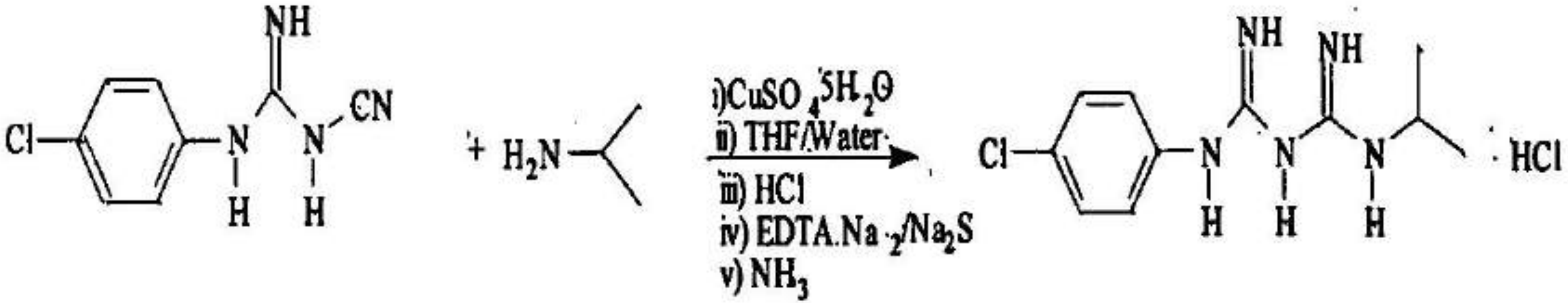
Urea

Paludrine

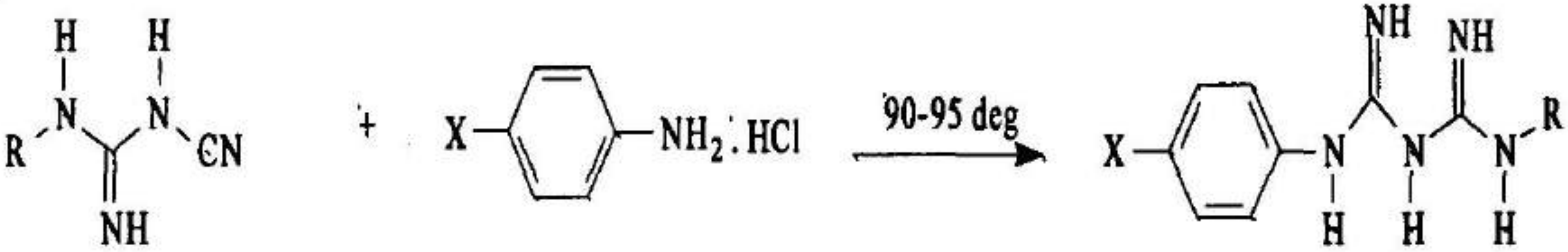
Uses :

Paludrine contains a medicine called proguanil hydrochloride. This belongs to a group of medicines called ‘anti-malarials’.

‘Anti-malarials’ can be used in certain parts of the world to help **prevent malaria** caused due to mosquitoes.



Synthesis of Paludrine：Another methods

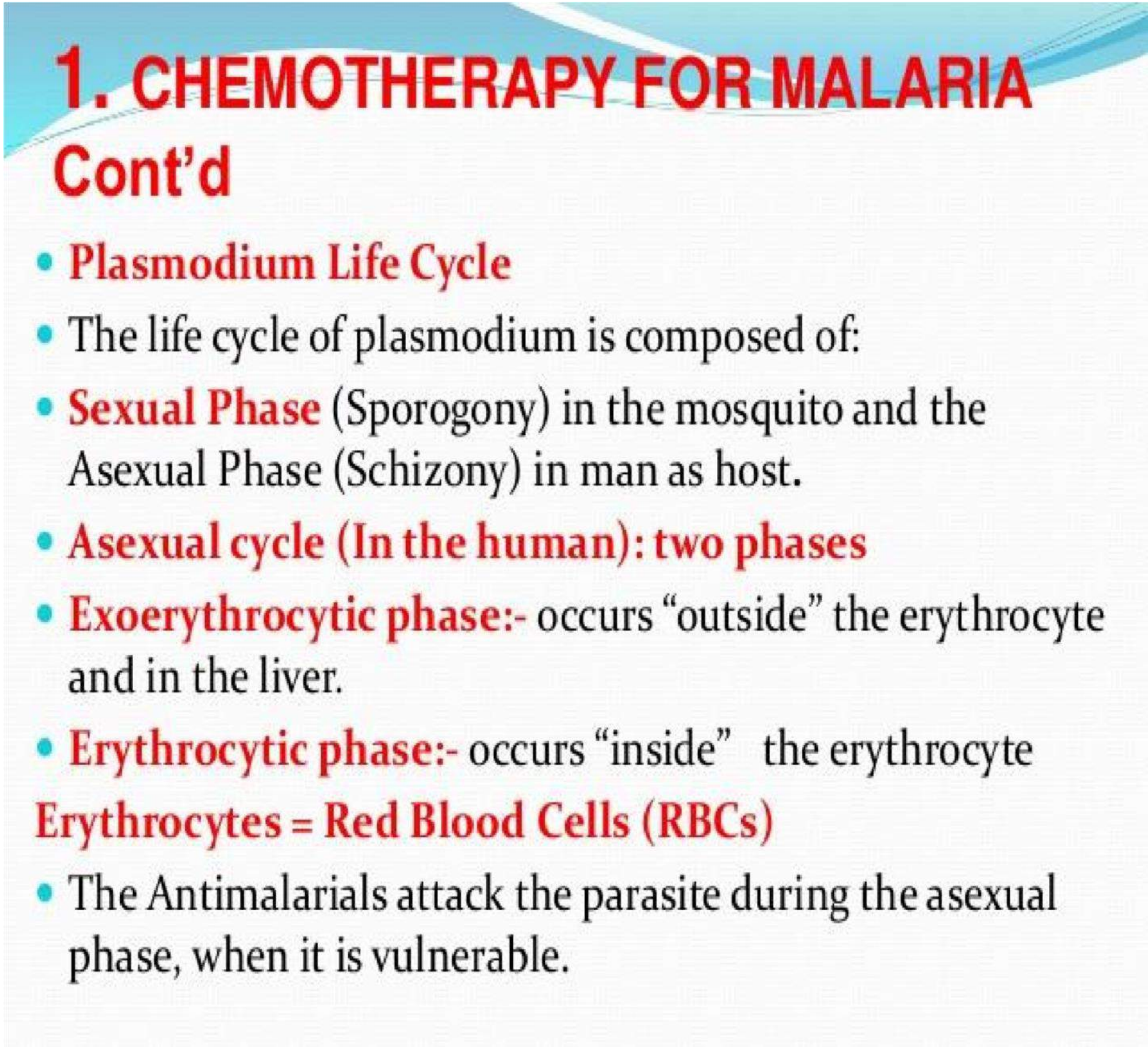

90-95 deg

Action of drug :

Clinical features:-

The clinical features of malaria are due to the blood stage parasites.

There is fever with rigor, and abdominal pain seen in malaria. Due to rupture of RBC there is anaemia, Mild enlargement of spleen is seen, head ache, myalgia, arthralgia, nausea.



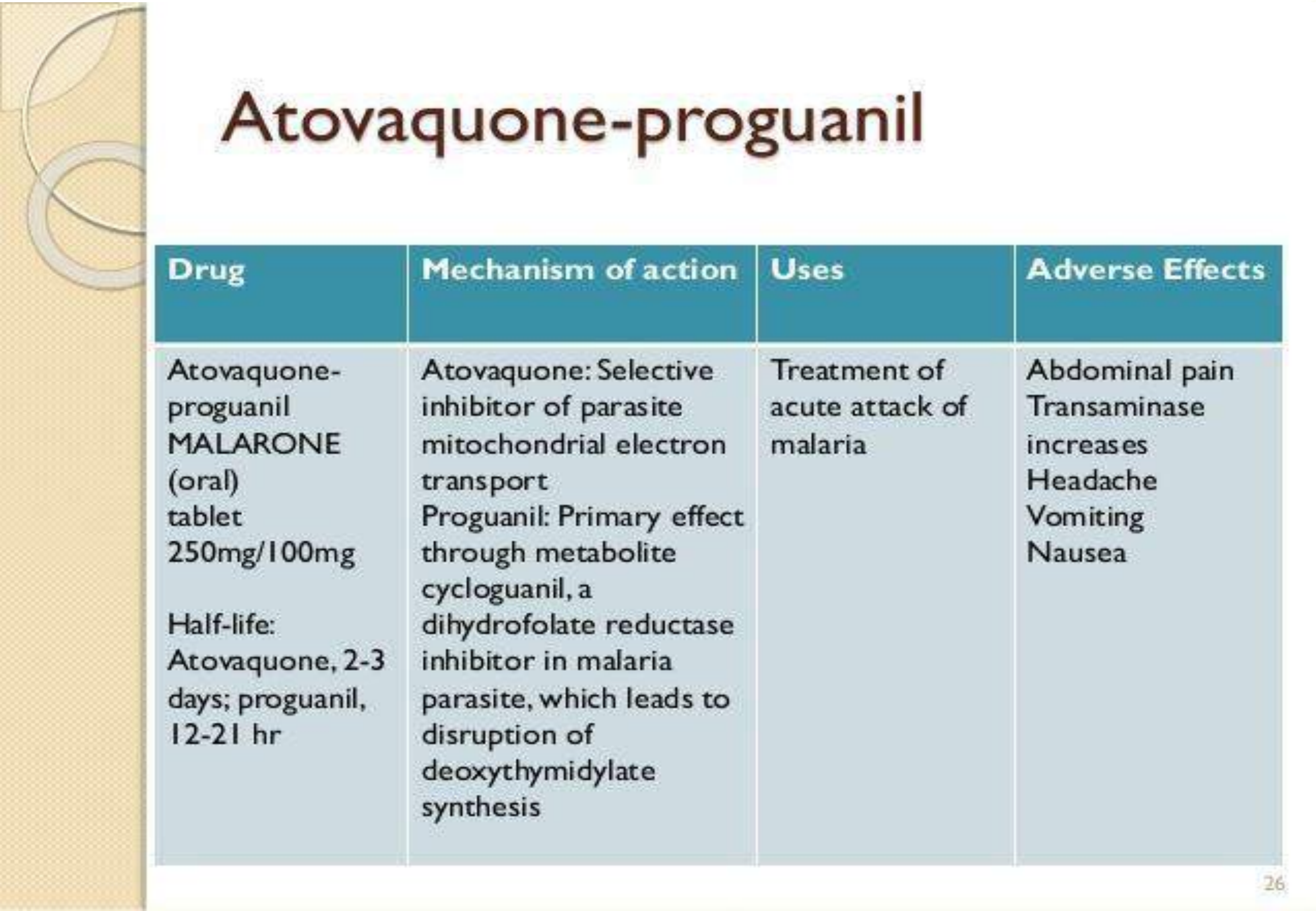
1. CHEMOTHERAPY FOR MALARIA Cont'd

- **Plasmodium Life Cycle**
- The life cycle of plasmodium is composed of:
- **Sexual Phase** (Sporogony) in the mosquito and the Asexual Phase (Schizony) in man as host.
- **Asexual cycle (In the human): two phases**
- **Exoerythrocytic phase:-** occurs "outside" the erythrocyte and in the liver.
- **Erythrocytic phase:-** occurs "inside" the erythrocyte

Erythrocytes = Red Blood Cells (RBCs)

- The Antimalarials attack the parasite during the asexual phase, when it is vulnerable.

Examples :



Atovaquone-proguanil

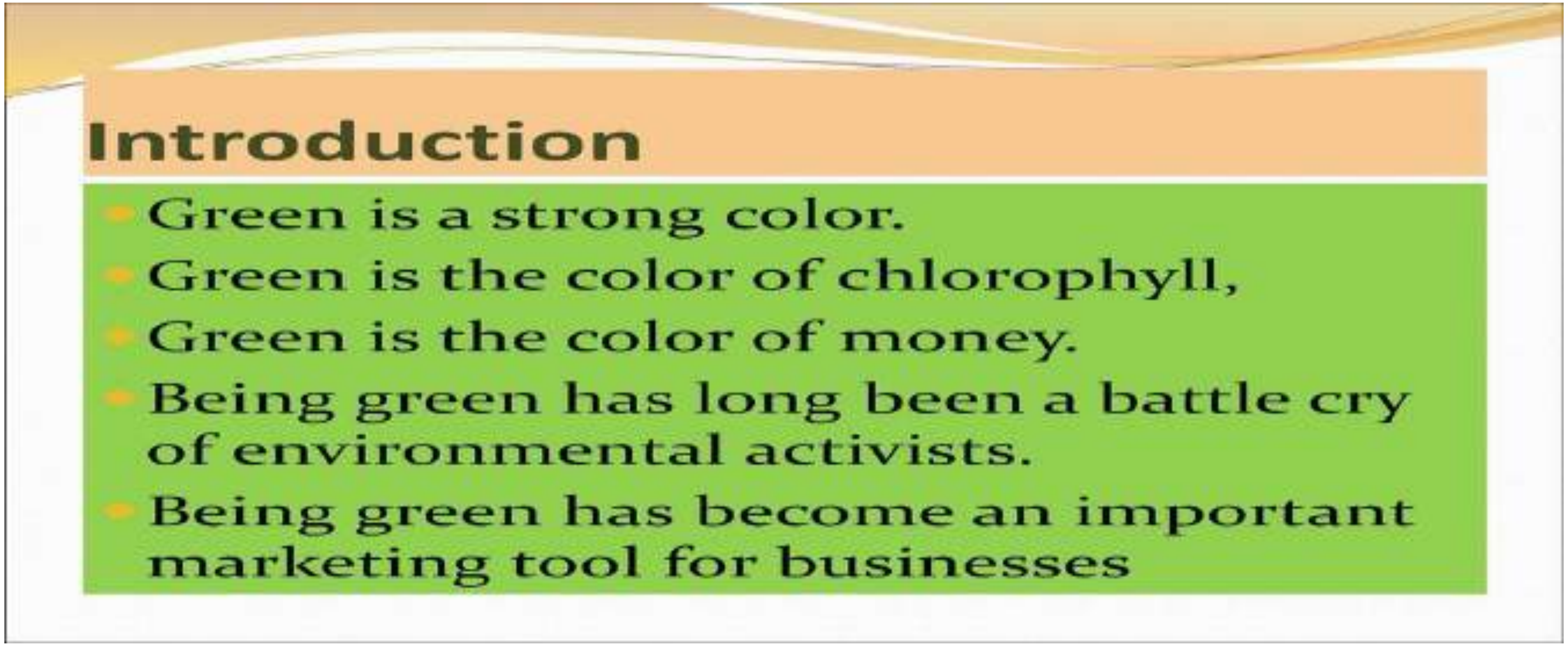
Drug	Mechanism of action	Uses	Adverse Effects
Atovaquone-proguanil MALARONE (oral) tablet 250mg/100mg Half-life: Atovaquone, 2-3 days; proguanil, 12-21 hr	Atovaquone: Selective inhibitor of parasite mitochondrial electron transport Proguanil: Primary effect through metabolite cycloguanil, a dihydrofolate reductase inhibitor in malaria parasite, which leads to disruption of deoxythymidylate synthesis	Treatment of acute attack of malaria	Abdominal pain Transaminase increases Headache Vomiting Nausea

Green Chemistry

Cutting-edge research for a greener sustainable future

RSC Publishing

Green Chemistry



Introduction

- Green is a strong color.
- Green is the color of chlorophyll,
- Green is the color of money.
- Being green has long been a battle cry of environmental activists.
- Being green has become an important marketing tool for businesses

Green chemistry is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances. ... Reduces the negative impacts of chemical products and processes on human health and the environment. Lessens and sometimes eliminates hazard from existing products and processes.

Father of Green Chemistry

The concept of green chemistry was formally established at the ENVIRONMENTAL PROTECTION AGENCY 15 years ago in response to the Pollution Prevention Act of 1990.

Paul T. Anastas for the first time in **1991** coined the term Green Chemistry. Though it is said that the concept was originated by Trevor Kletz in his **1978** paper where he proposed that chemists should seek alternative processes to those involving more dangerous substances and conditions.

Continued…

- What is green chemistry ?

Green chemistry is the approach in chemical sciences that efficiently uses renewable raw materials, eliminating waste and avoiding the use of toxic and hazardous reagents and solvents in the manufacture and application of chemical products.

Plants and animals suffer less harm from toxic chemicals in the environment. Lower potential for global warming, ozone depletion, and smog formation. Less

chemical disruption of ecosystems. Less use of landfills, especially hazardous waste landfills.

DEFINITION

Green Chemistry is the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products .

Some light upon the term-Green Chemistry:

Definition- "The design of chemical products and processes that are more environmentally friendly and reduce negative impacts to human health and the environment."

Green chemistry looks at pollution prevention on the molecular scale and is an extremely important area of Chemistry due to the importance of Chemistry in our world today and the implications it can show on our environment.

The *Green Chemistry* program supports the invention of more environmentally friendly chemical processes which reduce or even eliminate the generation of hazardous substances.

Green chemistry

- **Green chemistry**, also called **sustainable chemistry**, is an area of chemistry and chemical engineering focused on the designing of products and processes that minimize the use and generation of hazardous substances. Whereas environmental chemistry focuses on the effects of polluting chemicals on nature, green chemistry focuses on technological approaches to preventing pollution and reducing consumption of nonrenewable resources

Principles :

- **Use of Renewable Feedstocks**

  A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

- **Reduce Derivatives**

  Unnecessary derivatization (use of blocking groups, protection/de-protection, and temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

- **Catalysis**

  Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

Significance of green chemistry :

- Plants and animals suffer less harm from toxic chemicals in the environment. Lower potential for global warming, ozone depletion, and smog formation. Less chemical disruption of ecosystems. Less use of landfills, especially hazardous waste landfills.

Green chemistry aims to design and produce cost-competitive chemical products and processes that attain the highest level of the pollution-prevention hierarchy by reducing pollution at its source.

*Chemicals that are less hazardous to human health and the environment are less toxic to organisms.

SIGNIFICANCE

- Major tool in accomplishing Pollution prevention
- Leads to reduction in waste
- Reduced use of energy and other perishable resources
- Carrying out chemical activities leading to safer products

Choice of biocompatible, renewable, safe & non-toxic reagents

Minimise energy usage

Less of certain scarce raw resources

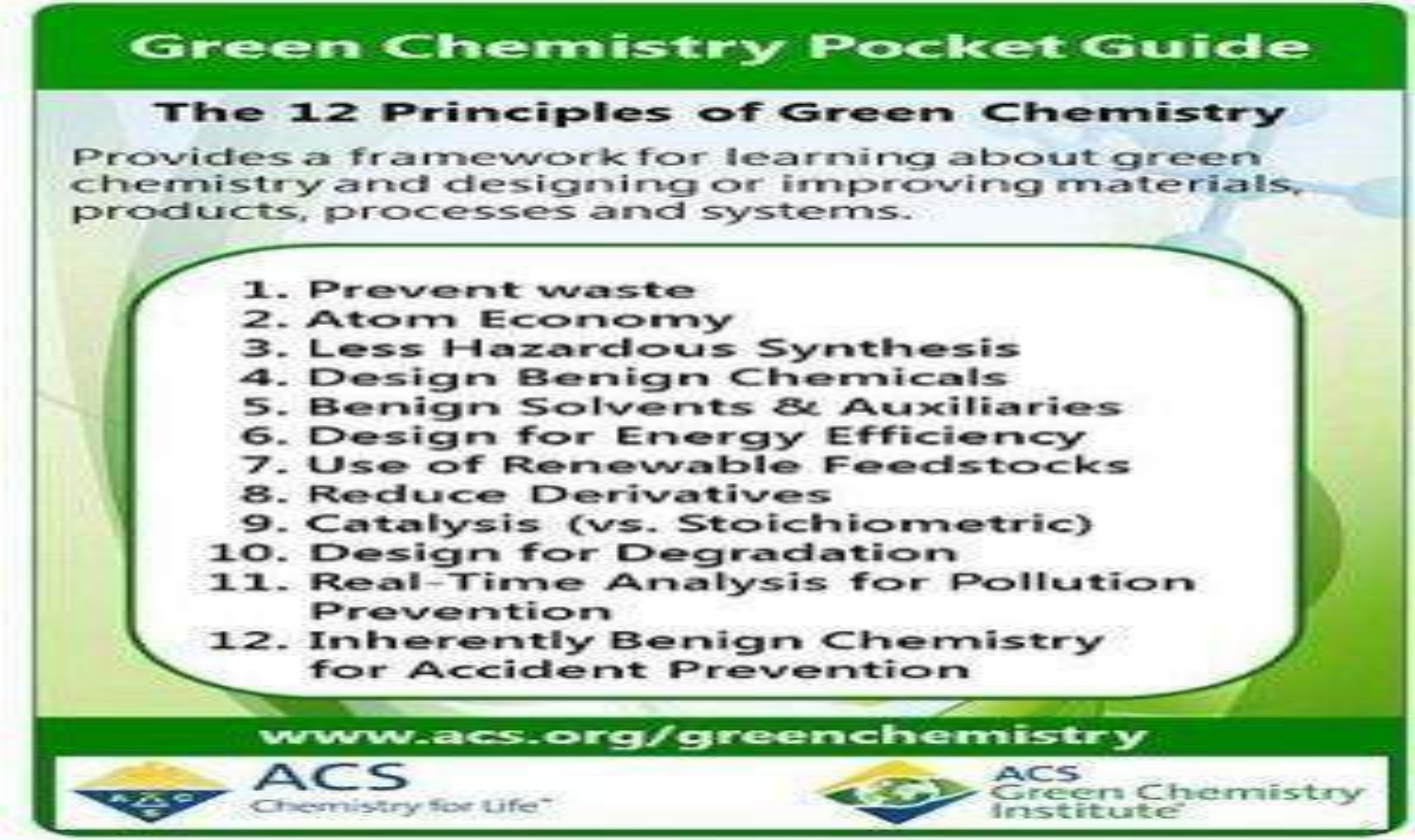
Safer disposal & recycling

Minimise byproducts & hazardouse waste

Green Chemistry

MEANING OF GREEN CHEMISTRY

- MAKING CHEMICAL PRODUCTS THAT DONOT HARM OUR ENVIRONMENT
- USING INDUSTRIAL PROCESS THAT REDUCE HAZARDOUS SUBSTANCES
- EFFICIENT PROCESS TO MINIMIZE WASTE PRODUCTION



Green Chemistry Pocket Guide

The 12 Principles of Green Chemistry

Provides a framework for learning about green chemistry and designing or improving materials, products, processes and systems.

1. Prevent waste
2. Atom Economy
3. Less Hazardous Synthesis
4. Design Benign Chemicals
5. Benign Solvents & Auxiliaries
6. Design for Energy Efficiency
7. Use of Renewable Feedstocks
8. Reduce Derivatives
9. Catalysis (vs. Stoichiometric)
10. Design for Degradation
11. Real-Time Analysis for Pollution Prevention
12. Inherently Benign Chemistry for Accident Prevention

www.acs.org/greenchemistry

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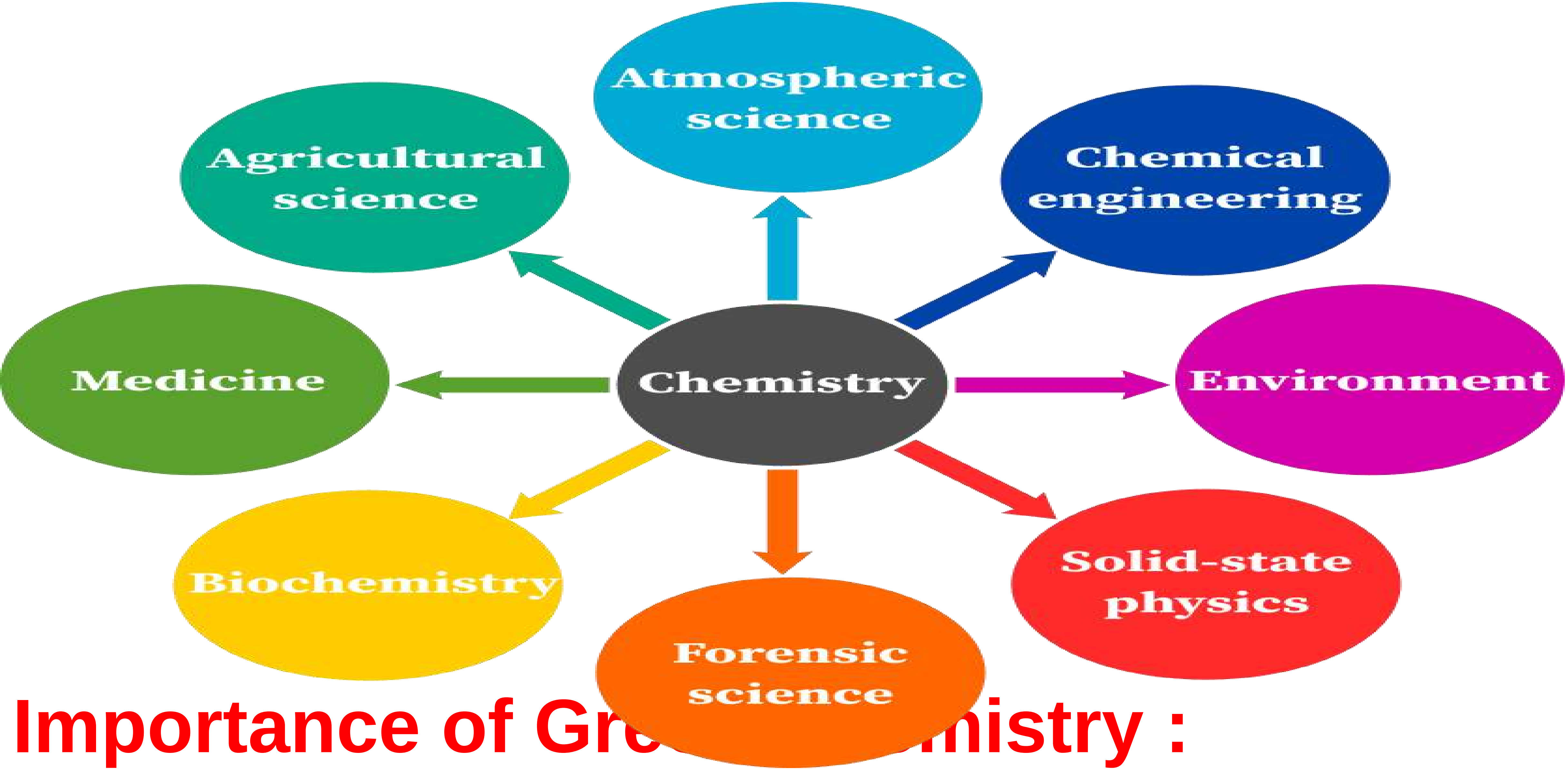
ACS Green Chemistry Institute®

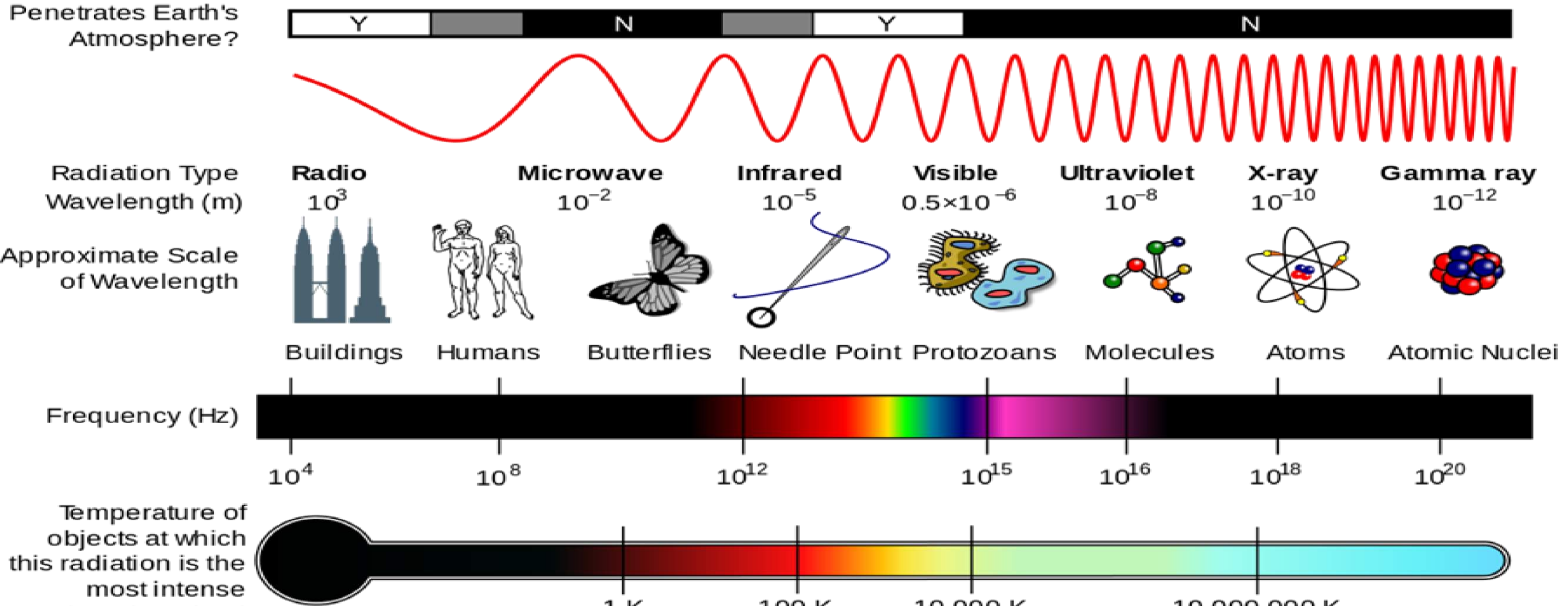


Importance of Gre mistry :

12 PRINCIPLES OF GREEN CHEMISTRY

1. Reduce Waste
2. Atom Economy
3. Less Hazardous Chemical Synthesis
4. Designing Safer Chemicals
5. Safer Solvents and Auxiliaries
6. Design for Energy Efficiency
7. Use of Renewable Feedstocks
8. Reduce Derivatives
9. Catalysis
10. Design for Degradation
11. Real-Time Pollution Prevention
12. Safer Chemistry for Accident Prevention

APPLICATIONS OF MICROWAVES

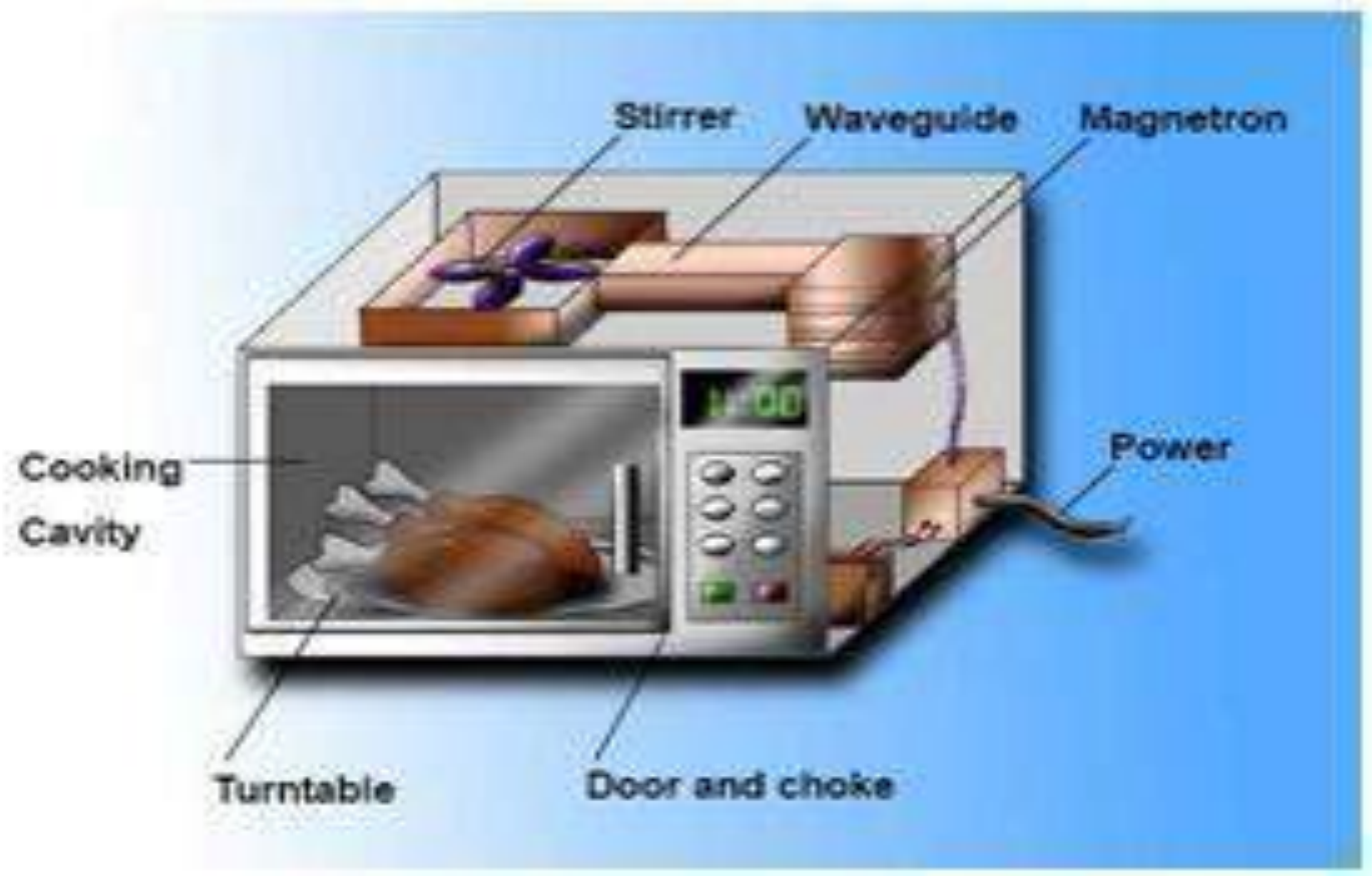


What are Microwaves ?

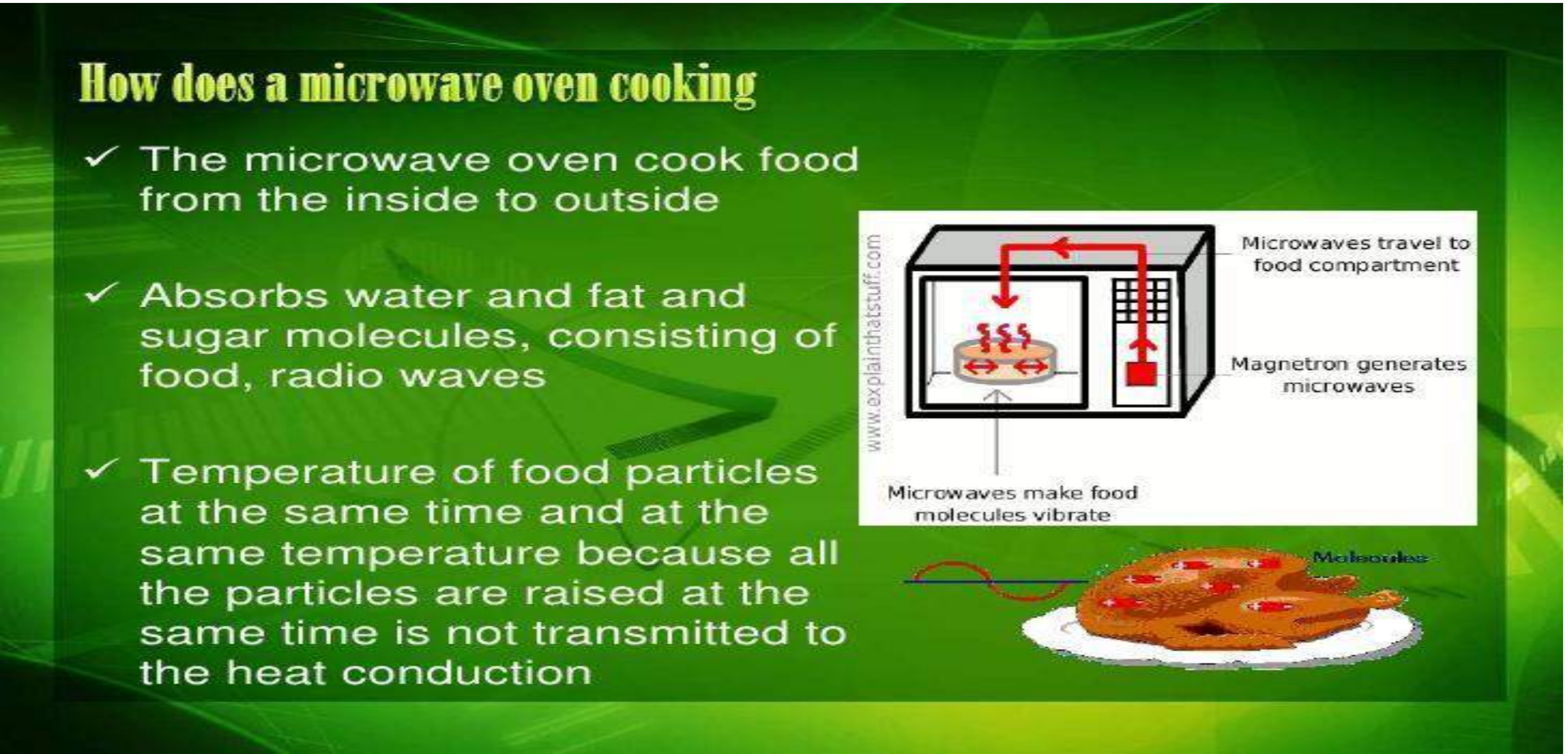
Microwave is a form of electromagnetic radiation with wavelengths ranging from about one meter to one millimeter; with frequencies between 300 MHz and 300 GHz. Different sources define different frequency ranges as microwaves;.

The name Microwave is derived from the energy used to cook the food, microwaves, which pass through the cells and molecules of the food, the frequency of the waves causes the water molecules to vibrate, this movement generates heat. These microwaves are produced by a device called a magnetron within the microwave oven.

Microwave Oven :



- Microwave Oven is commonly used for cooking purposes without using water. The high energy of the microwave rotates the polar molecules of water, fat, and sugars of the foodstuff.
- This rotation causes friction that results in heat generation. This process is called Dielectric heating. The excitation by the microwave



How does a microwave oven cooking

- ✓ The microwave oven cook food from the inside to outside
- ✓ Absorbs water and fat and sugar molecules, consisting of food, radio waves
- ✓ Temperature of food particles at the same time and at the same temperature because all the particles are raised at the same time is not transmitted to the heat conduction

is almost uniform so that the food will heat up uniformly. The cooking in the microwave oven is fast, efficient, and safe.

Working Principle:

A microwave oven uses microwaves to heat food. Microwaves are radio waves. In the case of microwave ovens, the commonly used radio wave frequency is 2.5 gigahertz. Radio waves in this frequency range have an interesting property ,they are absorbed by water, fats and sugars. When they are absorbed they are converted directly into atomic motion and motion is converted into heat.

Microwaves in this frequency range have another interesting property, they are not absorbed by most plastics, glass or ceramics. And metal reflects microwaves, which is why metals cause spark in a microwave oven. The reason that metal reflects microwaves is that no electronic waves resident in inside of conductor because conductor's conductivity is infinity.

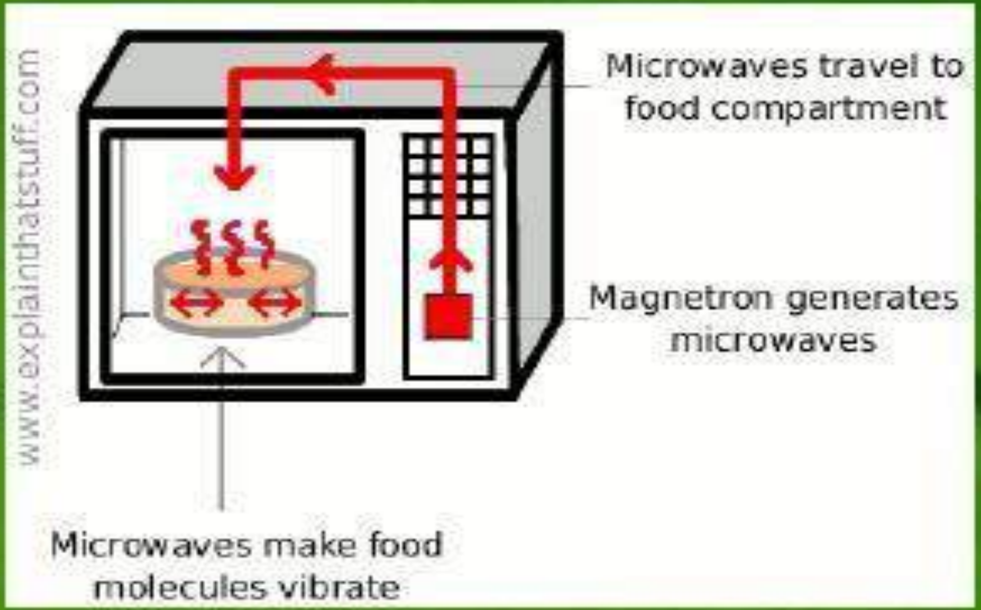
- Microwave ovens cook food by generating intermolecular friction between the molecules of the food. The microwaves cause water molecules to vibrate; the increased friction between the molecules results in heat. Microwaves could affect your tissue in a similar way if they were able to escape from the microwave oven.

Microwaves are produced inside the oven by an electron tube called a magnetron. The microwaves are reflected within the metal interior of the oven where they are absorbed by food. Microwaves

cause water molecules in food to vibrate, producing heat that cooks the food.

How does a microwave oven cooking

- ✓ The microwave oven cook food from the inside to outside
- ✓ Absorbs water and fat and sugar molecules, consisting of food, radio waves
- ✓ Temperature of food particles at the same time and at the same temperature because all the particles are raised at the same time is not transmitted to the heat conduction



Applications :

- Most common applications are within the range of 1 to 40 GHz. Microwaves are suitable for wireless transmission (wireless LAN protocol Ex- Bluetooth) signals having higher bandwidth. Microwaves are commonly used in radar systems where radar uses microwave radiation to detect the range, distance, and other characteristics of sensing devices and mobile broadband applications.
- Microwave technology is used in radio for broadcasting and telecommunication of transmission because due to their small wavelength, these are highly directional waves and therefore more practical than they would be at longer wavelengths (lower frequencies) .

- **Microwaves are generally used in telephone for long-distance communication.**

Microwave Applications

- **Communication**
  - Before the advent of fiber-optic transmission, most long-distance telephone calls were carried via networks of microwave radio relay links using FDM.
  - Wireless LAN protocols, such as Bluetooth and the IEEE 802.11 specifications, also use microwaves in the 2.4 GHz ISM band.
  - Wireless internet access IEEE 802.11a uses microwaves at 3.5-4 GHz range.
  - Metropolitan area network (MAN) protocols, such as WiMAX (Worldwide Interoperability for Microwave Access) are based on standards such as IEEE 802.16, designed to operate between 2 to 11 GHz.
  - Mobile Broadband Wireless Access (MBWA) protocols based on standards specifications such as IEEE 802.20 operate between 1.6 and 2.3 GHz.

Applications Of Microwaves

- Wireless Communications (space, cellular phones, cordless phones, WLANs, Bluetooth, satellites etc.)
- Radar and Navigation (Airborne,vehicle, weather radars, GPS etc.)
- Remote sensing (Meteorology, mining, land surface, aviation and marine traffic etc.)
- RF Identification (Security, product tracking, animal tracking, toll collection etc.)
- Broadcasting (AM,FM radio, TV etc.)
- Heating (Baking, Food process, Ovens, Drying, Mining, rubber industry)
- Bio-medical application(Diagnostics)

continued :

- Microwaves are most commonly used in satellite communications, radar signals, phones, and navigational applications.

- The microwaves used are medical treatments, drying materials, and in households preparation.

- Microwave is a form of electromagnetic radiation with wavelengths ranging from about one meter to one millimeter; with frequencies between 300 MHz and 300 GHz.

Applications continued:

Microwaves are used in number of industrial processes including ...

i) Meat tempering ii) Potato chips drying iii) Rubber vulcanization iv) Drying of pharmaceutical compounds…etc.

The reactants can be simply mixed together with little or no solvent .

1) The peptide hydrolysis using conventional heating has to run overnight in a sealed tube containing HCl, but due to microwave this time is reduced to 15 min. and reaction is carried out in open vessel inside the ordinary microwave oven. 2) Under solvent free conditions microwave energy develops the new procedures for conducting cleaner and efficient chemical transformations and destroying the hazardous wastes in the environment.

3) The contaminated solids can be treated with catalysis and microwaves to destroy the toxic compounds.

Ionic Liquids :

Ionic liquids are organic salts, usually consisting of wide range of polyatomic inorganic anions with asymmetrically substituted N containing organic cation , which are liquid under 100°C.

Ionic liquids have been recognized as environmental benign alternative to volatile organic solvents.

An ionic liquid is a salt in the liquid state. In some contexts, the term has been restricted to salts whose melting point is below some arbitrary temperature, such as 100 °C.

Ionic liquids, because of their negligible vapour pressures, have been generally recognized as green solvents.

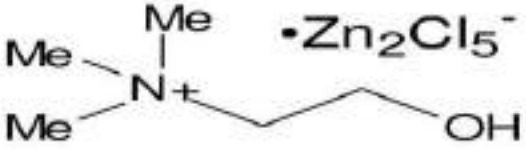
Introduction - Ionic Liquids

- Salts that are liquid at ambient temperatures.
- Have stable liquid range of over 300 K.
- Very low vapour pressure at room temperature.
- Selective solubility of water and organics.
- Potential to replace volatile organic solvents used in processes
- Often associated with Green Chemistry. Has been a major driving force behind the intense interest in ionic liquids

Ionic liquids (IL's)

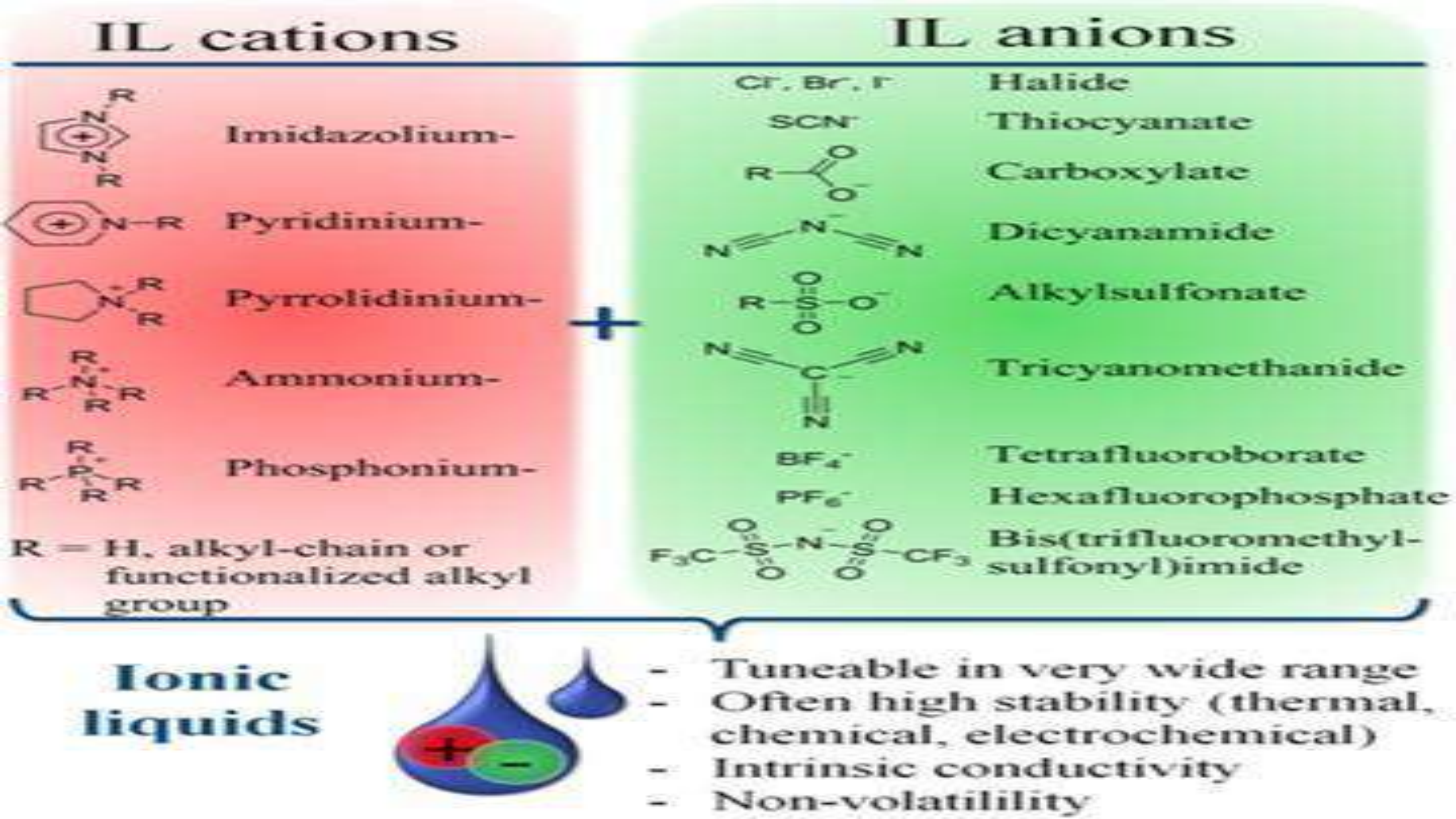
- Typically consist of organic cation (often ammonium or phosphonium salt) and inorganic anion

1. Ethylmethylimidazolium tetrafluoroborate, [emim][BF$_4$]



2.Choline chloride/Zinc chloride ionic liquid

- Usually only consider IL's which are liquid at room temperature
- Great variety of structures possible
- Very low vapour pressure – attractive alternative to VOCs.



IL cations

- Imidazolium-
- Pyridinium-
- Pyrrolidinium-
- Ammonium-
- Phosphonium-

R = H, alkyl-chain or functionalized alkyl group

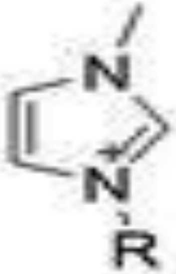
+

IL anions

Cl^-, Br^-, I^-	Halide
SCN^-	Thiocyanate
	Carboxylate
	Dicyanamide
	Alkylsulfonate
	Tricyanomethanide
BF_4^-	Tetrafluoroborate
PF_6^-	Hexafluorophosphate
	Bis(trifluoromethylsulfonyl)imide

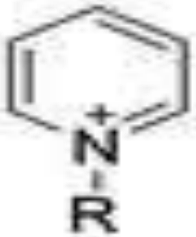
Ionic liquids

- Tuneable in very wide range
- Often high stability (thermal, chemical, electrochemical)
- Intrinsic conductivity
- Non-volatilility



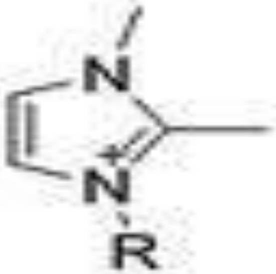
1-Alkyl-3-methylimidazolium

$[C_nC_1im]^+$



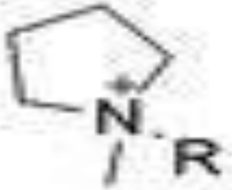
1-Alkylpyridinium

$[C_npyr]^+$



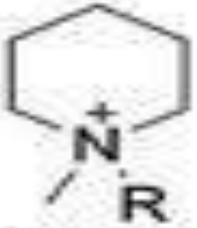
1-Alkyl-2,3-dimethylimidazolium

$[C_nC_1C_1im]^+$



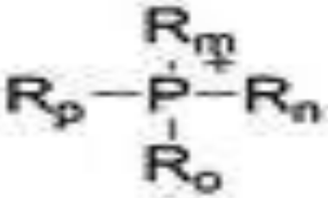
1-Alkyl-1-methylpyrrolidinium

$[C_nC_1pyrr]^+$



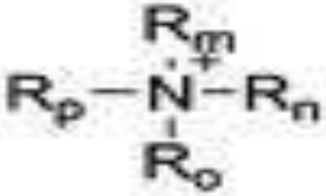
1-Alkyl-1-methylpiperidinium

$[C_nC_1pip]^+$



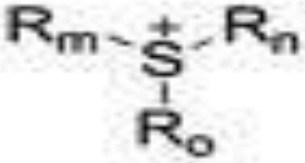
Tetraalkylphosphonium

$[C_mC_mC_oC_pP]^+$



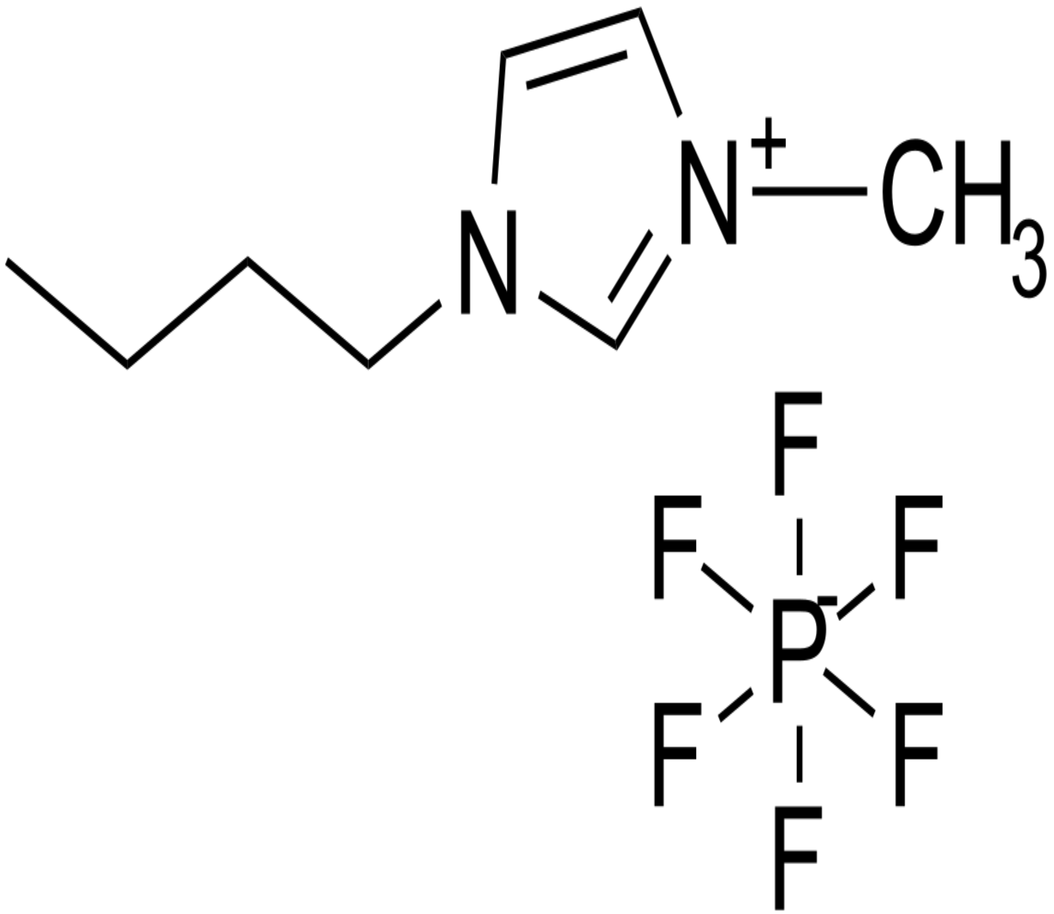
Tetraalkylammonium

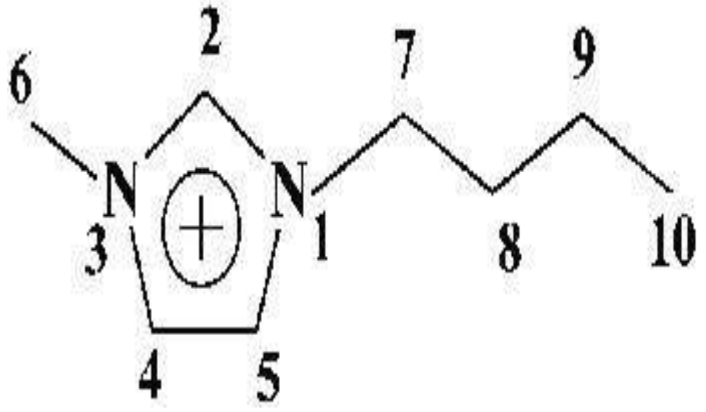
$[C_mC_nC_oC_pN]^+$



Trialkylsulfonium

$[C_nC_mC_oS]^+$




6
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Properties

- Easy separation
- Very low vapor pressure
- Non-flammable substance
- High thermally stable
- High mechanically stable
- Electrochemically stable
- Low toxicity
- Non-volatile

Ionic Liquids(ILs)

Definition: Ionic liquids are molten salts entirely composed of ions(+ve,-vely charged) that are liquid at or below room temperature, i.e. MP < 100°C.

Example: 1-ethyl-3-methyl imidazolium bis(trifluoro methyl sulfonyl) limide-M.P.= -17°C.

Properties of ILs :

- Non- flammable
- Very low/negligible vapor pressure
- Wide liquid range, high thermal stability
- Wide electro-chemical window(> 4 V)
- High ion conductivity
- Designer solvents
- Green solvents
- Viscosity= 10cP to above 1000 cP
- Density = 0.8-3.3 g/cc

Physical Properties of the Ionic Liquids

(1) They are good solvents for a wide range of both inorganic and organic materials

(2) They are often composed of poorly coordinating ions, so they have the potential to be highly polar yet noncoordinating solvents.

(3) polar alternative for two-phase systems

(4) Ionic liquids are nonvolatile, hence they may be used in high-vacuum systems

(1) they are used in huge amounts and

(2) they are usually volatile liquids that are difficult to contain.

Welton, T. *Chem. Rev.* **1999**, *99*, 2071-2083.

Ionic liquids cont….

- Good solvents for a wide range of organic, inorganic and polymeric compounds
- Anion and cation can be fine tuned to give a wide range of solvent properties (e.g. hydrophilic, hydrophobic) which can be exploited
- Wide range of reactions already demonstrated in this medium
- Can be used in conjunction with other alternative solvents (particularly CO_2)
- Claimed to be recyclable (essential for widespread use) although there may be regulatory problems with this.
- Effectively, properties similar to many other high boiling, polar solvents.

Application

- Ionic liquids –used in microreactors to synthesize & purify extremely reactive organometallic compounds (using the Green Chemistry principles.)
- Ionic liquids -used for efficient heat storage and transfer in solar thermal energy systems.
- Ionic Liquids -dispersing agents in paints to enhance appearance and drying properties
- 1-butyl-3-methylimidazolium hexafluorophosphate-used-non aqueous electrolyte medium -recovery of uranium in spent fuel rods.
- Some ionic liquids -advantage of both homogeneous and heterogeneous catalysts.

Examples of common Ionic Liquids:

- Ethyl-3-methylimidazolium (EMIM) Chloride,
- EMIM dicyanamide,
- 1-butyl-3,5-dimethylpyridinium bromide,
- 1-Butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF_6]

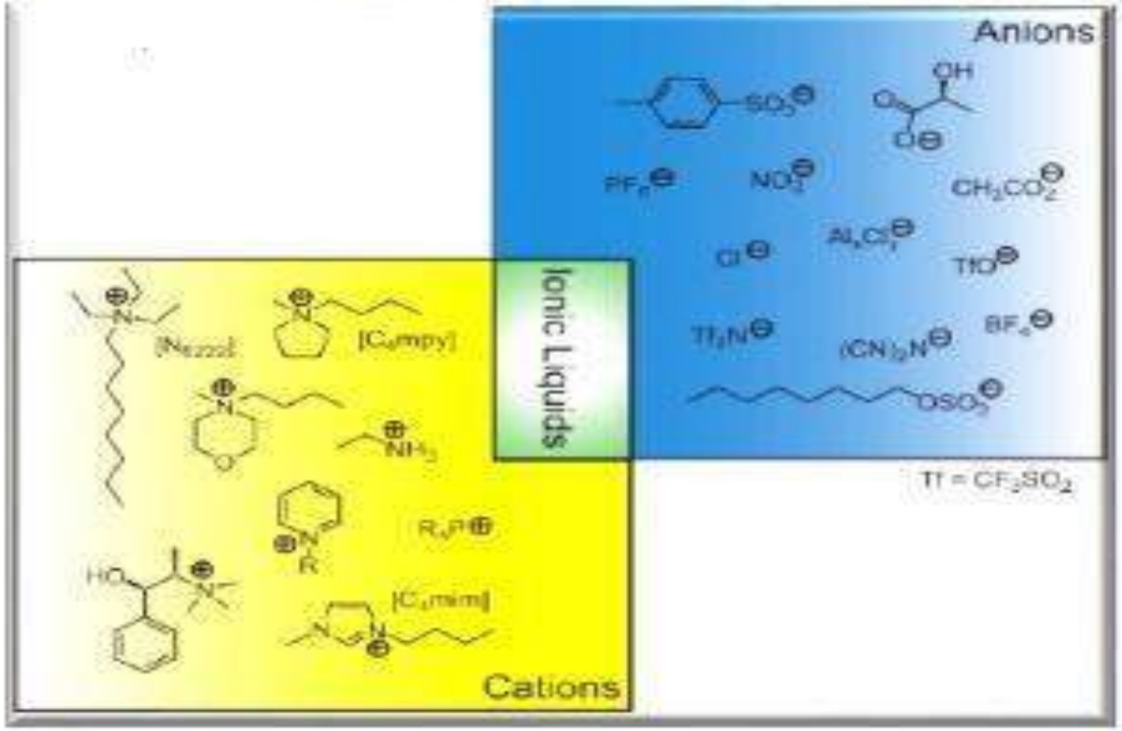

Fig: Some common cations in Ionic Liquids

* [PF_6] for moisture stable, water immiscible IL

* [BF_4]$^-$ for moisture stable, but water miscible IL.

* [$AlCl_4^-$] (or other Lewis acids) decomposes in water

IONIC LIQUIDS

- thermal stability
- low vapor pressure
- electric conductivity
- interesting solvent properties
- biphasic systems possible
- liquid crystalline structures
- high electroelasticity
- high heat capacity
- non flammability

LUBRICANTS & ADDITIVES
- lubricants
- fuel additives

ELECTROELASTIC MATERIALS
- artificial muscles
- robotics

ANALYTICS
- MALDI-TOF-matrices
- GC-head-space-solvents
- protein-crystallization

SOLVENTS
- bio-catalysis
- organic reactions & catalysis
- Nano-particle-synthesis
- polymerization

LIQUID CRYSTALS
- displays

HEAT STORAGE
- thermal fluids

ELECTROLYTES
- fuel cells
- sensors
- batteries
- supercaps
- metal finishing
- coating

SEPARATION
- gas seperations
- extractive distillation
- extraction
- membranes

Applications :

Ionic Liquids

Separation media
- Liquid membranes
- Extraction
- Carbon Capture

Electrolytes
- Fuel cells
- Batteries
- Sensors
- Metal plating
- Solar cells

Working fluids
- Heat storage
- Lubricants
- Surfactants

Green solvents
- Biocatalysis
- Chemical processing
- Protein crystallization

Advanced materials
- Liquid crystal displays
- Artificial muscles
- Pharmaceuticals

Applications of Microwaves :

- Microwaves are used in number of industrial processes including
- i) Meat tempering ii) Potato chips drying iii) Rubber vulcanization iv) Drying of pharmaceutical compounds…etc.
- The reactants can be simply mixed together with little or no solvent .
- 1) The peptide hydrolysis using conventional heating has to run overnight in a sealed tube containing HCl, but due to microwave this time is reduced to 15 min.and reaction is carried out in open vessel inside the ordinary microwave oven.
- 2) Under solvent free conditions microwave energydevelops the new procedures for conducting cleaner and efficient chemical transformations and destroying the hazardous wastes in the environment.

- **3) The contaminated solids can be treated with catalysis and microwaves to destroy the toxic compounds.**

THE END

Agrochemicals

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Department of Chemistry
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Kolhapur

M.Sc.-II : Organic Chemistry (2020-21)
SEM - IV

- **Paper No. 1152B : APPLIED ORGANIC CHEMISTRY**

UNIT-I: Agrochemicals - Syllabus

- **a. Carbamate pesticides**: Introduction and synthesis of carbaryl, carbofuran,
- Baygon, Aldicarb, Ziram, Zineb.
- **b. Organophosphorus pesticides:** Malathion, monocrotophos, dimethoate, phorate, mevinphos, chloropyriphos.
- **c. Natural and synthetic pyrethroids**: Isolation and structures of natural allethrin, fenvalerate, cypermethrin.
- **d. Plant growth regulators:** General survey and synthesis of simple compounds and applications.
- **e. Juvenile hormones:** Introduction & structures JHA importance synthesis
- **f. Insect repellents**: General survey, synthesis and applications.
- **g. Insect attractants /Pheromones**: Introduction, examples, and importance in IPM. Synthesis of juvabione, bombykol, grandisol and disparlure.

Introduction

Agrochemicals are pesticides, herbicides, or fertilizers used for the management of ecosystems in agricultural sectors.

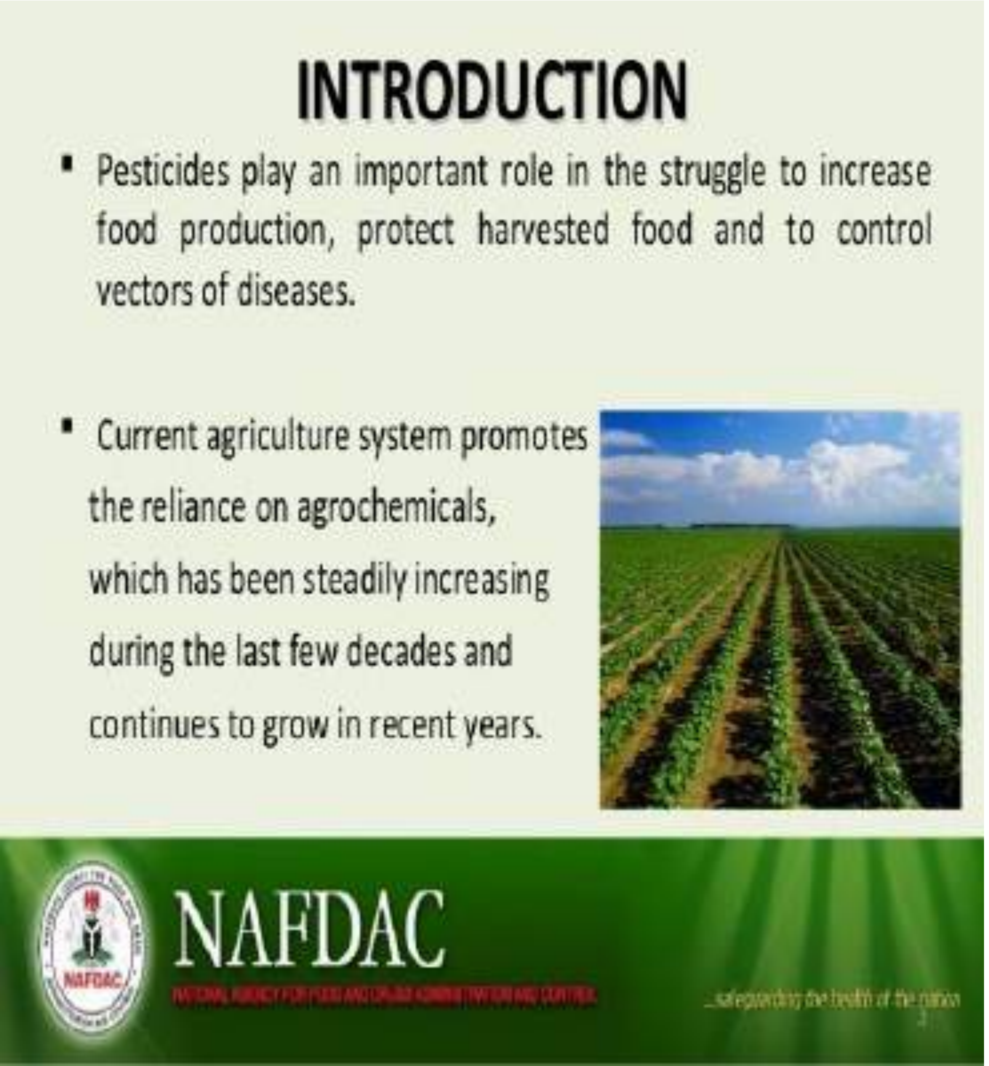
This is the generic name given to chemicals such as fertilizers, pesticides and insecticides. Agrochemicals, as the name suggests, is used in agriculture to facilitate plant growth and protection.

Agrochemicals are chemical agents used on farmlands to improve the nutrients in the field or crops. They improve crop growth by killing damaging insects. They are implemented in all forms of farming sectors such as horticulture, dairy farming, poultry, crop shifting, commercial planting, etc.

It is the chemical used to improve the quality and quantity of farm products.

Agrochemicals include insecticides, fungicides and herbicides which are collectively known as agrochemicals or crop protection products.

Agrochemicals is a wide term used for the various chemical products used in agriculture. e. g. pesticides ,insecticides, herbicides, fungicides and nematocides, rodenticides etc.



INTRODUCTION

- Pesticides play an important role in the struggle to increase food production, protect harvested food and to control vectors of diseases.
- Current agriculture system promotes the reliance on agrochemicals, which has been steadily increasing during the last few decades and continues to grow in recent years.

NAFDAC

NATIONAL AGENCY FOR FOOD AND DRUG ADMINISTRATION AND CONTROL

...safeguarding the health of the nation

Agro-chemicals and their Effects

Agro- chemicals are the chemicals that are used in agriculture as pesticide, fertiliser, soil conditioners etc.

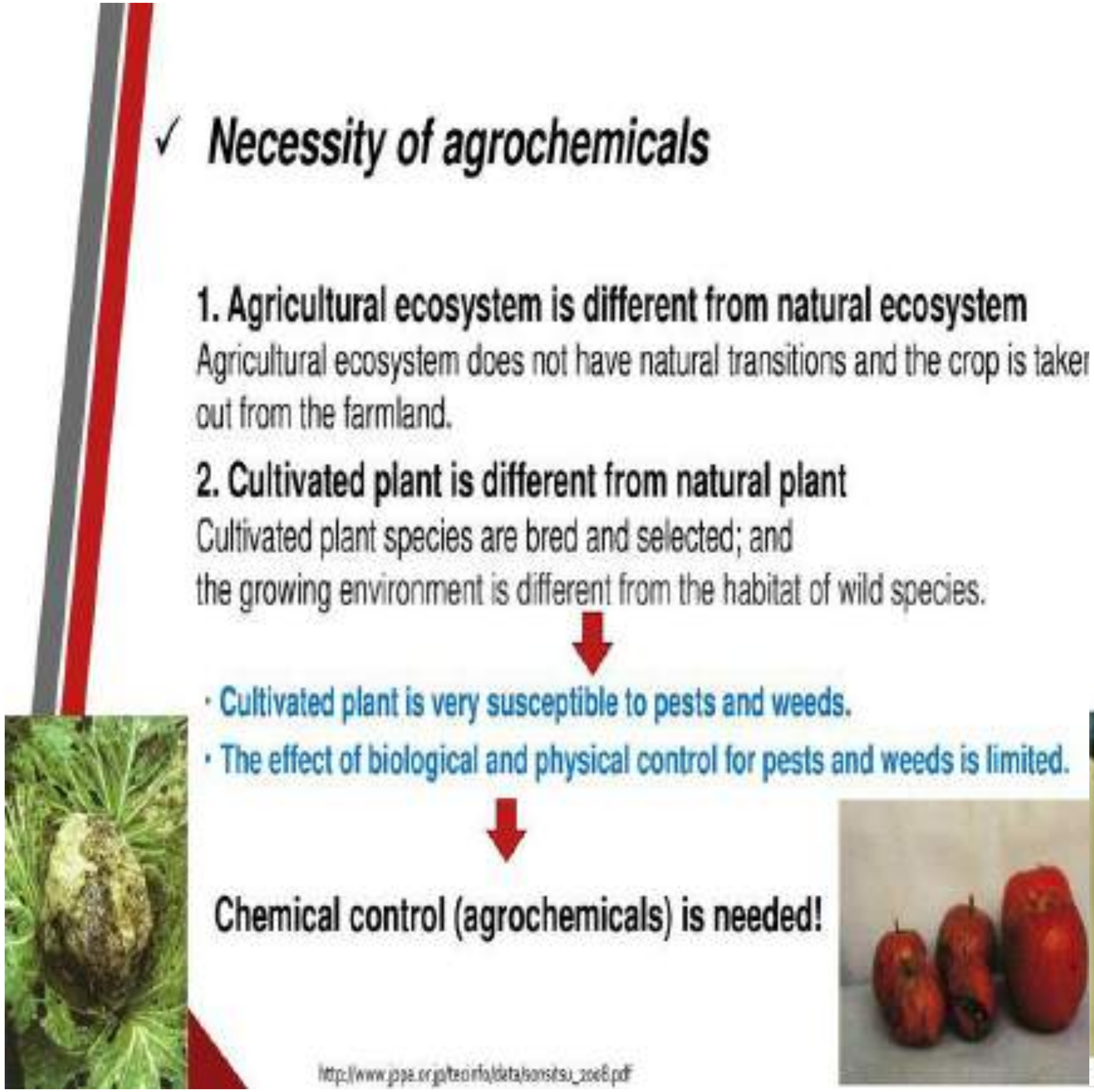
Types of Agro- chemicals:

Fertilisers:

These are the substances which are used to increase the nutrient amount in the land, it increases the rate of crop production.

The most commonly used compounds i fertiliser are phosphorus, nitrogen and potassium.

Why need of Agrochemicals ?



✓ *Necessity of agrochemicals*

1. Agricultural ecosystem is different from natural ecosystem
Agricultural ecosystem does not have natural transitions and the crop is taken out from the farmland.

2. Cultivated plant is different from natural plant
Cultivated plant species are bred and selected; and
the growing environment is different from the habitat of wild species.

⬇

- **Cultivated plant is very susceptible to pests and weeds.**
- **The effect of biological and physical control for pests and weeds is limited.**

⬇

Chemical control (agrochemicals) is needed!

http://www.jppa.or.jp/tecinfo/data/sonsitsu_2008.pdf

2. **The use of agrochemicals has environmental benefits:**

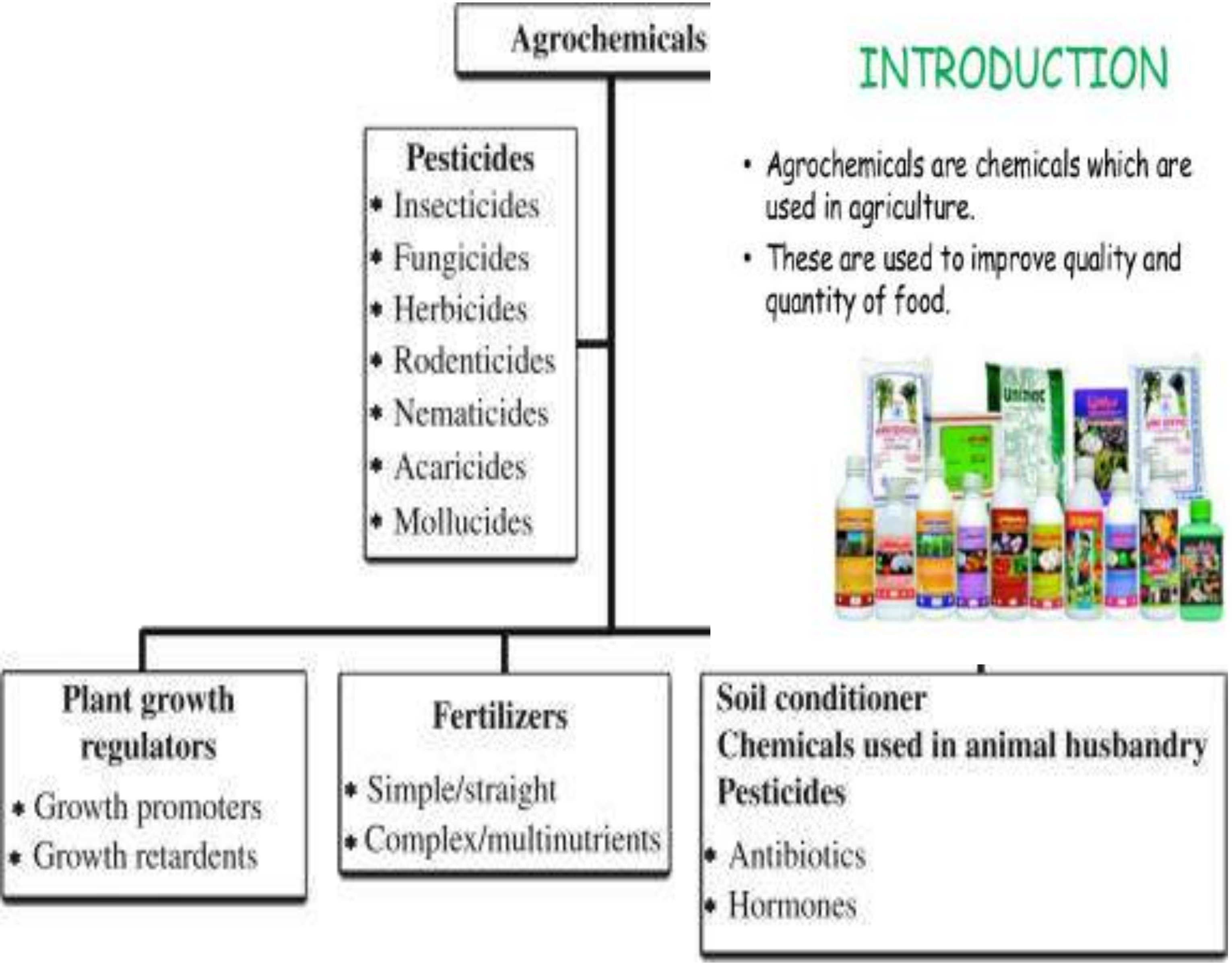
Because agrochemicals allow farmers to grow more per acre, less land is needed to supply the global food market. The rate of deforestation is declining and reforestation has started in several countries.

3. **The use of agrochemicals can reduce the cost of food:** With crop protection chemicals, food production would increase, many fruits and vegetables would be in large supply and prices would drop.

4. **Consumer benefits exist**: Agrochemicals allow consumers to consume high-quality products that are free of insect blemishes and contamination.

https://yellow.co.ke/bi[illegible]blogs/advantages-of-using-agrochemicals

Classification of Agrochemicals



Agrochemicals

Pesticides

- Insecticides
- Fungicides
- Herbicides
- Rodenticides
- Nematicides
- Acaricides
- Mollucides

Plant growth regulators

- Growth promoters
- Growth retardents

Fertilizers

- Simple/straight
- Complex/multinutrients

Soil conditioner

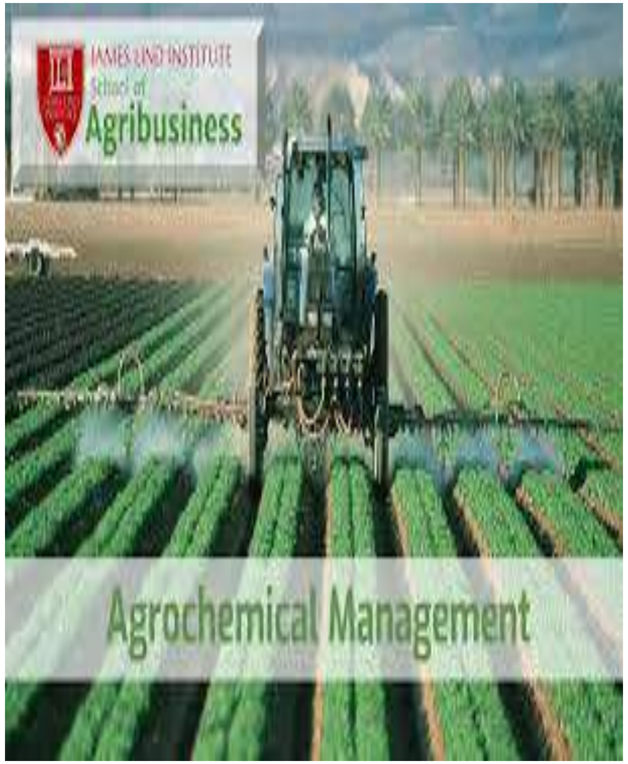
Chemicals used in animal husbandry

Pesticides

- Antibiotics
- Hormones

INTRODUCTION

- Agrochemicals are chemicals which are used in agriculture.
- These are used to improve quality and quantity of food.



Pest and Pesticides

DEFINITIONS

The NAFDAC **Pesticide Registration Regulation (2005)** defines

- **Pest** as any insect, rodent, nematode, fungus, weed or any other form of plant or virus or bacteria or other microorganism.
- **Pesticide** as any chemical substance or mixture of substance intended for preventing, destroying, repelling, mitigating the effect of any pest of plants and animals.
- **Agrochemical** is a term used to refer to the various chemical products used in agriculture and animal husbandry such as fertilisers, pesticides and soil conditioners.

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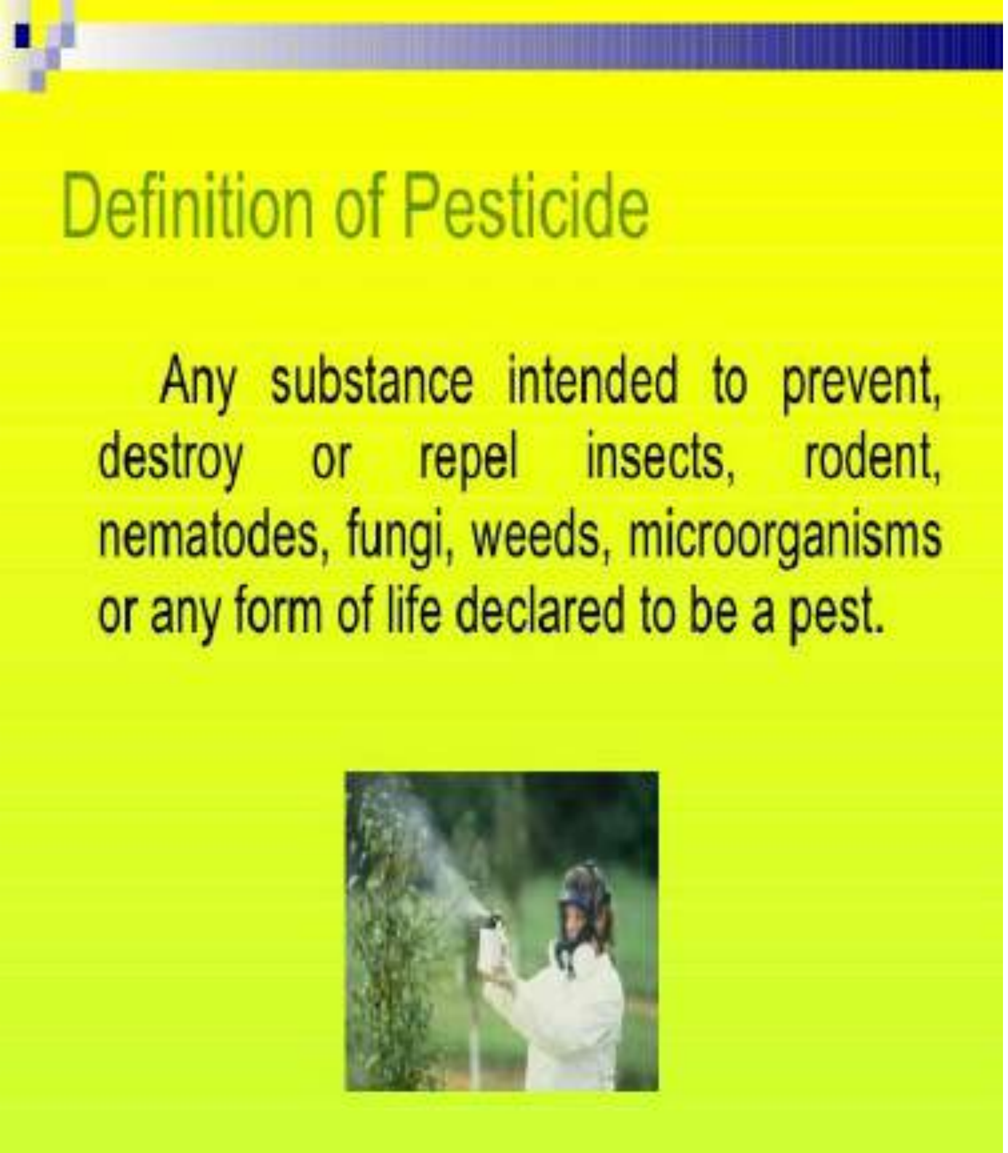
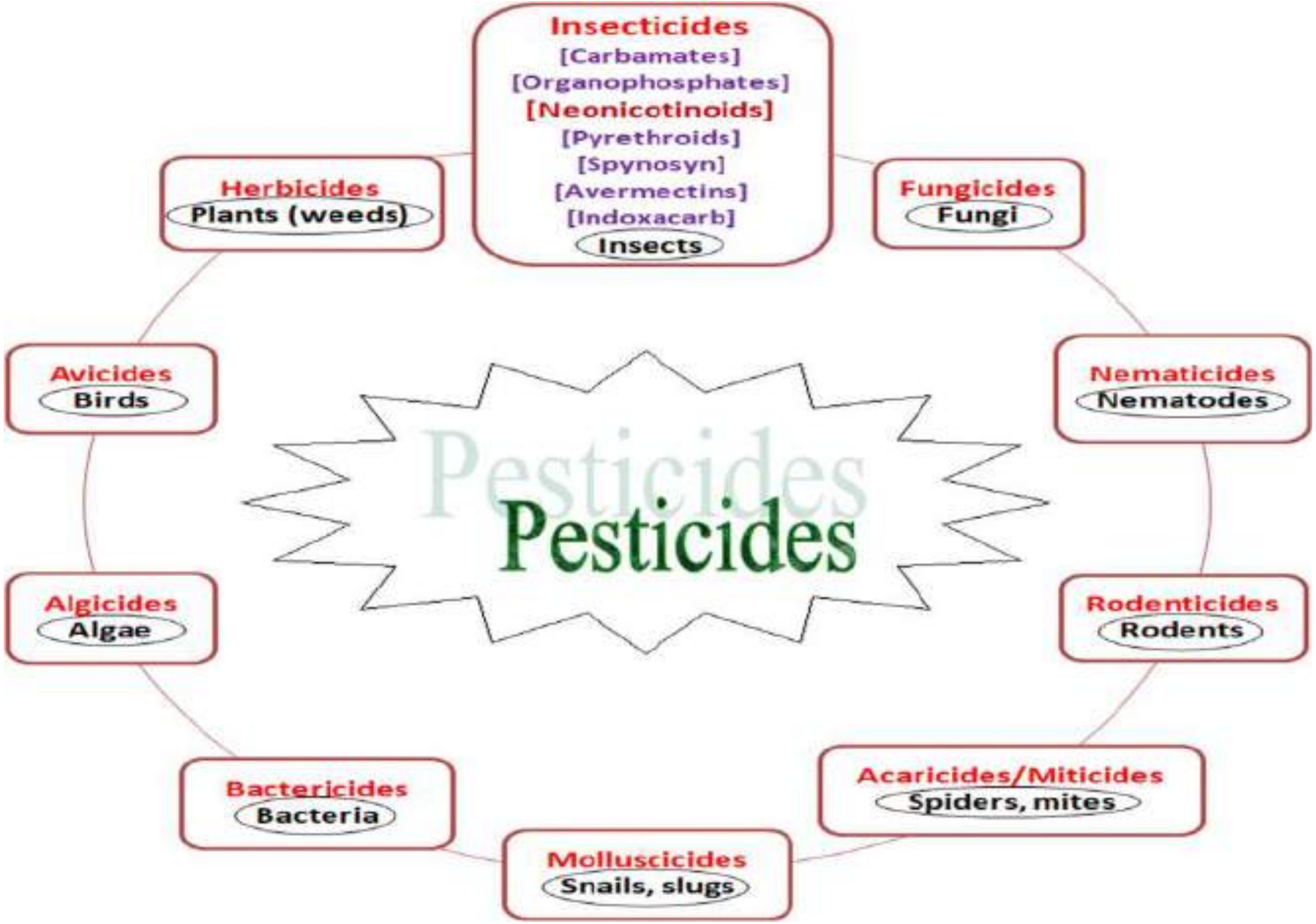


Definition of Pesticide

Any substance intended to prevent, destroy or repel insects, rodent, nematodes, fungi, weeds, microorganisms or any form of life declared to be a pest.

Classification of Pesticides



Pesticides

Insecticides
[Carbamates]
[Organophosphates]
[Neonicotinoids]
[Pyrethroids]
[Spynosyn]
[Avermectins]
[Indoxacarb]
Insects

Fungicides
Fungi

Nematicides
Nematodes

Rodenticides
Rodents

Acaricides/Miticides
Spiders, mites

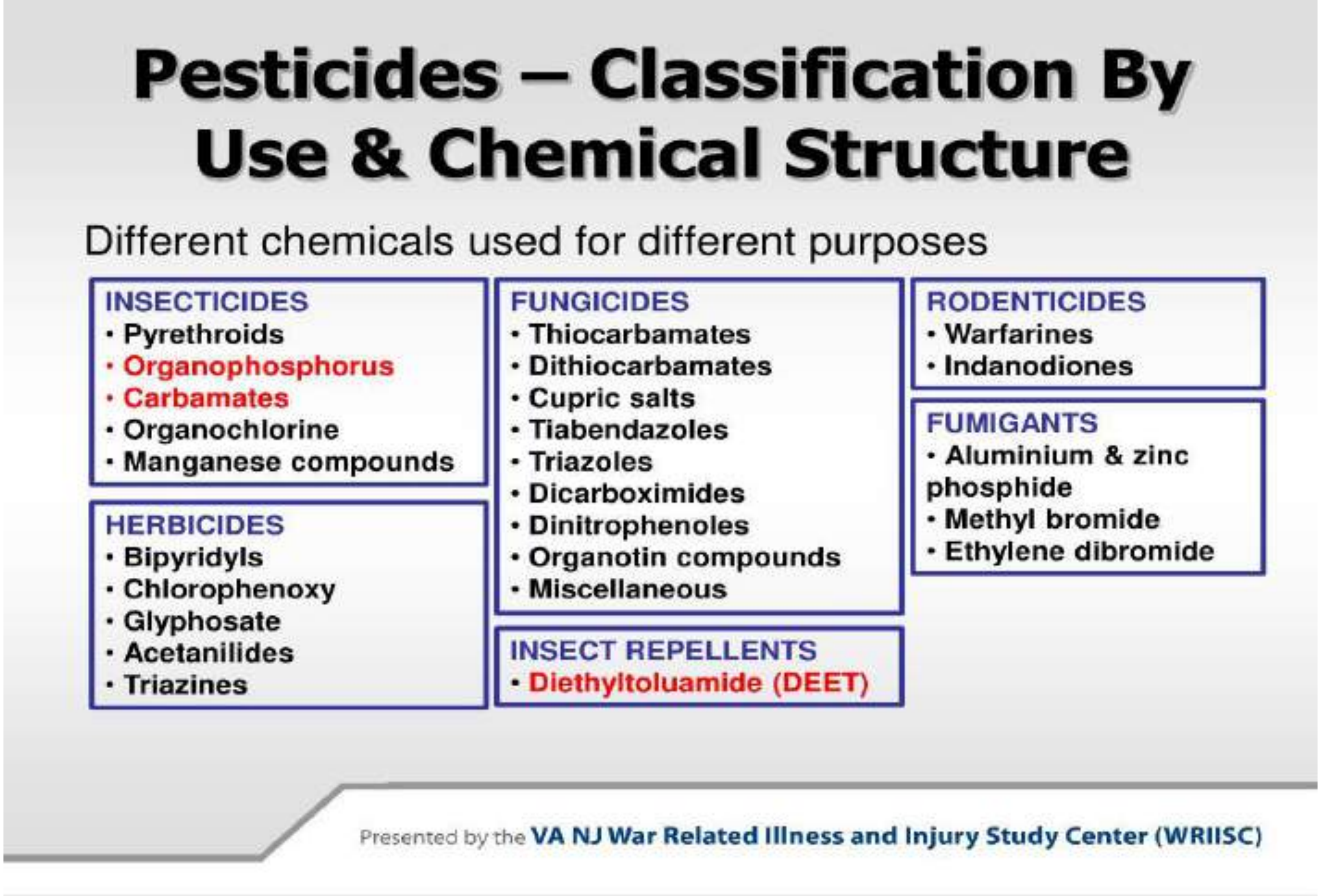
Molluscicides
Snails, slugs

Bactericides
Bacteria

Algicides
Algae

Avicides
Birds

Herbicides
Plants (weeds)



Pesticides – Classification By Use & Chemical Structure

Different chemicals used for different purposes

INSECTICIDES
- Pyrethroids
- Organophosphorus
- Carbamates
- Organochlorine
- Manganese compounds

HERBICIDES
- Bipyridyls
- Chlorophenoxy
- Glyphosate
- Acetanilides
- Triazines

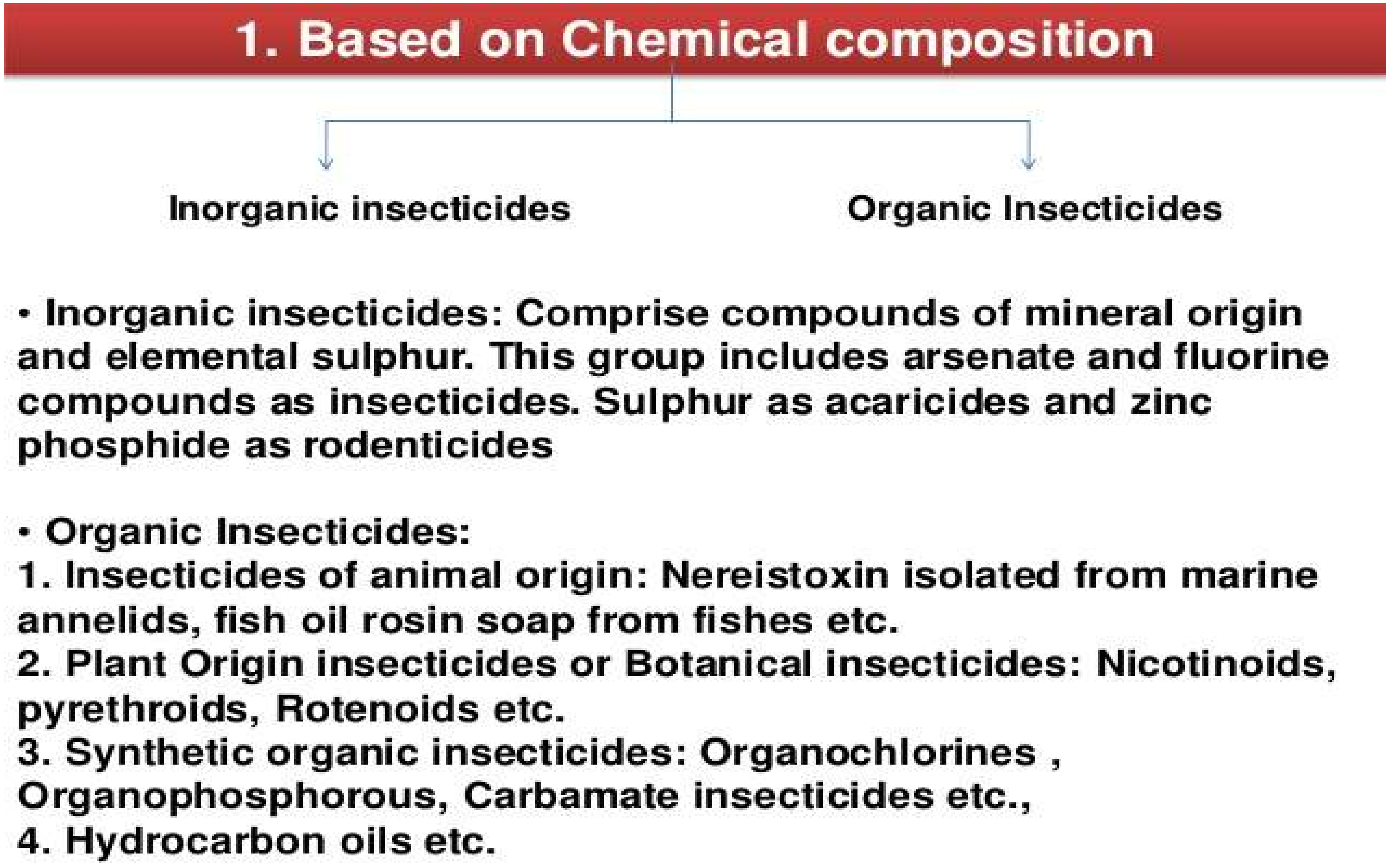
FUNGICIDES
- Thiocarbamates
- Dithiocarbamates
- Cupric salts
- Tiabendazoles
- Triazoles
- Dicarboximides
- Dinitrophenoles
- Organotin compounds
- Miscellaneous

INSECT REPELLENTS
- Diethyltoluamide (DEET)

RODENTICIDES
- Warfarines
- Indanodiones

FUMIGANTS
- Aluminium & zinc phosphide
- Methyl bromide
- Ethylene dibromide

Classification



1. Based on Chemical composition

Inorganic insecticides

Organic Insecticides

- Inorganic insecticides: Comprise compounds of mineral origin and elemental sulphur. This group includes arsenate and fluorine compounds as insecticides. Sulphur as acaricides and zinc phosphide as rodenticides

- Organic Insecticides:

1. Insecticides of animal origin: Nereistoxin isolated from marine annelids, fish oil rosin soap from fishes etc.
2. Plant Origin insecticides or Botanical insecticides: Nicotinoids, pyrethroids, Rotenoids etc.
3. Synthetic organic insecticides: Organochlorines , Organophosphorous, Carbamate insecticides etc.,
4. Hydrocarbon oils etc.

Soil conditioners

- Definition :

Soil conditioning means improving several aspects of the quality of **soil**: Tilth. This refers to the **soil's** physical **condition** and larger-scale structure. It includes whether the **soil** has aggregates (clumps) and what size they **are**, whether it has channels where water can enter and drain, and its level of aeration.

A wide variety of materials have been described as **soil conditioners** due to their ability to improve **soil** quality. Some examples include biochar, bone meal, blood meal, coffee grounds, compost, compost tea, coir, manure, straw, peat, sphagnum moss, vermiculite, sulfur, lime, hydroabsorbant polymers, and biosolids. Compost is the best all-round soil conditioner.

A **soil conditioner** is a product which is added to soil to improve the soil's physical qualities, usually its fertility (ability to provide nutrition for plants)

Organic matter helps **soil** become spongey and porous, which leads to a healthy balance of moisture retention and drainage, as well as creating a structure that

Natural and Synthetic Pesticides

Pesticides are chemicals that may be used to kill fungus, bacteria, insects, plant disease, etc. These chemicals work by ingestion or touch and death may occur immediately or over a long period of time. An **insecticide** is used to specifically target and kill insects.

Natural Pesticides:

Pyrethrum Flower ,
Neem leaves and oil ,
Tobacco leaves,
Nuxvomica seed,
Sabadilla seeds,
Ryania root and stem
Derris root and rhizome

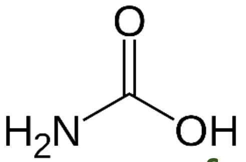
Types of Insecticides
(Synthetic Insecticides)

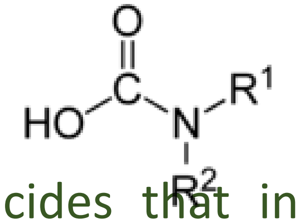
a. Carbamate Insecticides

- A carbamate is a category of organic compounds that is formally derived from carbamic acid. The term includes organic compounds, formally obtained by replacing one or more of the hydrogen atoms by other organic functional groups as well as salts with the carbamate anion H_2NCOO^- .

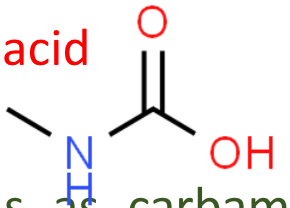
- **Carbamic acid**, which might also be called aminoformic **acid** or aminocarboxylic **acid**, is the chemical compound with the formula H_2NCOOH. It can be obtained by the reaction of ammonia NH_3 and carbon dioxide CO_2 at very low temperatures, which also yields an equal amount of ammonium **carbamate**.

Carbamic acid



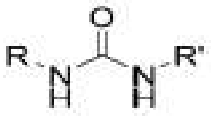


Methyl carbamic acid

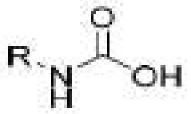


- The carbamates are a group of insecticides that includes such compounds as carbamyl, methomyl, and carbofuran. They are rapidly detoxified and eliminated from animal tissues.

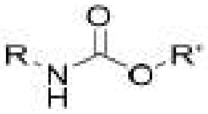
- The so-called **carbamate insecticides** feature the carbamate ester functional group included in this group are aldicarb (Temik), carbofuran (Furadan), carbaryl.



urea



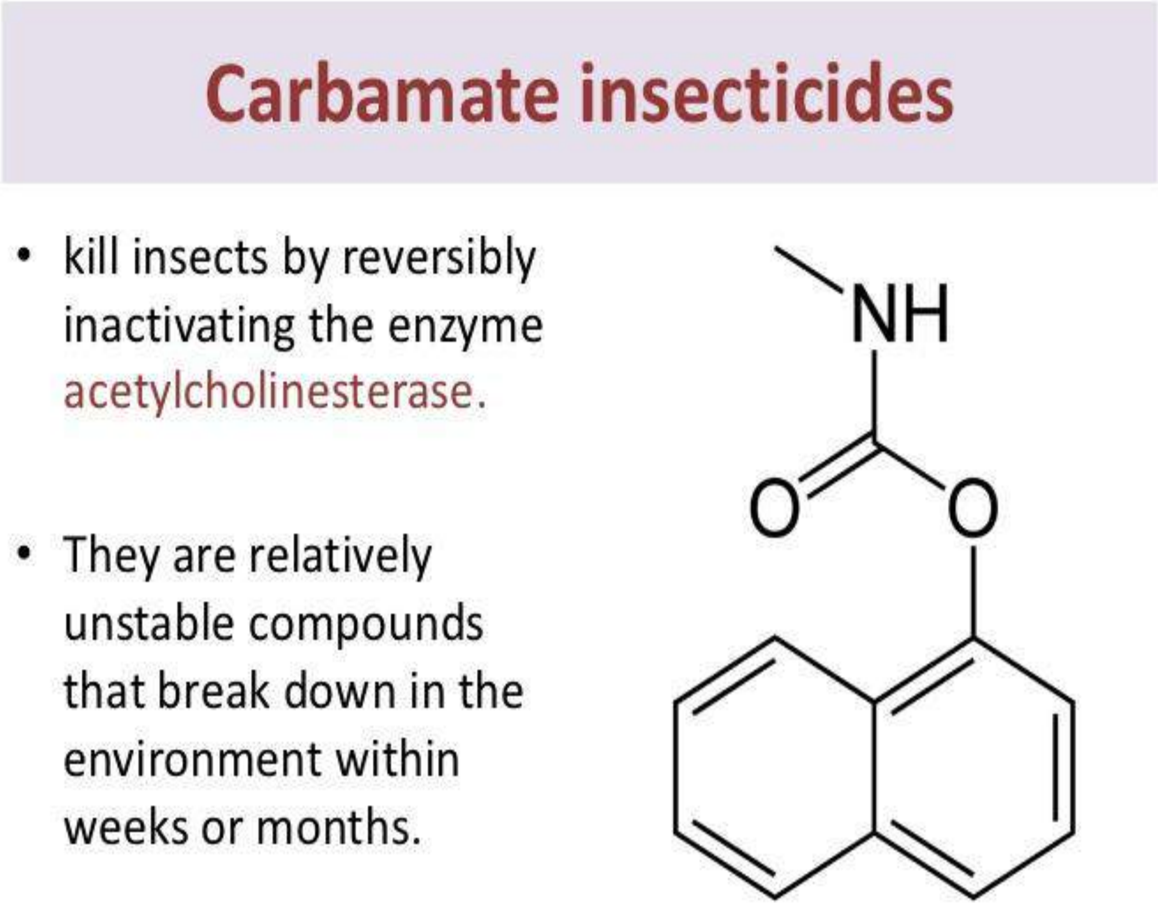
carbamic acid



carbamic ester

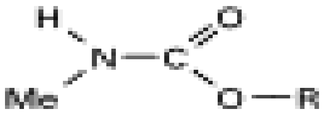
What are carbamate Insecticides ?

- **Carbamates are** a class of insecticides structurally and mechanistically similar to organophosphate (OP) insecticides. **Carbamates are** N-methyl **carbamates** derived from a carbamic acid .



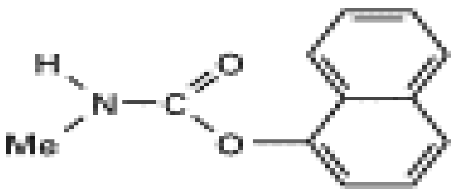
Carbamate insecticides

- kill insects by reversibly inactivating the enzyme acetylcholinesterase.
- They are relatively unstable compounds that break down in the environment within weeks or months.

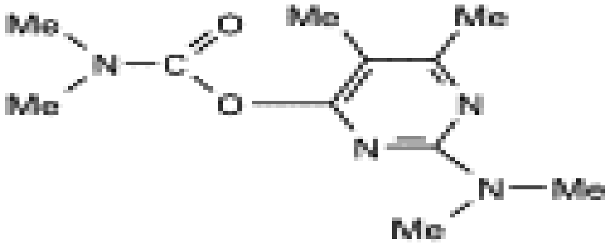


R is PhR′ or N=CR′

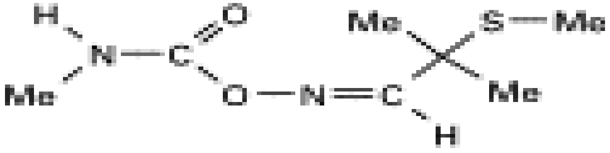
Carbamate insecticide: general structure



Carbaryl



Pirimicarb (an *N,N*-dimethyl carbamate)

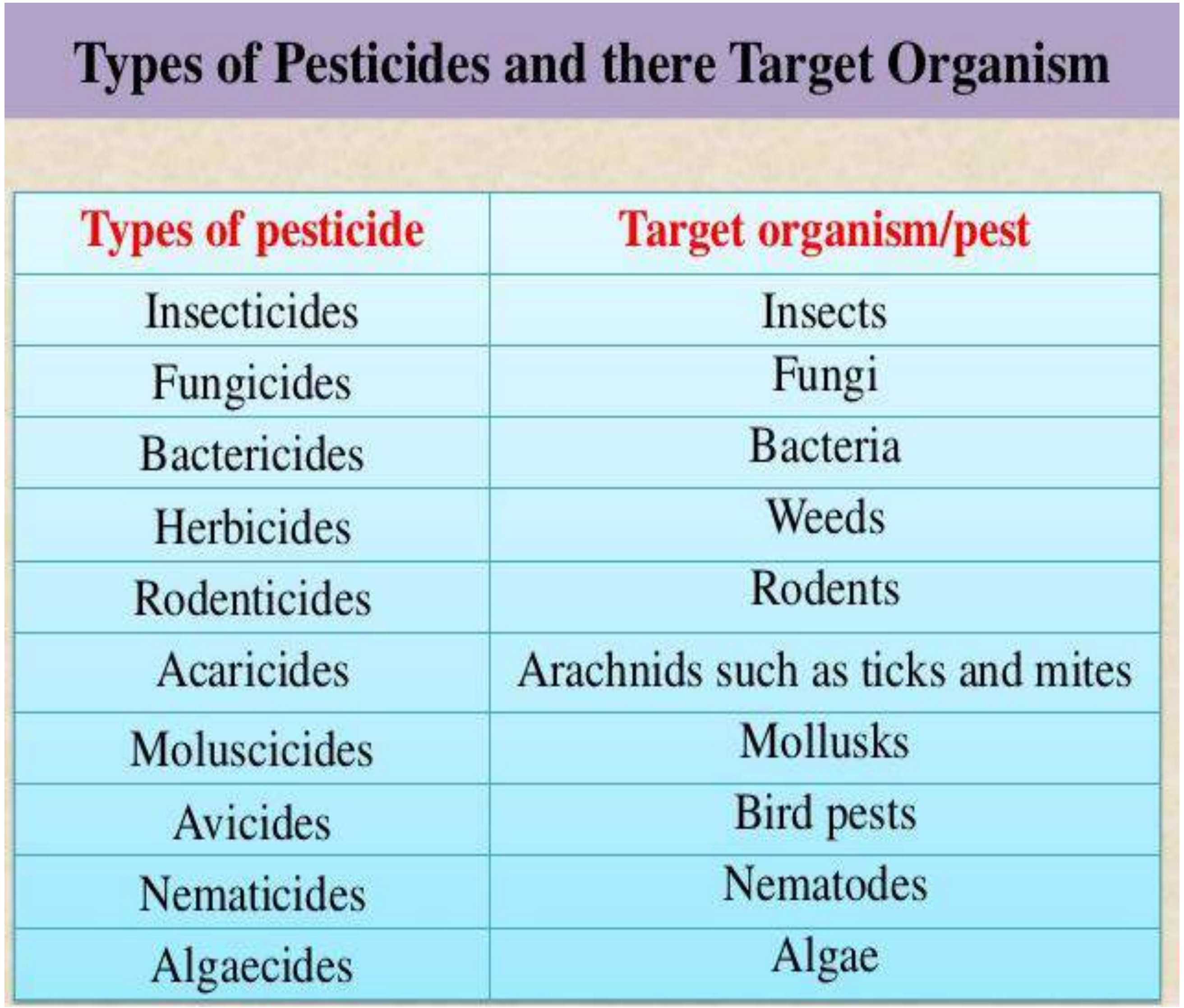


Aldicarb (an *N*-methyl oxime carbamate)

Carbamates continued

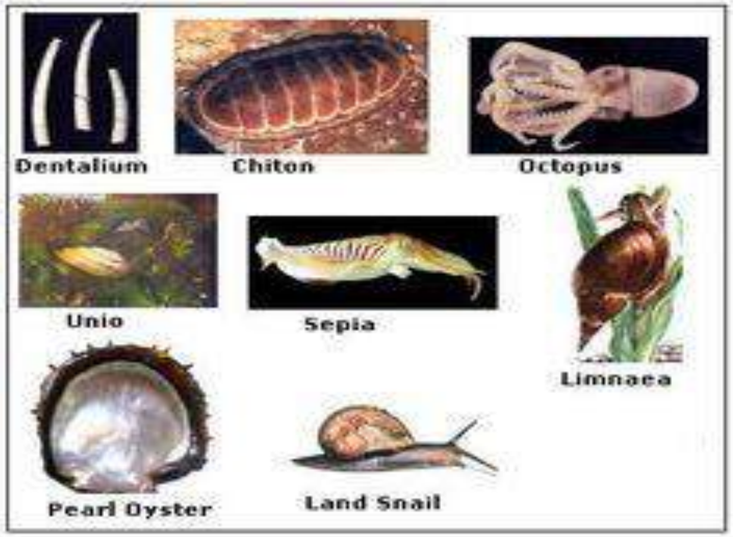
- **Carbamate pesticides** are derived from carbamic acid and kill insects in a similar fashion as organophosphate insecticides. They are widely used in homes.
- **Carbamate** compounds are esters of carbamic acid that are commonly used as **insecticides**. These compounds are referred to as N-methylcarbamates. Derivatives of carbamic acid, thiocarbamic acid, and dithiocarbamic acid which are used as **herbicides**. **Carbamate herbicides** are of low mammalian toxicity.

Continued…



Types of Pesticides and there Target Organism

Types of pesticide	Target organism/pest
Insecticides	Insects
Fungicides	Fungi
Bactericides	Bacteria
Herbicides	Weeds
Rodenticides	Rodents
Acaricides	Arachnids such as ticks and mites
Moluscicides	Mollusks
Avicides	Bird pests
Nematicides	Nematodes
Algaecides	Algae



Continued…

- Carbamate compounds are esters of carbamic acid that are commonly used as insecticides. These compounds are referred to as *N*-methylcarbamates. Derivatives of carbamic acid, thiocarbamic acid, and dithiocarbamic acid are used as herbicides. When used properly, carbamate pesticides offer significant benefits to society, as they protect and increase agricultural production, as well as protect human and animal health from insect-vector-mediated diseases. However, overexposure of humans and animals to these pesticides often results in poisonings.

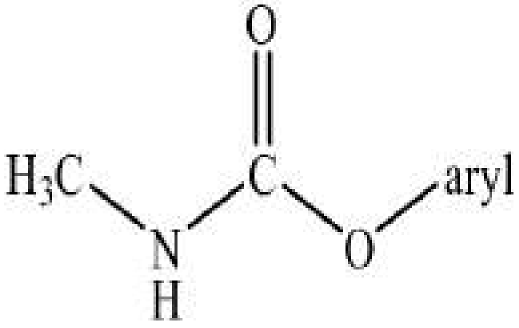
The first carbamate insecticide, carbazyl was introduced in 1956.

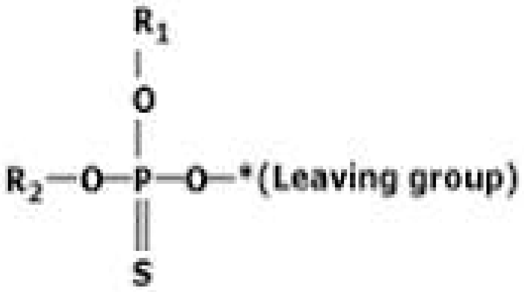
Because of very low mammalian toxicity together with short half-life in the environment carbaryl are the most popular insecticide and effectively acts against 160 harmful insects.

Carbamate pesticides generally have the formula RHNCOOR’, and are relatively polar, highly soluble in water, and chemically reactive. Some Carbamates of importance are Aldicarb, Carbaryl, Carbofuran, Ferbam, and Captan.

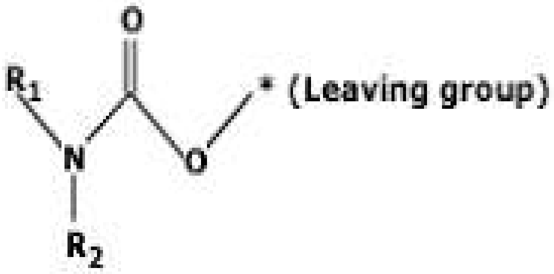
Continued…

- **Carbamate insecticides** are esters of carbamic acid (the monoamide of carbon dioxide), achieving chemical stability with the introduction of one or two N-alkyl substituents and with alkyl or aryl substituents .

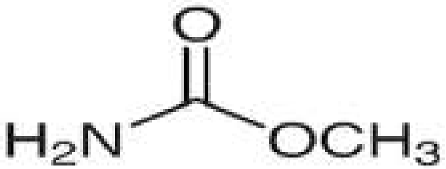




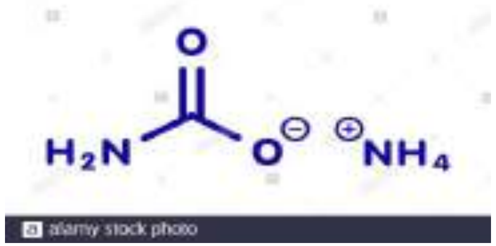
Organophosphate



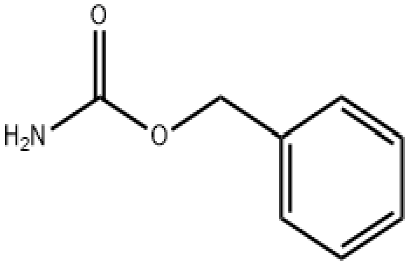
Carbamate



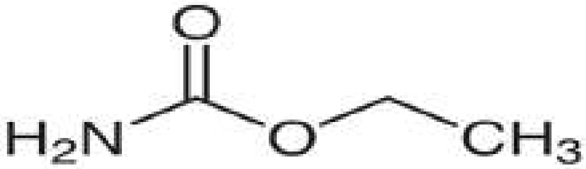
Methyl carbamate



Ammonium carbamate



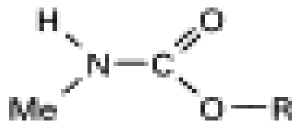
Benzyl carbamate



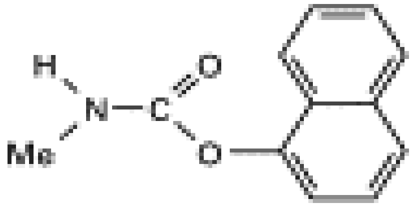
Ethyl carbamate

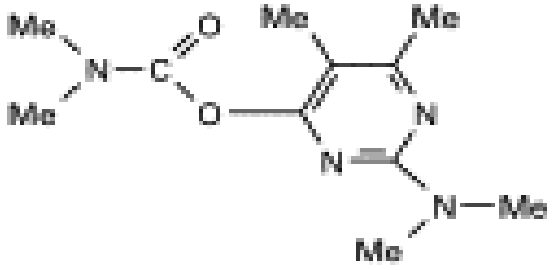
Examples of Carbamate Insecticides

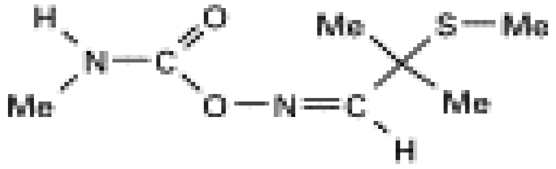
- They are also frequently used as household, garden, and farm insecticides. Chlorpyrifos, parathion, diazinon, famphur, phorate, terbufos, and malath
- These are, used to kill or control insects. There are many forms of **carbamates**, each different in the way they work and in their poisonous effects. **Carbamates** break down in the environment within weeks or months.
- **Carbamate insecticides** are esters of carbamic acid (the monoamide of carbon dioxide), achieving chemical stability with the introduction of one or two N-alkyl substituents at R4 and R5 and with alkyl or aryl substituents at R6.


R is PhR′ or N=CR′

Carbamate insecticide: general structure


Carbaryl

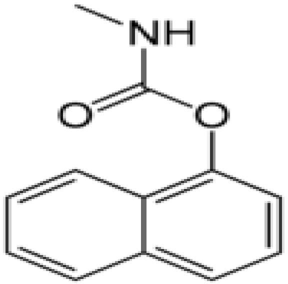

Pirimicarb (an *N,N*-dimethyl carbamate)


Aldicarb (an *N*-methyl oxime carbamate)

1. Synthesis and Uses of Carbaryl / Sevin

Carbaryl is often inexpensively produced by direct reaction of methyl isocyanate with 1-naphthol. Alternatively, 1-naphthol can be treated with excess phosgene to produce 1-naphthylchloroformate, which is then converted to **carbaryl** by reaction with methylamine. The former process was carried out in Bhopal.

Carbaryl is a carbamate ester obtained by the formal condensation of 1-naphthol with methylcarbamic acid. It has a role as an (acetylcholinesterase) inhibitor, a carbamate insecticide, (cholinesterase) inhibitor, an acaricide , an agrochemical and a plant growth retardant.



methylcarbamate
Naphthalen-1-yl
Other names
Sevin (Generic trademark)
α-Naphthyl N-methylcarbamate or
1-Naphthyl methylcarbamate

Synthesis: From 1) 1-naphthol and phosgene: 2) Using 1-naphthol and methyl isocyanate:

3) Using 1-naphthol and methylcarbamoyl chloride:

In these **routes** of **synthesis** of **Carbaryl** highly toxic substances such as phosgene, methyl isocyanate and methyl carbamoyl chloride are used.

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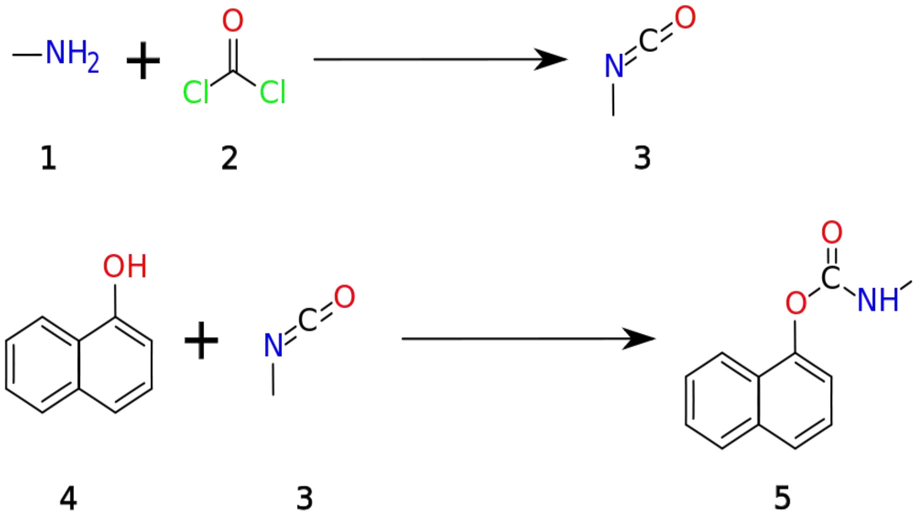
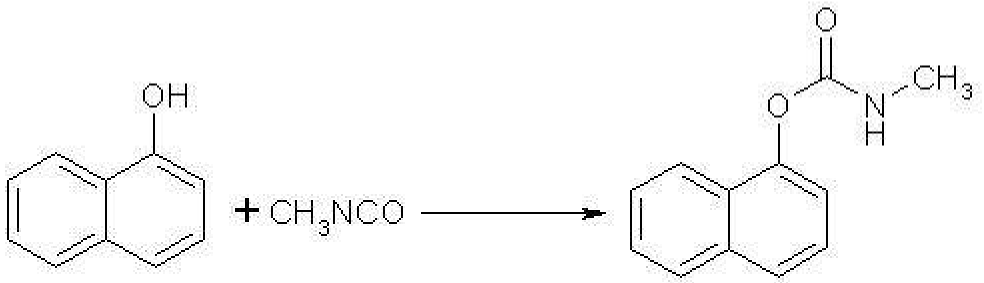
Synthesis of Carbaryl : sevin

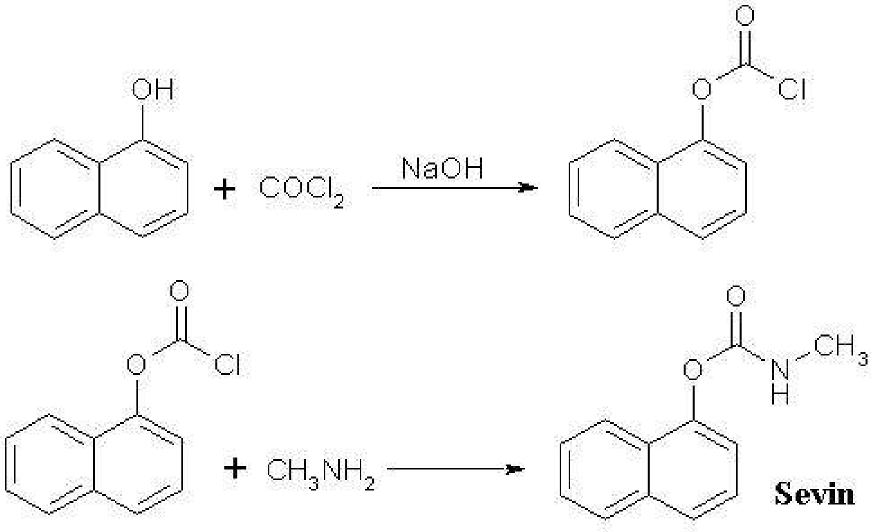


Uses : Carbaryl is a man-made pesticide that is toxic to insects. It is commonly **used** to control aphids, fire ants, fleas, ticks, spiders, and many other outdoor pests. It is also **used** in some orchards to thin out blossoms on fruit trees. **Carbaryl** has been registered for **use** in pesticide products since 1959.

1. From alpha – Naphthol and Methyl isocyanate



2. From alpha – Naphthol and carbonyl chloride

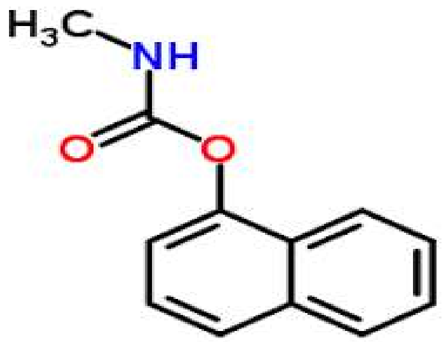


Toxicity and properties

Carbaryl is practically non-toxic or slightly toxic to birds, and slightly to moderately toxic to mammals. However, it is moderately to highly toxic to fish and highly toxic to earthworms and honey bees. **Carbaryl** is very highly toxic to shrimp, waterfleas, and stoneflies. The **LD50** for acute exposure is >2000 mg/kg .The **LD50** for acute exposure in pigeons ranges from 1000 to 3000 mg/kg (2). **Carbaryl** is a man-made pesticide that is toxic to insects. It is commonly used to control aphids, fire ants, fleas, ticks, .

It is a broad-spectrum N-methyl carbamate insecticide applied worldwide for control of agricultural and structural pests, and as a molluscicide.

Properties	
Chemical formula	$C_{12}H_{11}NO_2$
Molar mass	201.225 g·mol^{-1}
Appearance	Colourless crystalline solid
Density	1.2 g/cm^3
Melting point	142 °C (288 °F; 415 K)
Boiling point	decomposes
Solubility in water	very low (0.01% at 20°C)[1]

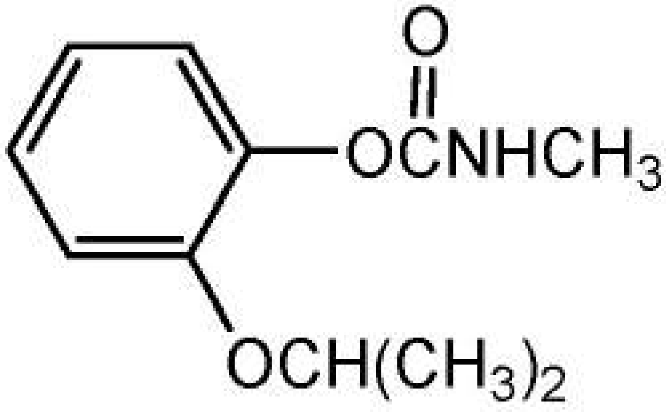


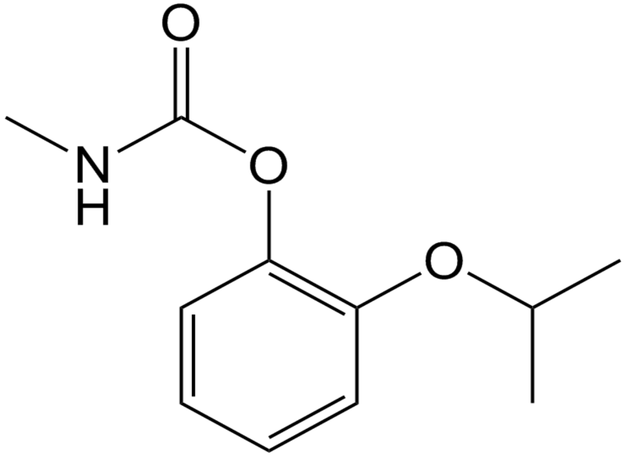
2. Baygon / Propoxure

Propoxure (**Baygon**®) is an insecticide with a broad spectrum of activity and a very low order of mammalian toxicity. Radio synthesis of propoxur was performed by the reaction of acetyl-1^{14}C chloride and sodium azide to produce methyl isocyanate which then reacted with o-isopropoxyphenol at 100°C.

Baygon products contain the pyrethroids - cyfluthrin, transfluthrin, prallethrin the carbamate propoxur and organophosphorus chlorpyrifos as **active ingredients**.

Propoxur is a nonfood carbamate **insecticide**, marketed under the registered trademark name Baygon. It is used to control cockroaches, flies, mosquitoes.





Baygon / Propoxur : Physical properties

- Propoxur is a carbamate non-systemic insecticide introduced in 1959 with a fast knockdown and long residual effect used against turf, forestry, and household pests and fleas. It is also used in pest control for other domestic animals, Anapheles mosquitoes, ants, gypsy moths, and other agricultural pests.
- **Formula**: $C_{11}H_{15}NO_3$
- **Molar mass**: 209.2417 g/mol
- **Solubility in water**: 0.2% (20°C) It is an N-methyl residual carbamate insecticide, a family of toxic chemicals that includes carbaryl, aldicarb and carbofuran. **Melting point**: 86 to 92 °C; 187 to 197 °F; 359 to 365 K
- **Boiling point**: decomposes
- **Flash point**: > 149 °C; 300 °F; 422 K

Synthesis

- **Propoxur** (**Baygon**®) is an **insecticide** with a broad spectrum of activity and a very low order of mammalian toxicity. Synthesis of **propoxur** was performed by the reaction of methyl isocyanate with o-isopropoxyphenol at 100°C to form baygon .