GREEN CHEMISTRY

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DEFINITION

Design of chemical Products & Processes that reduces or eliminates the use & generation of substances hazardous to the humans, plants, animals & environment.

Or

Environmental benign Chemical Synthesis

GREEN CHEMISTRY IS ABOUT

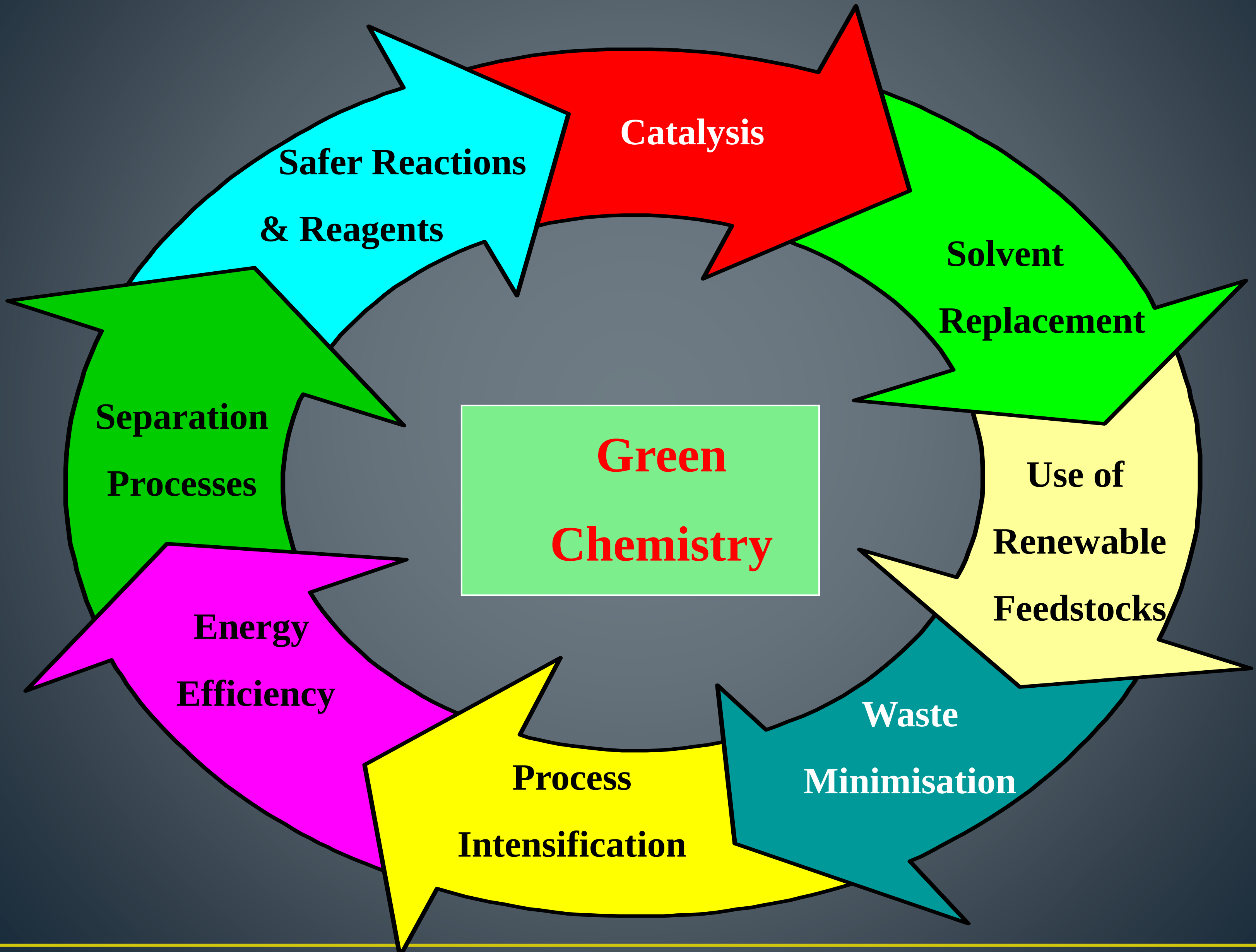
- **Waste Minimisation at Source**
- **Use of Catalysts in place of Reagents**
- **Using Non-Toxic Reagents**
- **Use of Renewable Resources**
- **Improved Atom Efficiency**
- **Use of Solvent Free or Recyclable Environmentally Benign Solvent systems**

Green Chemistry Is About...

Reducing

- **Waste**
- **Materials**
- **Hazard**
- **Risk**
- **Energy**
- **Cost**

Some Aspects of Green Chemistry

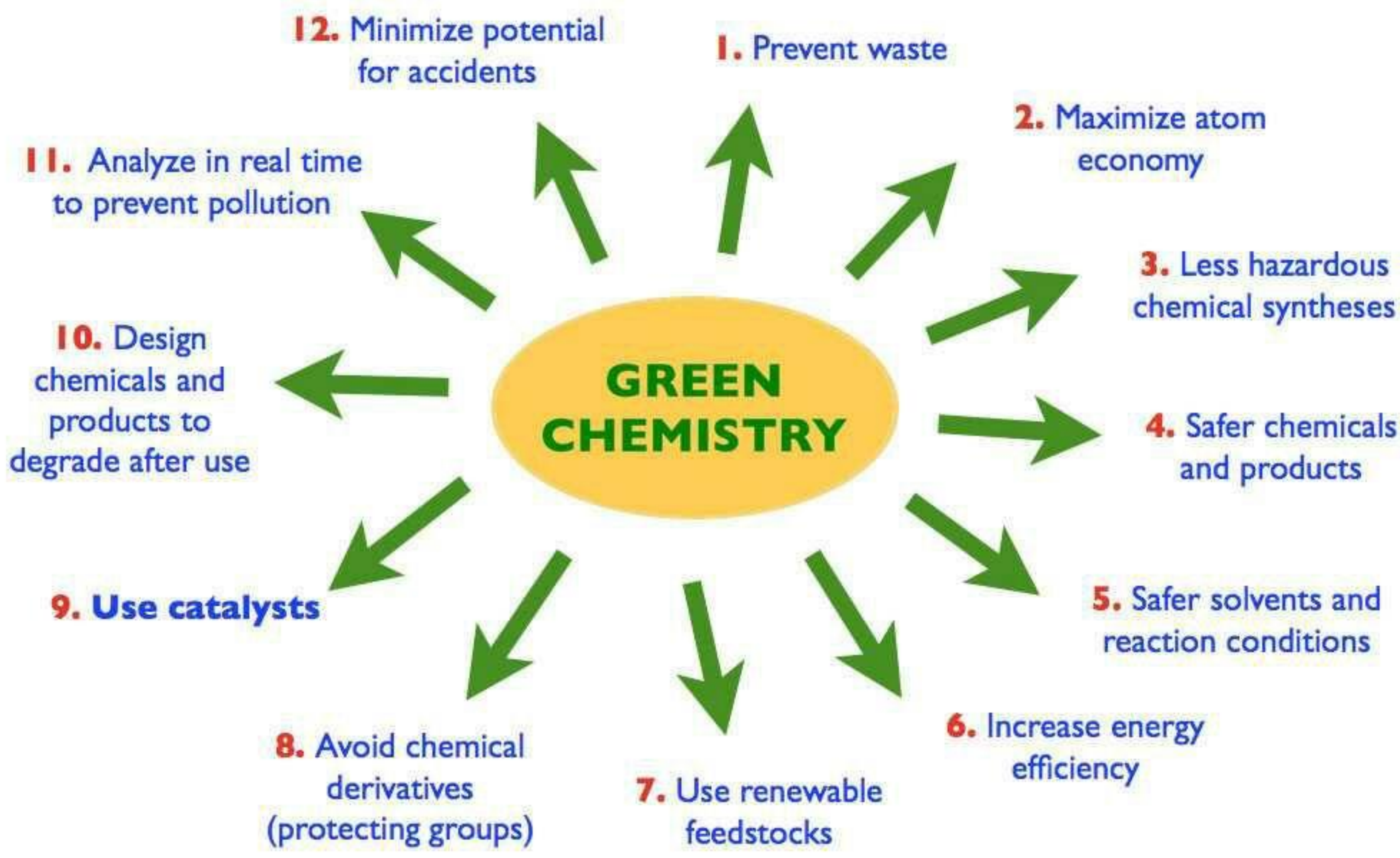


Why do we need Green Chemistry ?

- *Chemistry is a very prominent part of our daily lives.*
- *Chemical developments also bring new environmental problems and harmful unexpected side effects, which result in the need for 'greener' chemical products.*
- *A famous example is the pesticide DDT.*

(Insecticide),carcinogenic

Twelve Principles:



Anastas and Warner (1998)

The 12 Principles of Green Chemistry

Given by Paul Anastas & John warner

(U.S. Environmental Protection Agency)

1. Prevention: *It is better to prevent waste than to treat or clean up waste after it is formed.*

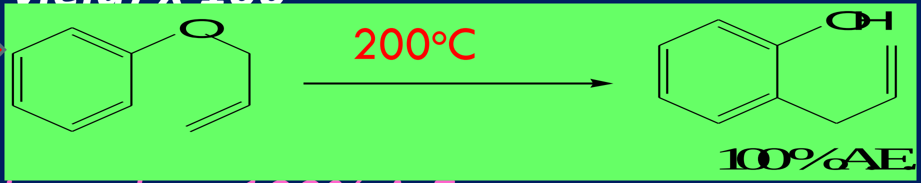
2.Atom Economy: *Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.*

Formula By, ***R.A. Sheldon***

% AE = (FW of atoms utilized/FW of all reactants) X 100

% yield = (Actual yield/Theoretical yield) x 100

Rearrangement



& addition Reaction: 100 % A.E.

Substitution & Ellimination reaction: Less than 100% A.E.

3. Less Hazardous Chemical Synthesis: *Whenever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.*

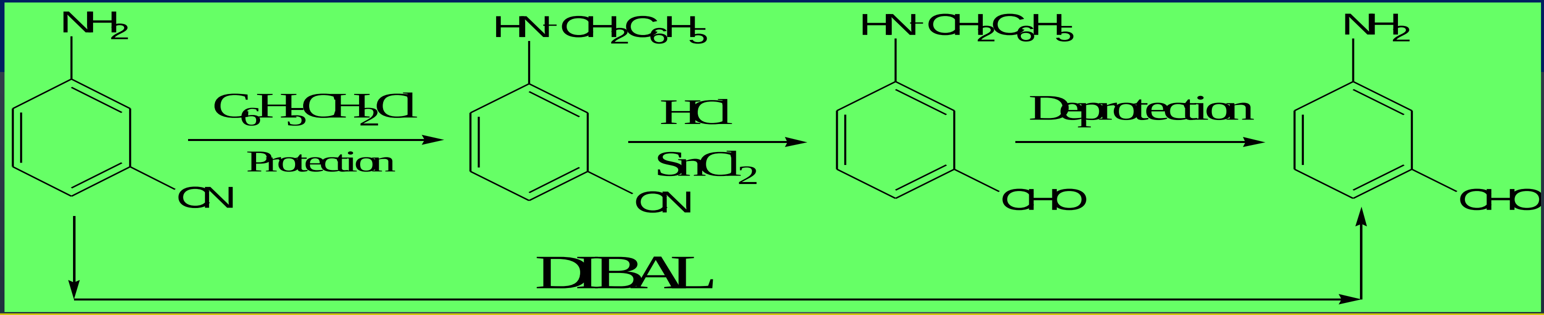
4. Designing Safer Chemicals : *Chemical products should be designed to preserve efficacy of the function while reducing toxicity.*

5. Safer Solvents and Auxiliaries: *The use of auxiliary substances (solvents, separation agents, etc.) should be made unnecessary whenever possible and, when used, innocuous.*

6. Design for Energy Efficiency. *Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.*

7.Use of Renewable Feedstocks: *A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.*

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



The 12 Principles of Green Chemistry

9 Catalysis

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

10 Design for Degradation

Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

11 Real-time Analysis for Pollution Prevention

Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

12 Inherently Safer Chemistry for Accident Prevention

Substances and the form of a substance used in a chemical process should be chosen to minimise the potential for chemical accidents, including releases, explosions, and fires.

eg- Tragedy in Bhopal, India – 1984 due to MIC

In arguably the worst industrial accident in history, 40 tons of methyl isocyanate (MIC) were accidentally released when a holding tank overheated at a Union Carbide pesticide plant, located in the heart of the city of Bhopal. 15,000 people died and hundreds of thousands more were injured.

Goals of Green Chemistry:

Retain mother earth in its natural form

Keep chemical manufacturing and their usage ecofriendly

1)Sustainability: *use ecofriendly ways to meet needs of society*

2) Cradle to Cradle design: *creation of reused product*

3)Source reduction: *reducing waste & pollution*

4)Innovation: *developing alternatives to technology*

5)Viability: *Creating ecofriendly center of economy activity around technologies and product*

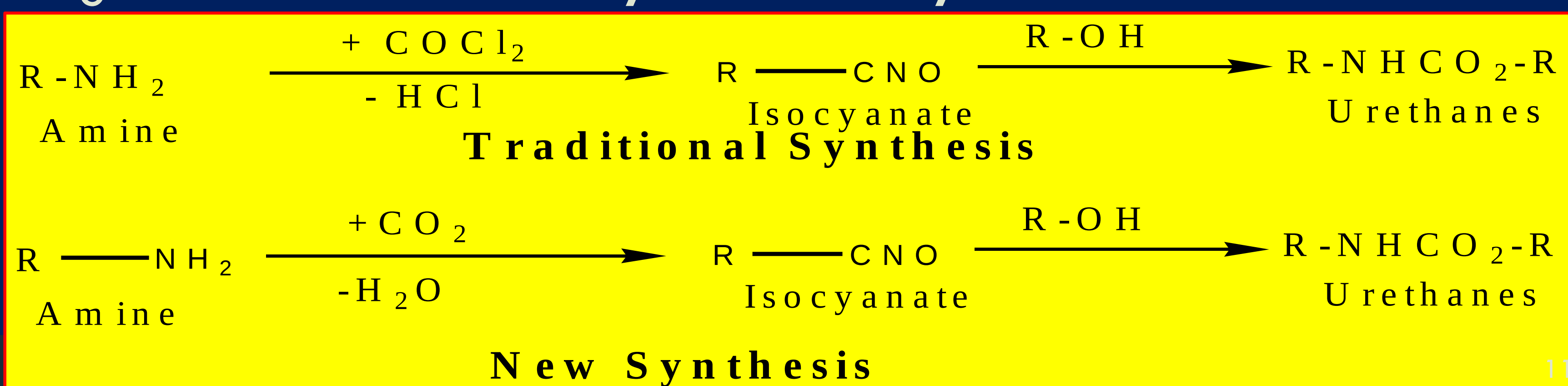
GREEN CHEMICALS

- **Chemicals used or produced that do not harm the user or environment**
- Its helps to achieve objectives of green chemistry

a) ***Green reagents:*** Nontoxic, biodegradable, produced by clean process

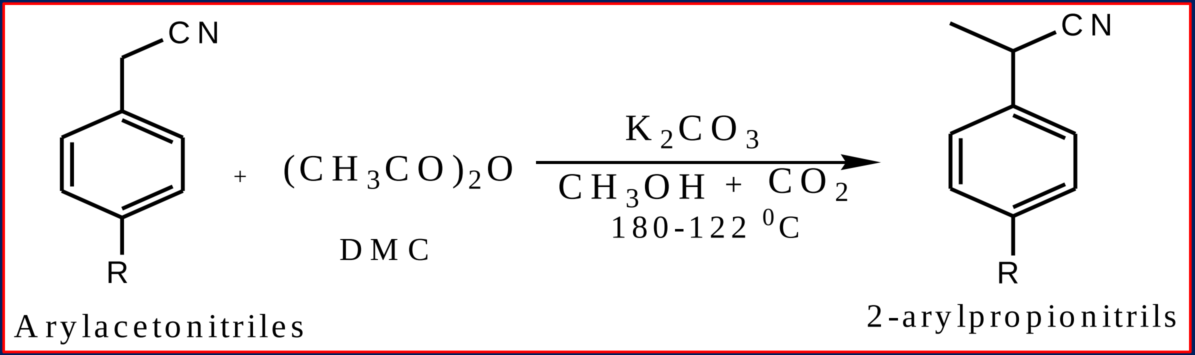
i) Carbon dioxide(CO_2): Instead of toxic CO & $COCl_2$

- **low reactivity.**
- eg: **New method for Polyurethanes synthesis**



ii) Dimethyl carbonate (DMC): *Instead of Methyl halide or DMS (methylation) or Phosgene(carbonylation)*

- *DMC have tunable reactivity (90^0C), good reactivity ($180\text{-}122^0C$)*
- *In Presence of K_2CO_3 selective methylation by DMC*
- *Unwanted Inorganic salts not formed*
- *Eg: Selective methylation of aryl acetonitriles*

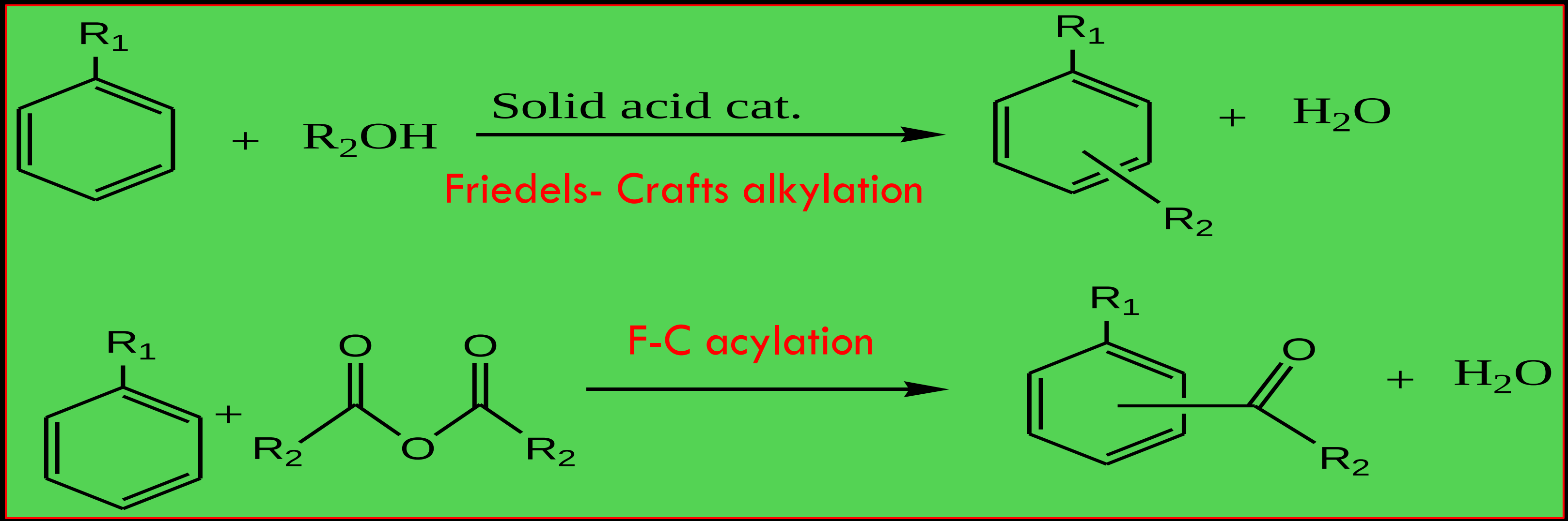


iii) Diphenyl carbonates: *instead of phosgene for production of polycarbonates*

iv)Oxidative transition metal complexes: *Extremely stable , long lasting, catalytic, recyclable oxidants of high oxidation state transition metal complexes*

b)Green Catalyst: Highly active, Selective, easy to handle, economical, helps to meet objective of green chemistry

- *enables clean catalysis, simple purification, safe operation of large scale processes.*
- *Eg: Solid acid catalyst as MCM-41, $Cs_2.5H_{0.5}PWO_{40}$, H^+-ZSM-5 & SO_4^{2-}/ ZrO_2*
- *Used for alkylation, isomerization, esterification, etherification, hydration, dehydration, Condensation, cracking etc*

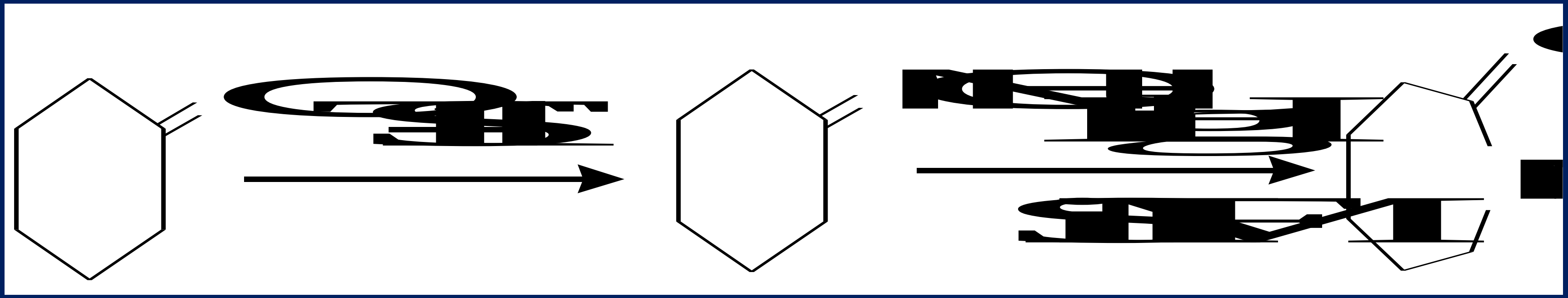


- ***Green Method:***

Eg- synthesis of Caprolactum, which is used for manufacture of Nylon

It eliminates use of $AlCl_3$

- Conventional process uses **oleum & hydroxylamine sulfate**
- *But now use of* ***Zeolite*** *as a green catalyst*
- $H_2 + O_2 \rightarrow H_2O_2$
- $N_2 + 3H_2 \rightarrow NH_3$



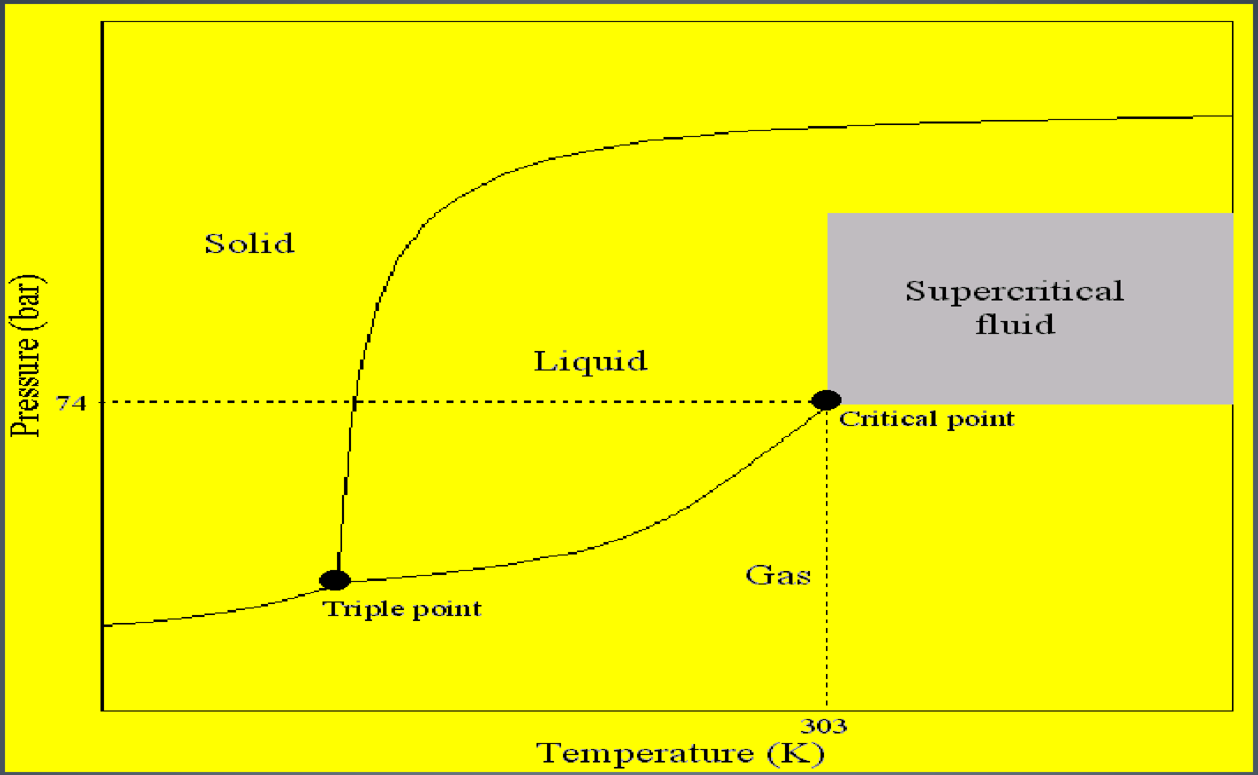
C) Green Solvents: *Cheap , nontoxic or less toxic, stable, readily available & recyclable*

- ***Eg-*** *Supercritical CO_2: cheap, benign, nonflammable, nonvolatile , dosent deplete ozone layer.*
- *Wide range of tempt. & pressure can be used*
- ***Conventional Solvent:*** *Costly , toxic, non biodegradable ,difficult to recycle, disposal is very expensive, risky to store, causing pollution.*
- *Eg- CCl_4, DMF, DMSO, DMAc, CS_2, $CHCl_3$, ether, acetone, pet ether, etc.*

Other green Solvent system:

- *Cyclodextrin with water, supercritical water, aqueous hydrogen peroxide, hydrogen, indium with water*
- *Free radical bromination by $ScCO_2$*
- *$ScCO_2$ is used as a solvent in decaffeination of coffee, oil extraction.*

What is Supercritical Fluid

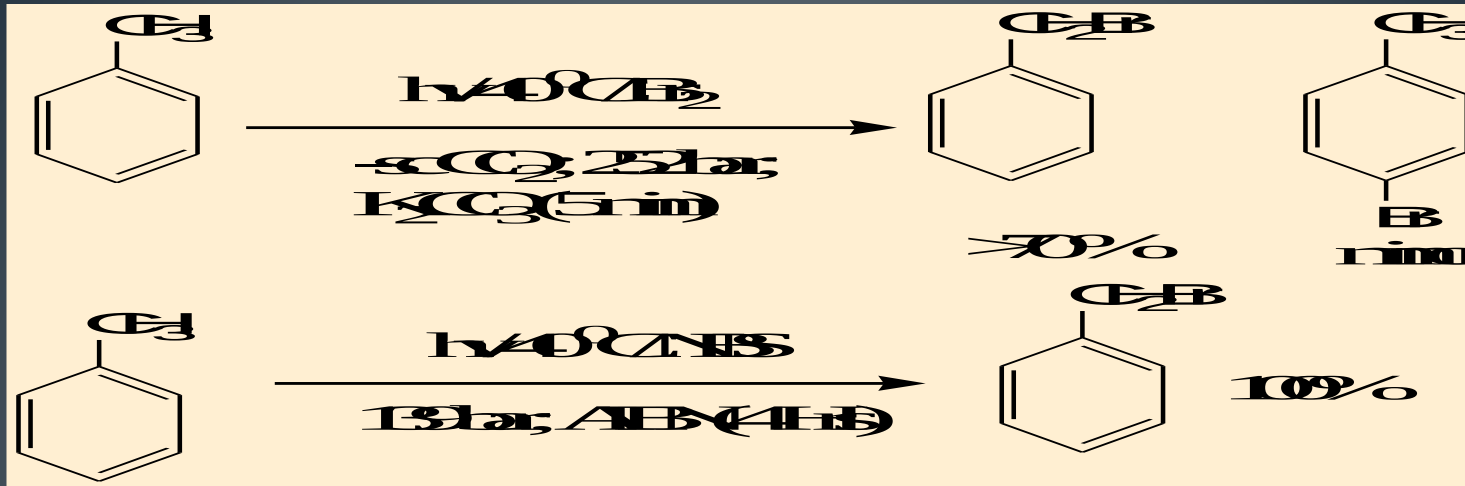


SCF is defined as a substance above its **critical temperature** (T_C) and **critical pressure** (P_C).

The critical point represents the **highest temperature and pressure** at which the substance can exist as a **vapor and liquid in equilibrium.**

http://www.chem.leeds.ac.uk/People/CMR/whatarescf.html

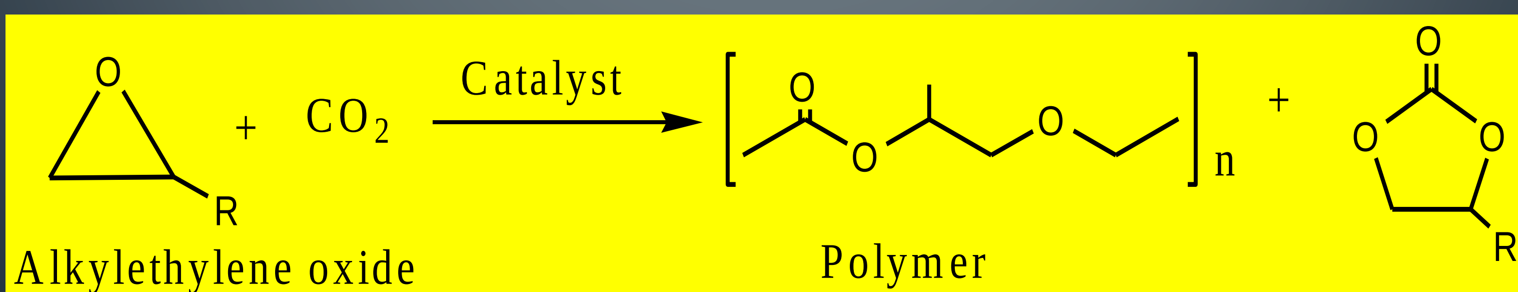
Bromination of toulene using Bromine & NBS



Use of Soapy CO2 in polymerization reaction:

Solvating power increases by hydrocarbon molecule

Eg- Polymerization of alkyl ethylene oxide-



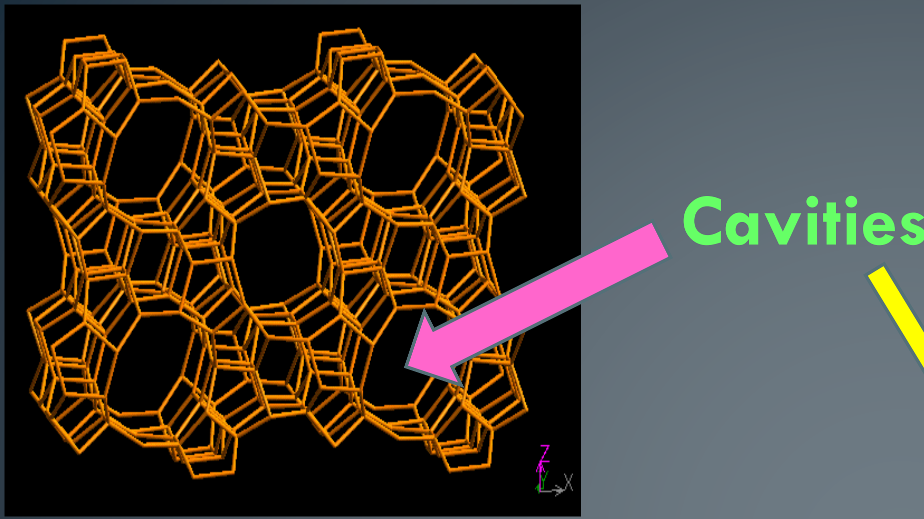
Green Organic Synthesis

- Waste generates while synthesizing tons of chemicals are polluting the environment & posing serious health hazardous
- Many Green technologies are developed to control manufacture & use of chemicals

a)Use of Zeolites: Microporous alumino silicates

- **They loosely hold wide variety of cations Na^{+}, K^{+},Ca^{2+}, Mg^{2+}, etc.**
- **Valuable as adsorbent , ion exchanger & catalysts.**
- **Used as heterogeneous catalyst, can be recovered & recycled**
- **Leading to less waste & fewer byproducts**
- **Zeolite confine molecules in their cavities causing changes in structure & reactivity.**
- **Hydrogen forms of zeolites are powerful solid state acids.**
- **Zeolite used in cracking of crude oil, isomerization, oxidation, reduction reaction as catalyst.**

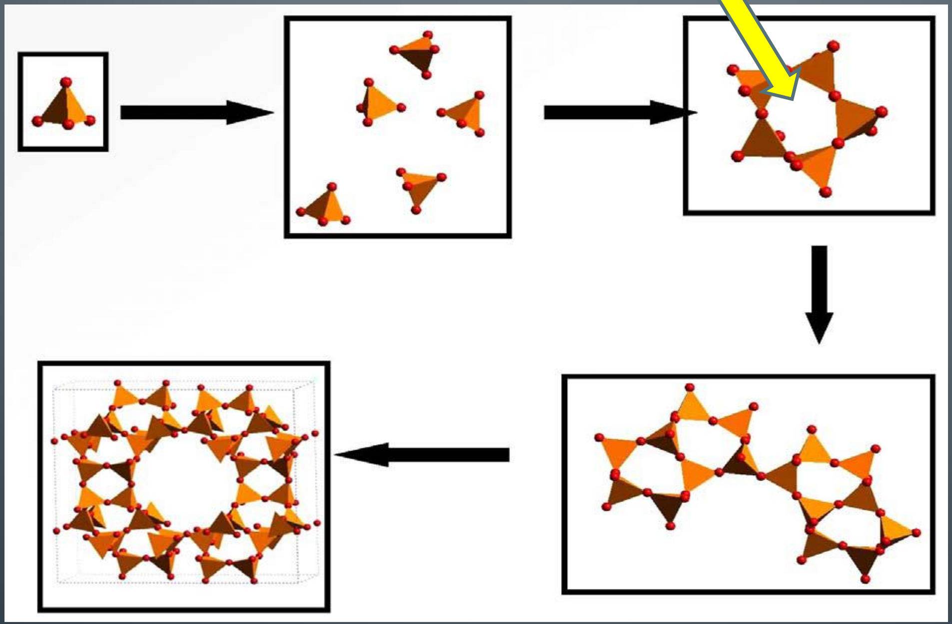
Zeolite framework:



ZSM-5 (MFI)

hydrated calcium aluminium silicate

How zeolites are built

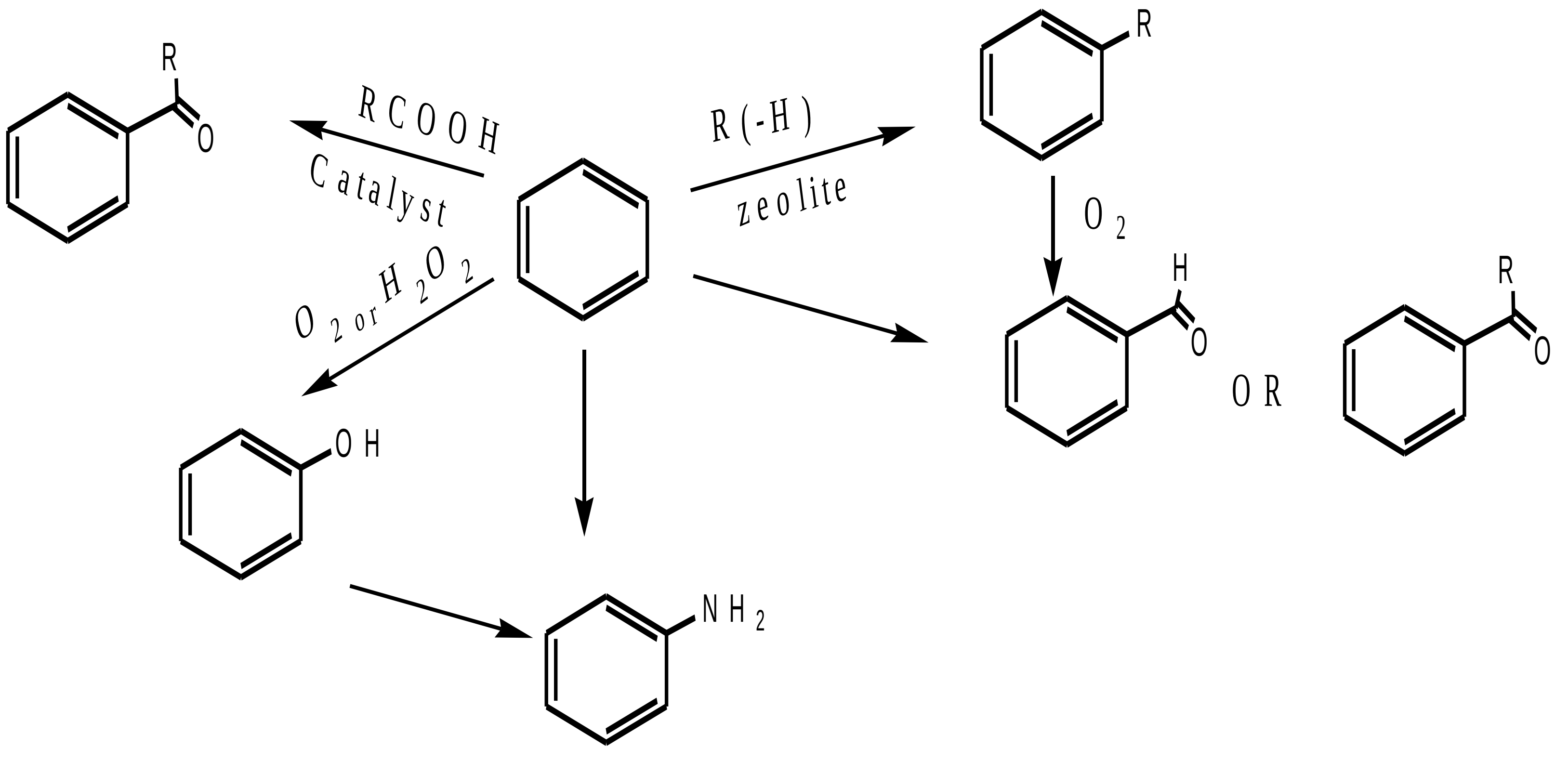


- Zeolites acts as ionic & molecular sieves by selectively sorting ions, molecules based on size, shape & polarity

  i.e used to separate & trap molecules

- **Eg- Use of Titanium ZSM-5 in production of caprolatum**

Some Zeolite catalysed reactions:

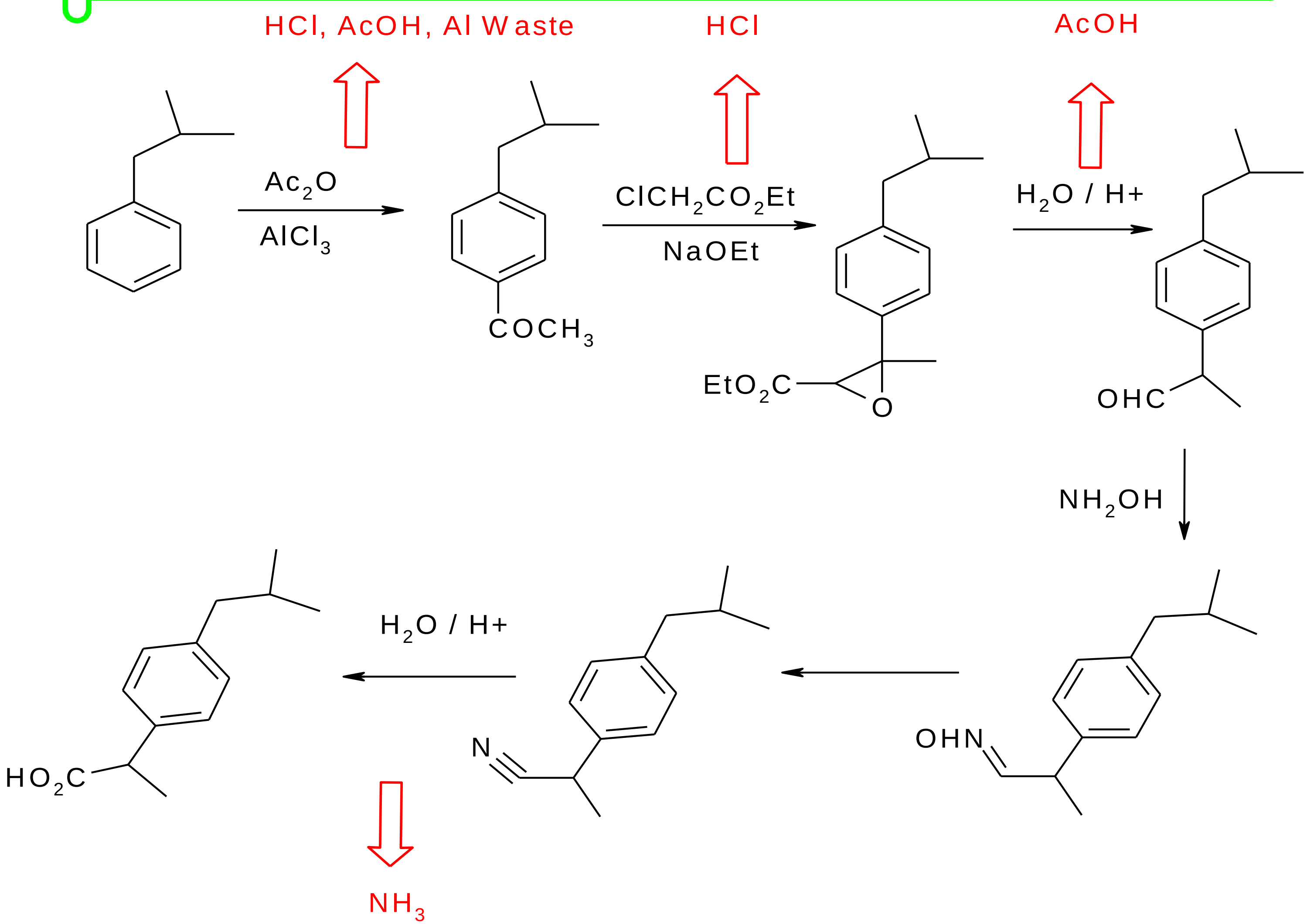


Non-Classical aromatic Chemistry

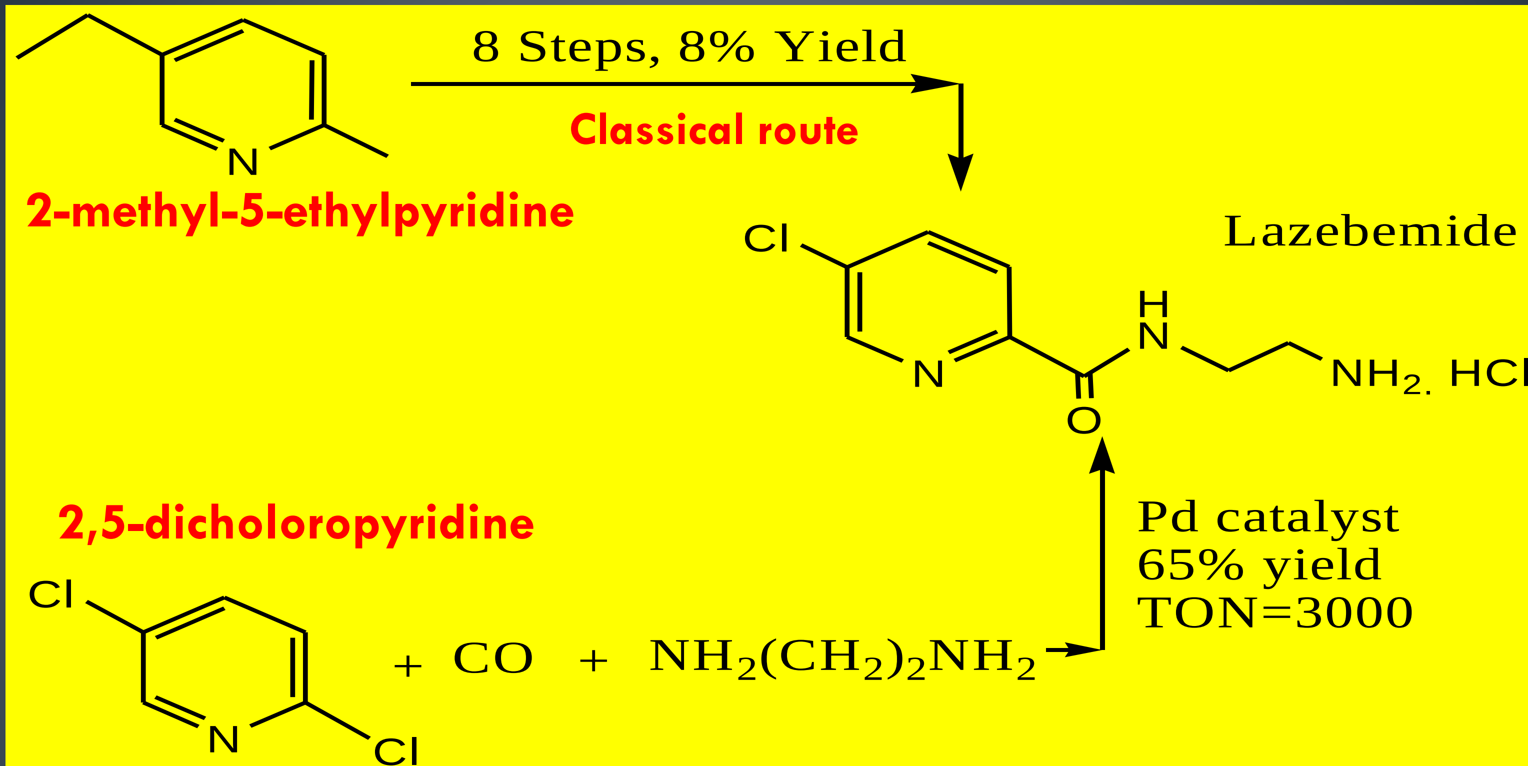
b)Use of natural catalyst:

- Major source of waste in chemical industry:
- Acids: HNO_3, H_2SO_4, HCl, etc
- Bases: KOH, NaOH, etc
- Metals: Na, Mg, Zn, MnO_2 & MnO_4^{-1}
- They all endup with huge quantity of inorganic salts.
- Therefore need of greener alternatives
- Eg- 1) Synthesis of Ibuprofen (Anti-inflamatory)

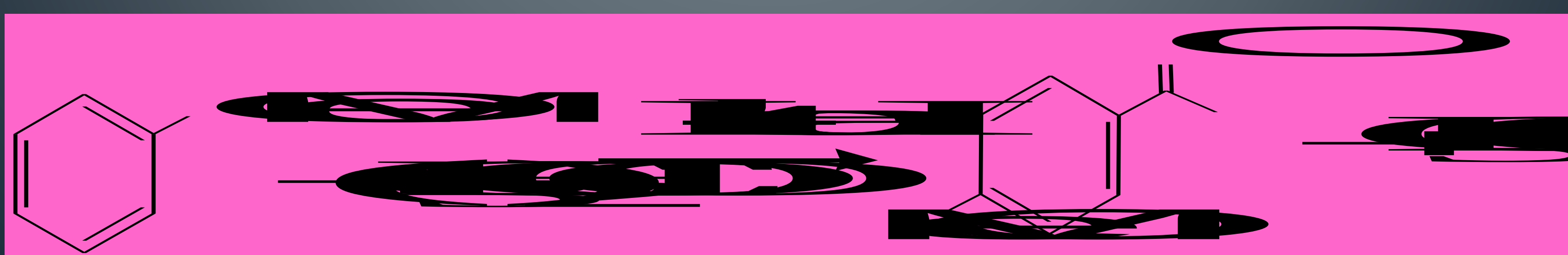
Classic Route to Ibuprofen



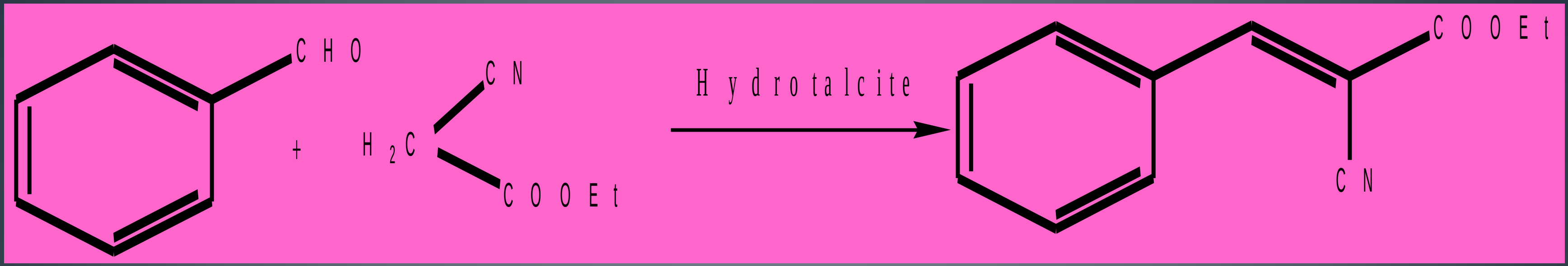
2)Synthesis of Lazabemide: Anti-parkinsonian drug

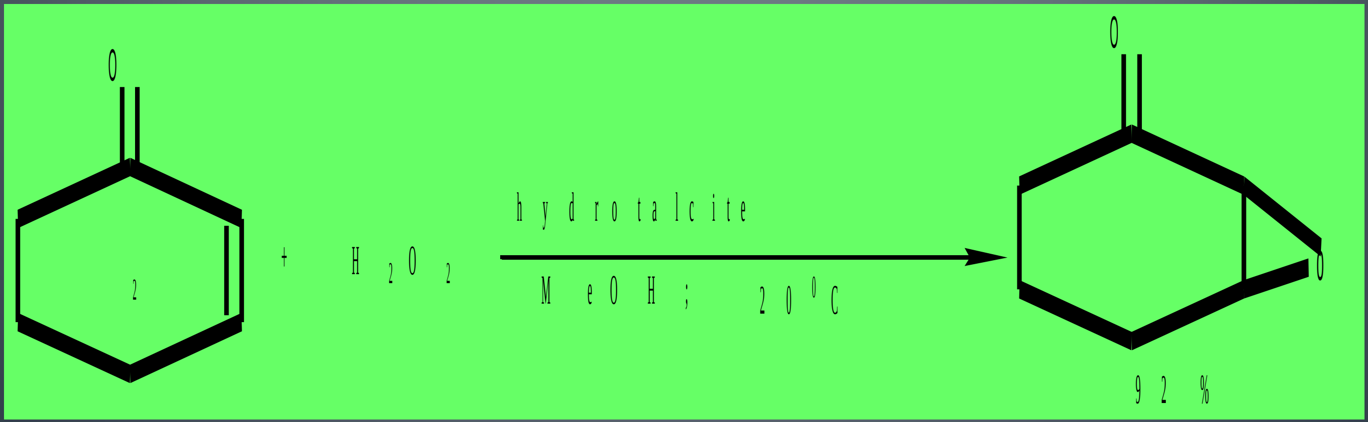


3)Zeolite Catalysed Friedel-Craft's reaction:

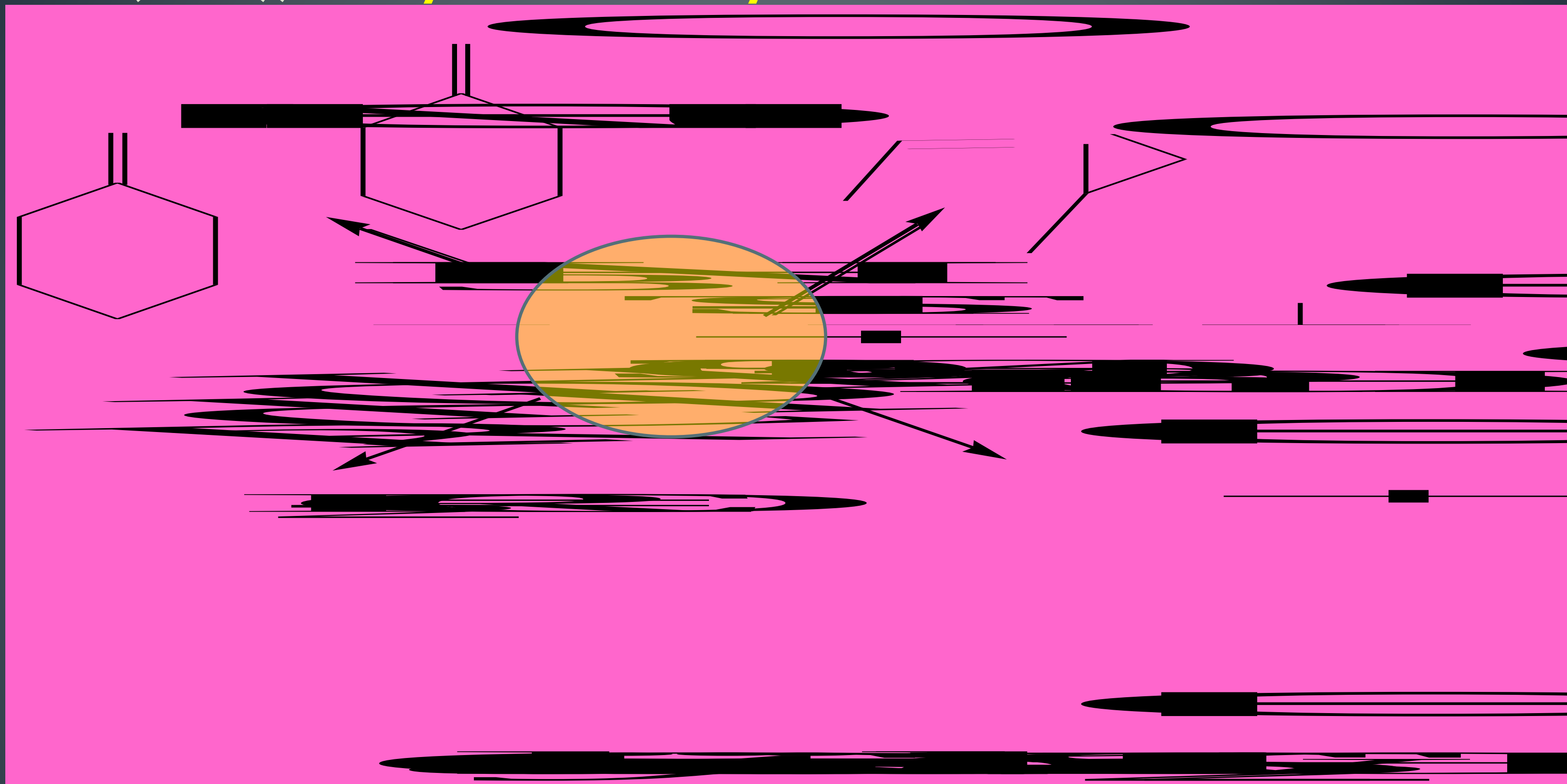


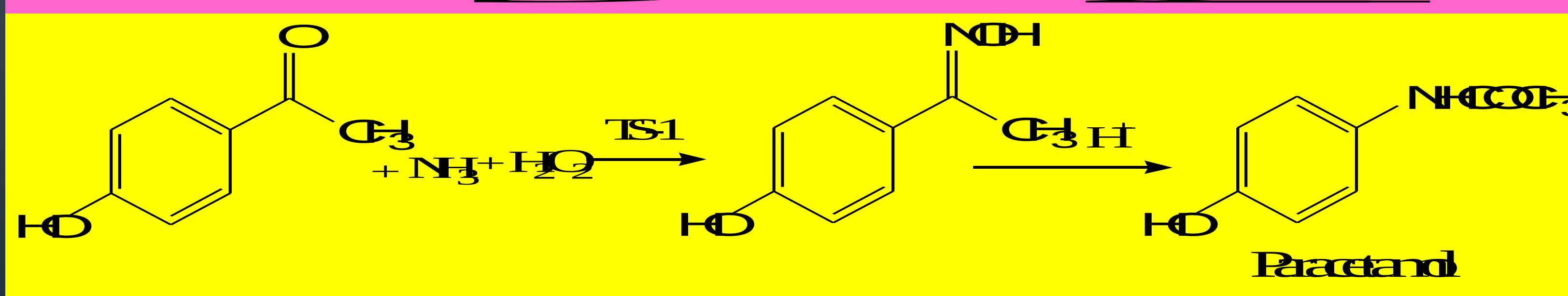
- **4) Conventional bases(KOH, NaOH) replaced by recyclable solid bases ie- hydrotalcite clays (aluminium magnesium hydroxide)**





5) Heterogeneous catalytic hydrogenation(Ni, Pd, Pt, Titanium silicate(TS-1)): Recyclable catalyst





Paracetamol intermediate via ammoximation

C) Use of Biocatalysts:

enzymes are most efficient, Pure catalyst present in all living forms

Reaction catalyzed by enzyme called as biocatalysis

- It carries wide range of chemical reactions
- **Advantages:**

i) Nontoxic, biodegradable , renewable catalysts, safe to use.

ii) Operate at ambient tempt., energy efficient

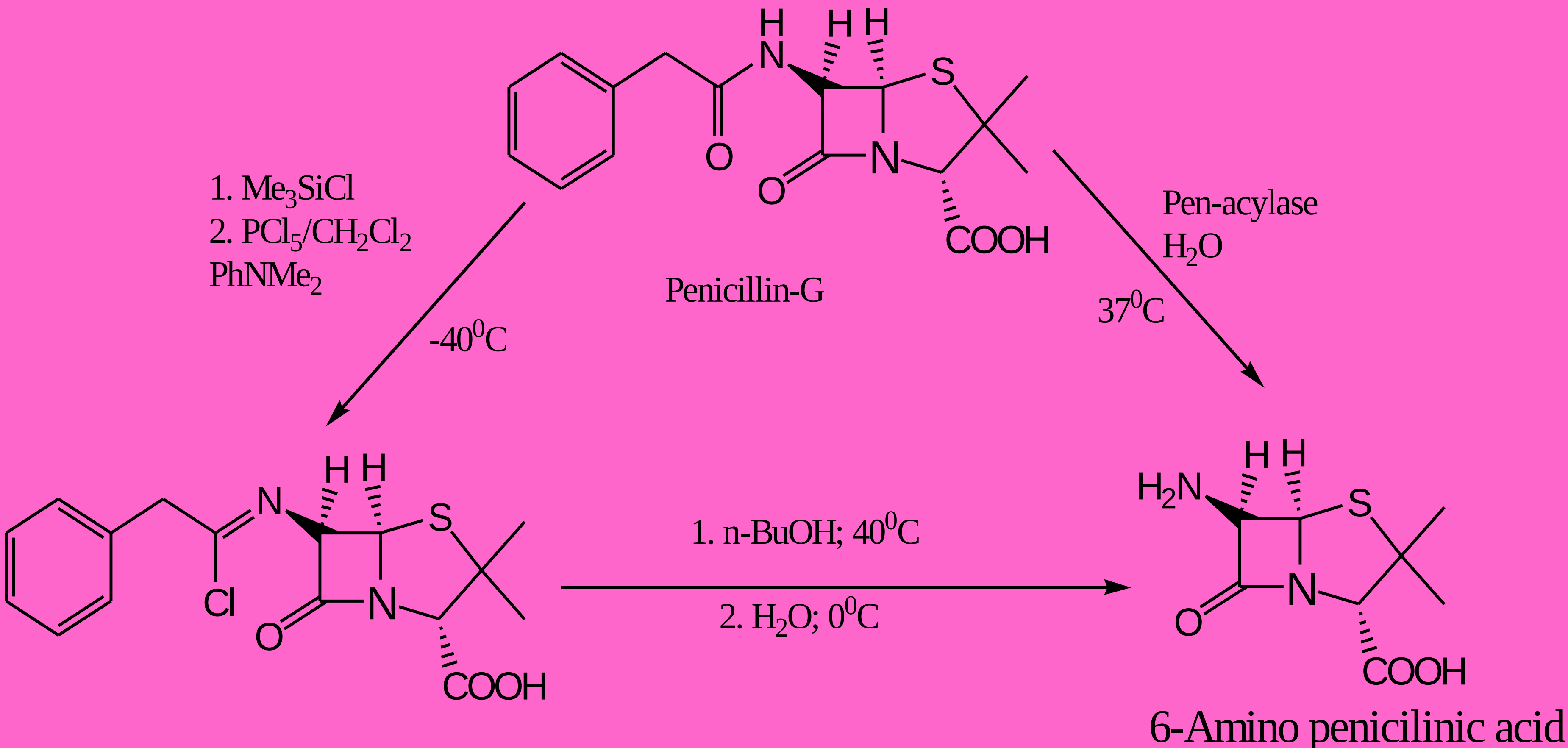
iii) acts in aqueous medium , help to avoid use of toxic, hazardous organic solvents

iv) Substrate Specificity of enzyme helps to use even in impure reaction mixture.

v) Stereospecificity helps to yield only one single isomer.

Eg- **i) Production of 6- Aminopenicillanic acid by enzymatic hydrolysis of Penicillin-G:**

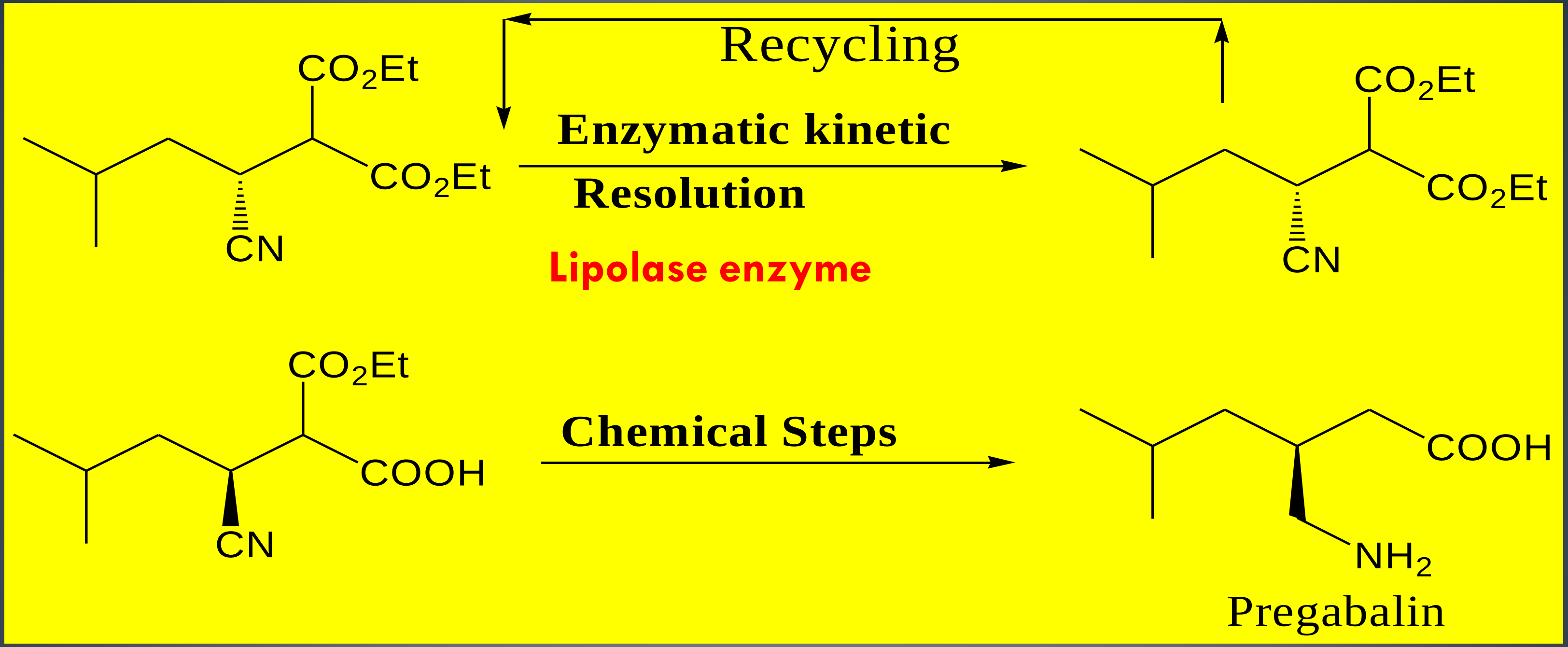
Enzyme: Penicillin-G-acylase



Enzymatic versus Chemical Deacylation of Penicillin G

ii) Synthesis of Pregabalin:

- **Used to treat Neuropathic pain**



Limitations:

i) Costly, availability is restricted to their isolation

ii) Can not be synthesized

iii) Sensitive to p^H, tempt, heavy metal ions, etc

iv) Water soluble so can not be recovered after use.

Emerging Green Technologies

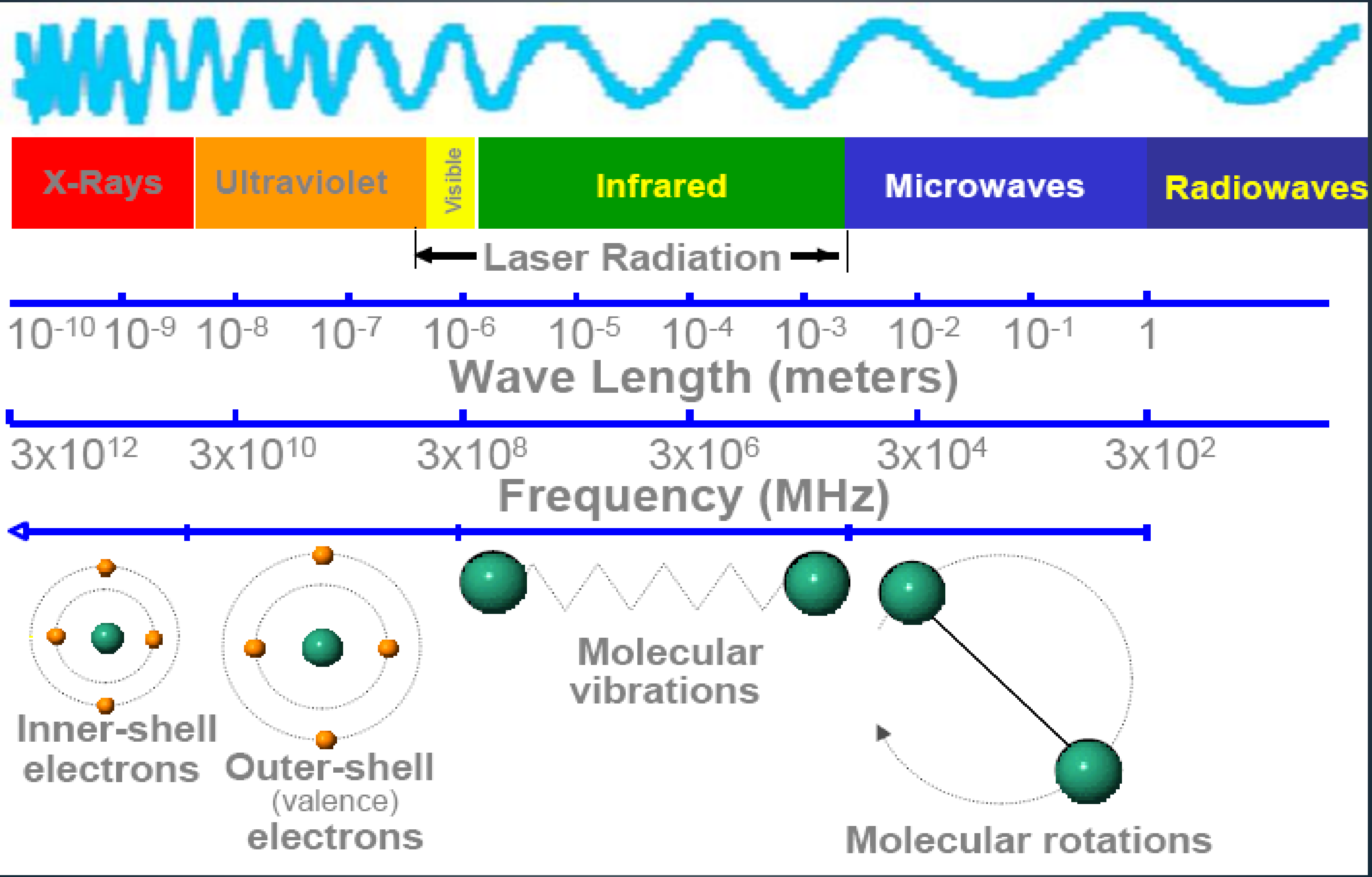
- **Conventional method : Disadvantages**
- Chemical processes use aggressive conditions with reactive & toxic chemicals & depleting energy sources.
- Energy input is also not directly targeted to chemical bond or molecule.
- So much of energy is wasted in heating up reactants, solvents.

Green Technology:

"Sustainable synthetic processes which meet the objectives of green chemistry are termed Green technologies."

So new technologies based on alternative energy sources like microwave, sonic, solar, mechanical & electrochemical energies are fast emerging.

1.Microwave Chemistry



1.Microwave Chemistry

- Use of microwave radiations(**0.3-300 MH_Z**) in chemical process
- **Nonionizing** (Hence not alter the molecular structure of the compounds

  being heated – it provides only thermal activation),

  high wavelength radiations.
- **Glass, ceramics, hydrocarbons transparent to MWs, but metal reflect.**

- **Instantaneous method, specific heating & no contact required between reaction vessel & energy source**
- **Works better for all conventional reactions that tooks hours or days to complete, can be performed in minutes with better yield.**

Principle

When a molecule is irradiated with microwaves, it aligns itself with the applied field.

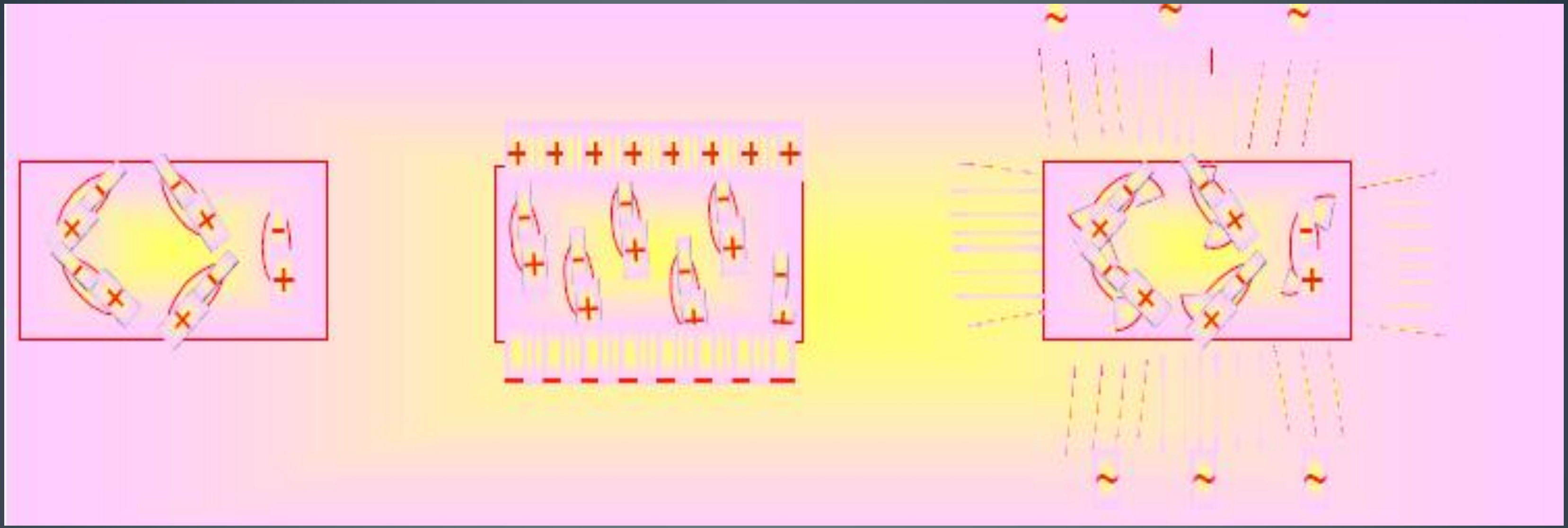
The rapidly changing electric field (2.45 x 109 Hz) affects the molecule *and* ***consequently the molecule continually attempts to align itself with the changing field and energy is absorbed.***

The ability of a material to convert electromagnetic energy into thermal energy is dependent on the dielectric constant.

The larger the dielectric constant the greater is the coupling with microwaves.

Thus, solvents such as water, methanol, DMF, ethyl acetate, acetone, acetic acid, etc. are all heated rapidly when irradiated with microwaves.

MW Heating Mechanism



No constraint

Continuous electric field

Alternating electric field With high frequency

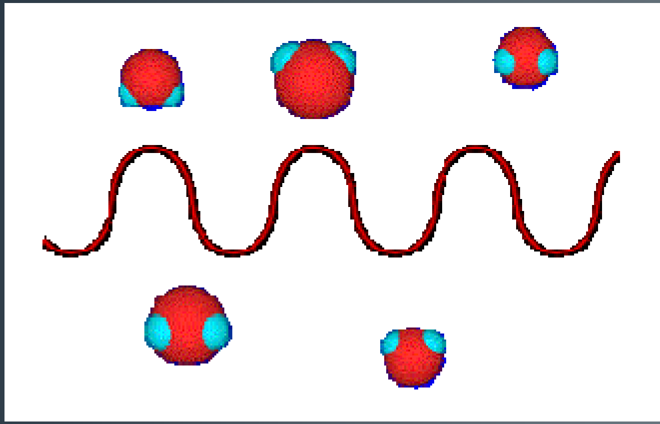
✓**Two mechanisms:**

❖ **Dipolar rotation / polarization**

❖**Ionic Conduction mechanism**

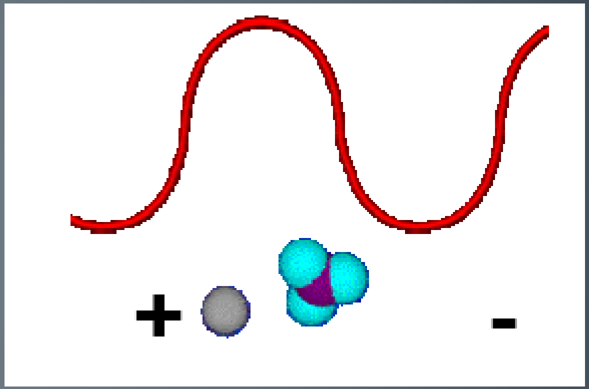
Microwave Dielectric Heating Mechanisms

Dipolar Polarization Mechanism



Dipolar molecules try to align to an oscillating field by rotation

Conduction Mechanism

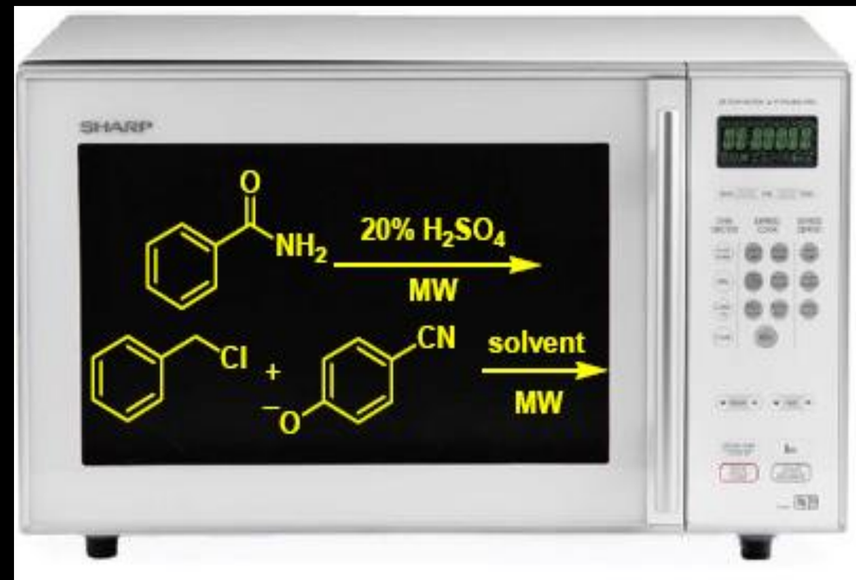


Ions in solution will move by the applied electric field

Microwave for Synthesis

- **Advantages:**
- Uniform heating throughout.
- Reaction acceleration
- Milder reaction conditions
- Higher yield
- High efficiency of heating
- Pure final product

Cooking Chemistry ???



a. Hydrolysis:

i) Hydrolysis of Benzyl chloride :MW -3 min, 97% ; Conventional: 35 min

ii) Hydrolysis of Benzamide: MW: 07 min, 99% yield ; conventional -1 hr,

b. Oxidation: Conventional-10-12 h

- **MWs- 5 min ,40% yield**

c. Esterification: MW- 6 min

2. Sonochemistry

- **Use of ultrasound to drive chemical reactions**
- **Widely developed for heterogeneous system**
- **Frequency: 20 KH_Z-1 MH_Z**
- Ultrasound influence on chemical reaction by **Accoustic cavitation mechanism**
- **Accoustic cavitation mechanism:**

When liquid-solid interface subjected to ultrasound sonication, compression of liquid is followed by rarefaction(expansion) occurs.

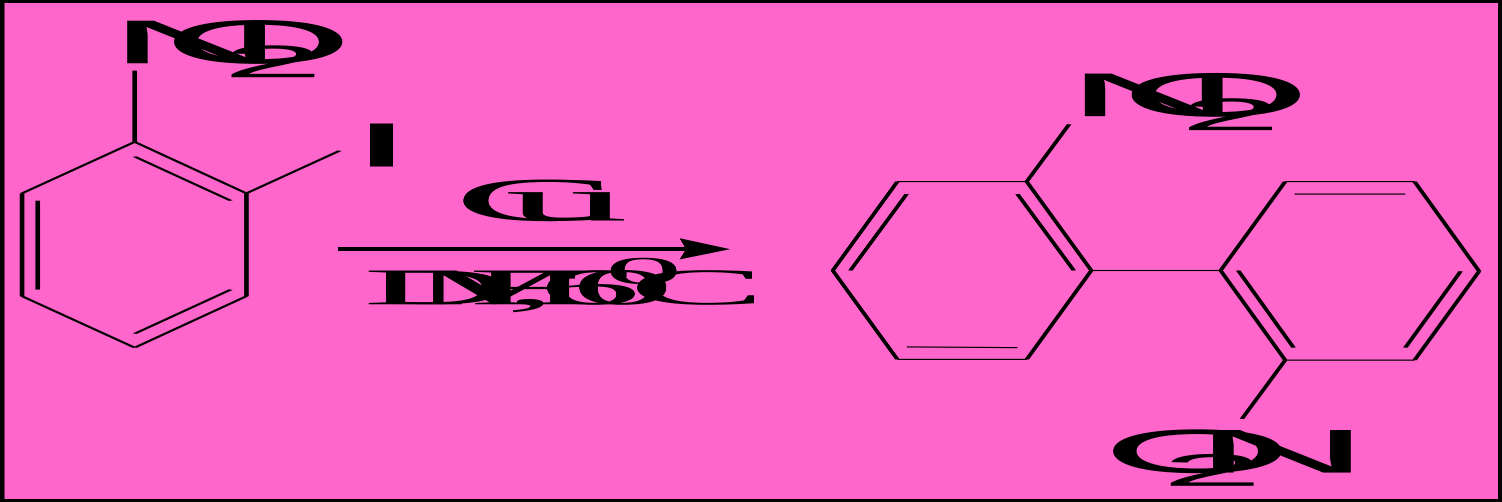
The sudden pressure drop gives rise to small ,oscillating bubbles of gaseous substances called Cavities.

These cavities expand by each cycle of ultrasonic energy until they reach an unstable size.

- **Then they can colloid or violently collapse.**
- **These collapsing releases high tempt., pressure, shock waves & particle accelerations.**
- **This energy is used to drive chemical reactions.**

- **Advantages:**
- **Better yield, faster rates, milder tempt.**
- **Most widely developed for heterogeneous reactions**
- **Finds many applications in many area & organic synthesis**

- **Eg- Ullman Reaction:**
- **Conventional: 48 h, Copper -10 fold**
- **Sonochemistry: 10 h , Copper -4 fold**



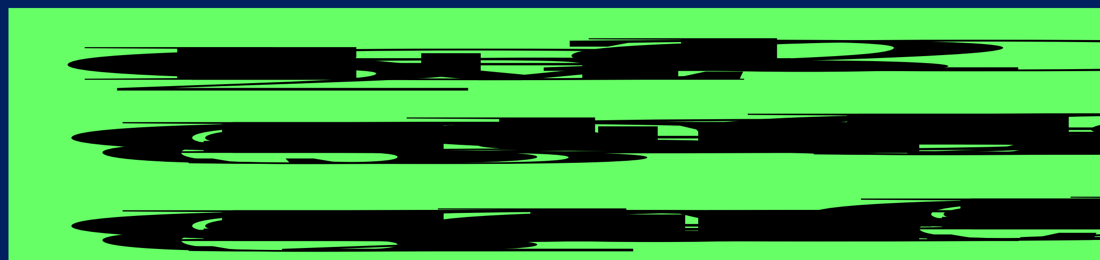
3. Photochemistry

- *Study of Chemical reactions initiated by absorption of energy in the form of light(200-800 nm) by atoms or molecules.*
- *Excitation of Molecules can initiate chemical reaction in many ways i.e. decompostion, rearrangement, combination, transfer of e-, H-atom, Protons, transfer of energy to other molecule, etc.*
- *Eg- Photosynthesis, formation of Vit-D, Degradation of plastics in sunlight*
- ***Advantages:***
- *Photons are clean reagent*
- *Reducing energy usage by targeting energy at a particular bond in molecule.*
- *Specific reactivity of electronically excited molecules*
- *Low thermal load on reaction system*
- *Extent control on radiation in terms of space, time & energy*
- *Selective activation of individual reactants.*
- *Performed in gas, liquid & solid phase*

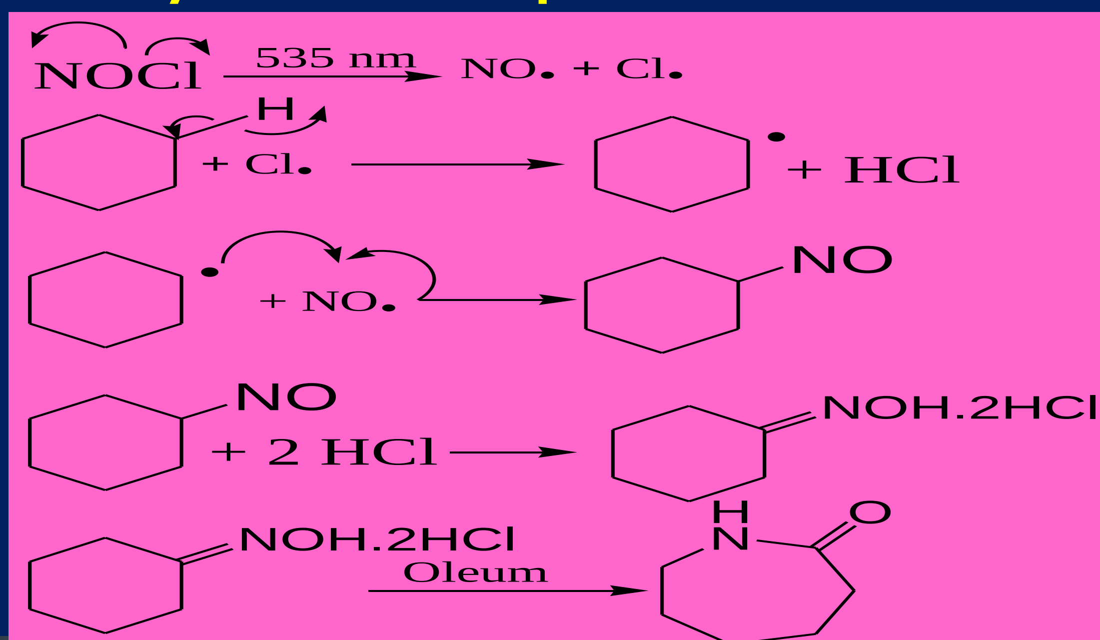
For practical reason most photochemical reactions are done in solution

- **Disadvantages:** Absorption characteristics, Internal & external light filters, Investment cost & electricity cost.
- **Eg.** i) Production of Vit-D_3

ii)Preparation of benzyl chloride by reaction of toluene with chlorine



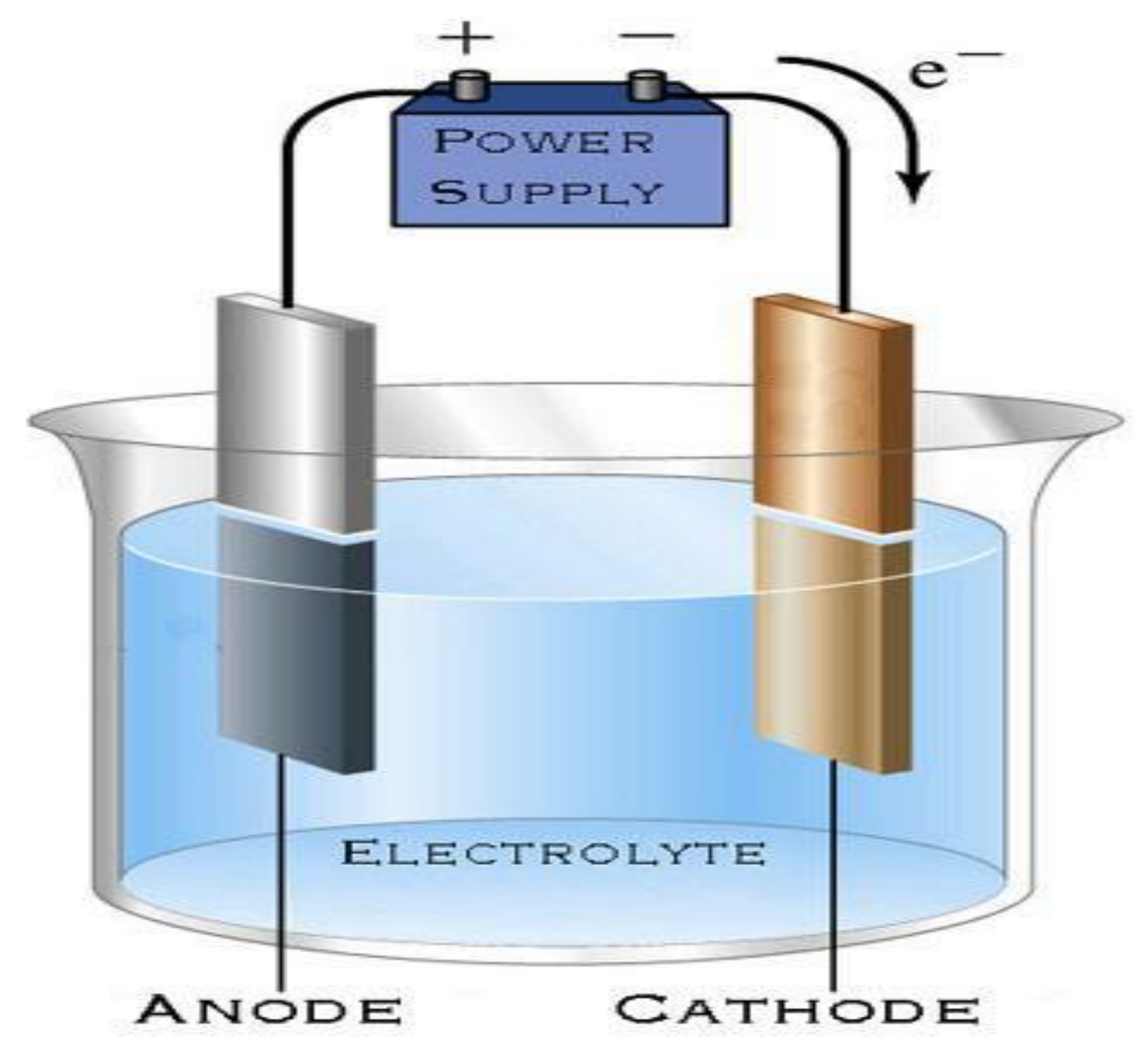
iii) Photochemical synthesis of caprolactum



4. Electrochemistry

- Electrochemistry involves the activation of molecules by transferring electrons from the surface of a heterogeneous electrode
- Synthesis of inorganic & organic chemical compounds in an electrochemical cell is termed as elctrosynthesis.
- Basic needs: Galvanic cell, potentiostat & two electrodes
- Advantages:
- i)water based process
- ii) Lower energy cost
- iii) Atom efficient- replacement of reagents by electrons
- iv) Novel chemistry possible
- v) Avoids wastage
- vi) Higher product selectivity than chemical routes

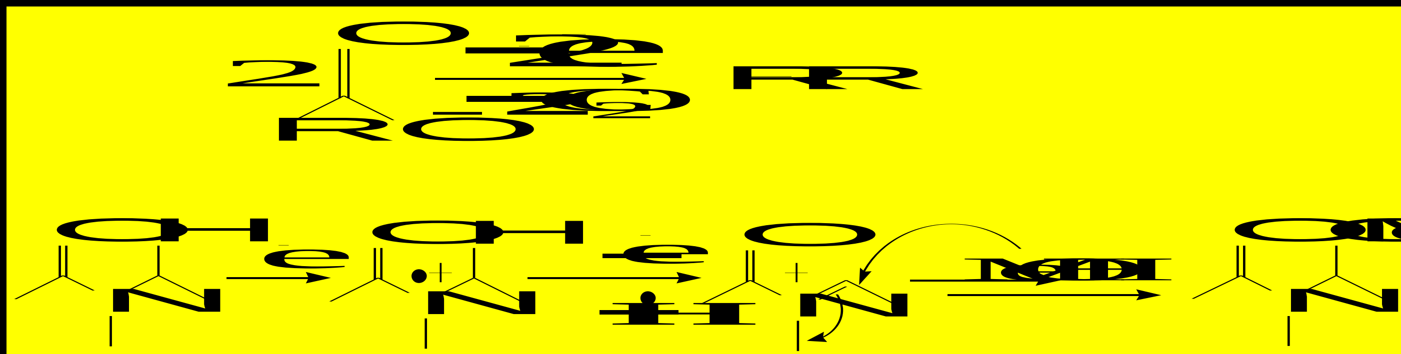
  vii) Minimum pollution problem
- Viii) Less hazardous route


+
−
e⁻
POWER
SUPPLY
ELECTROLYTE
ANODE
CATHODE

Eg- A) Anodic Oxidations

Kolbe electrolysis: Two carboxylic acids **decarboxylate** to form alkane

- Amide——→ N-acyliminium——→-captured by various nucleophiles.

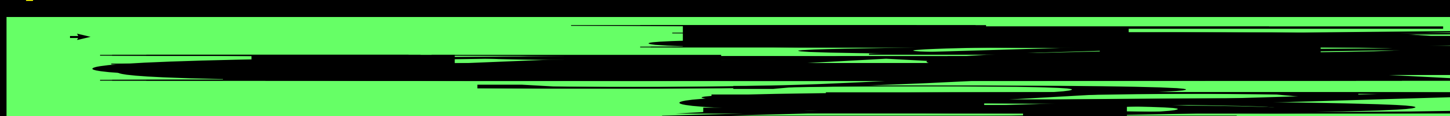


<u>B) Cathodic reductions:</u> eg- i)Production of Adiponitrile by electrohydro dimerisation of acrylonitrile. Oxygen is produced at anode.

ii) Cathodic reduction of arenes:

5. Mechanochemistry

- Use of mechanical energy or force to drive chemical reactions
- Based on transfer of mechanical energy to reacting particles.
- Eg-i) Combustion of rubbing sticks together, this motion creates tempt. to 200^{0}C leading to combustion reaction ii)Striking of flint on steel to make spark, heat is released.
- It is possible to synthesize chemical products by using mechanical energy only.
- Ball milling is used widely to achieve chemical processing
- Used for reactions using solid reagents not readily soluble in organic solvents
- Advantages: Simple, efficient, ecofriendly.
- Eg-Synthesis of Cellulose acetate used in films & textiles



- Traditional: Use of H_2SO_4 & expensive solvent

GREEN SYNTHESIS

- **Refers to a chemical process that meets criteria defined by green chemistry**

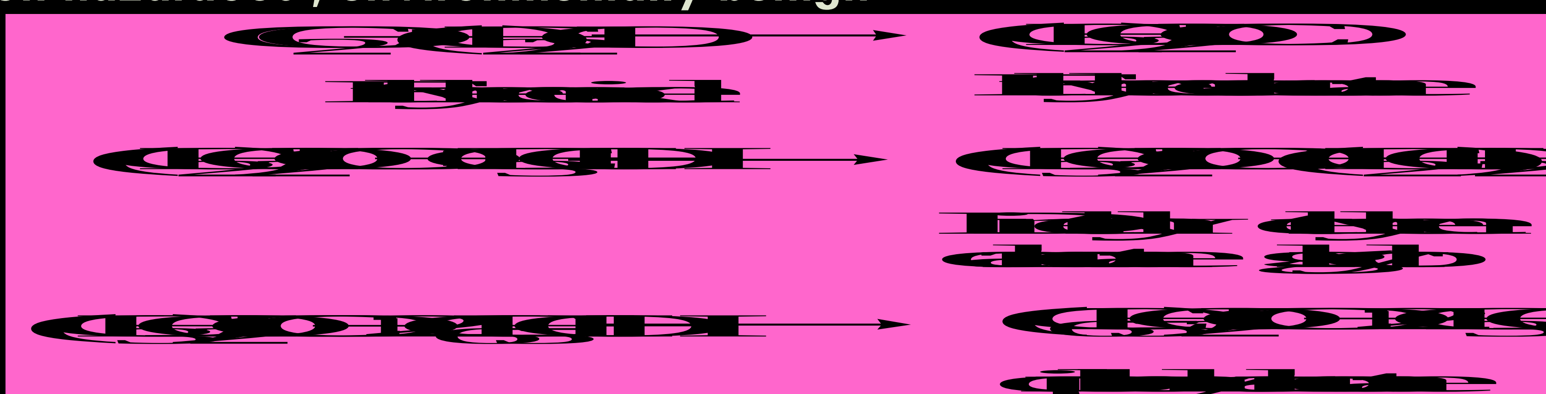
1. Polycarbonates:

Traditionally: Phosgene process, highly toxic ,corrosive, use of large amount of solvents(ethylene chloride & water)

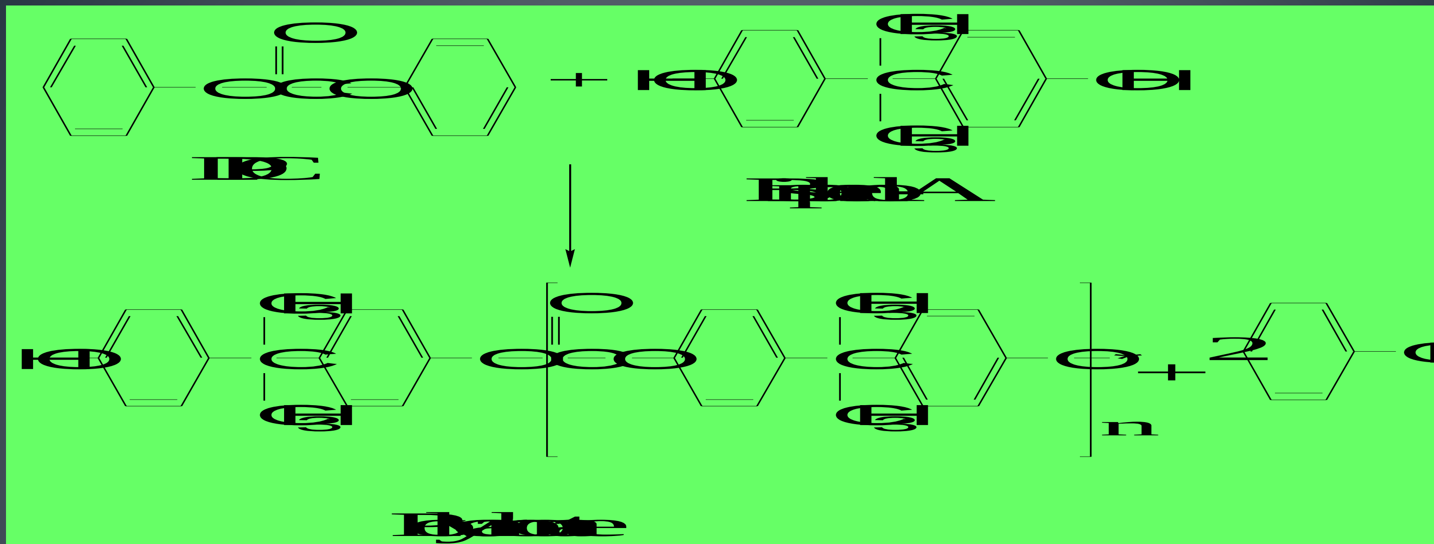
- Chlorine impurities found in PC.
- Process is Hazardous , uneconomical, not environmental benign.

New Method: Use of CO_2, ethylene oxide & bisphenol-A. gives high yield of PC & alongwith high purity monoethylene glycol(MEG)

- Non hazardous , environmentally benign



Polymerization: PC used as engineering plastics, etc.

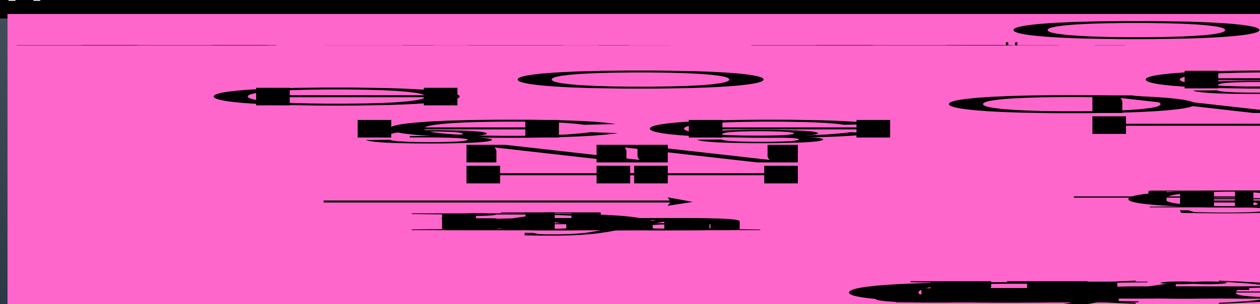


2.Carbaryl (1-naphthol N-methyl carbonate)/ Sevin

Insecticide, used to control 100 species of insects

Traditional Synthesis: Phosgene ,methyl isocyanate, methyl carbamoyl chloride. Its highly toxic & hazardous chemicals.

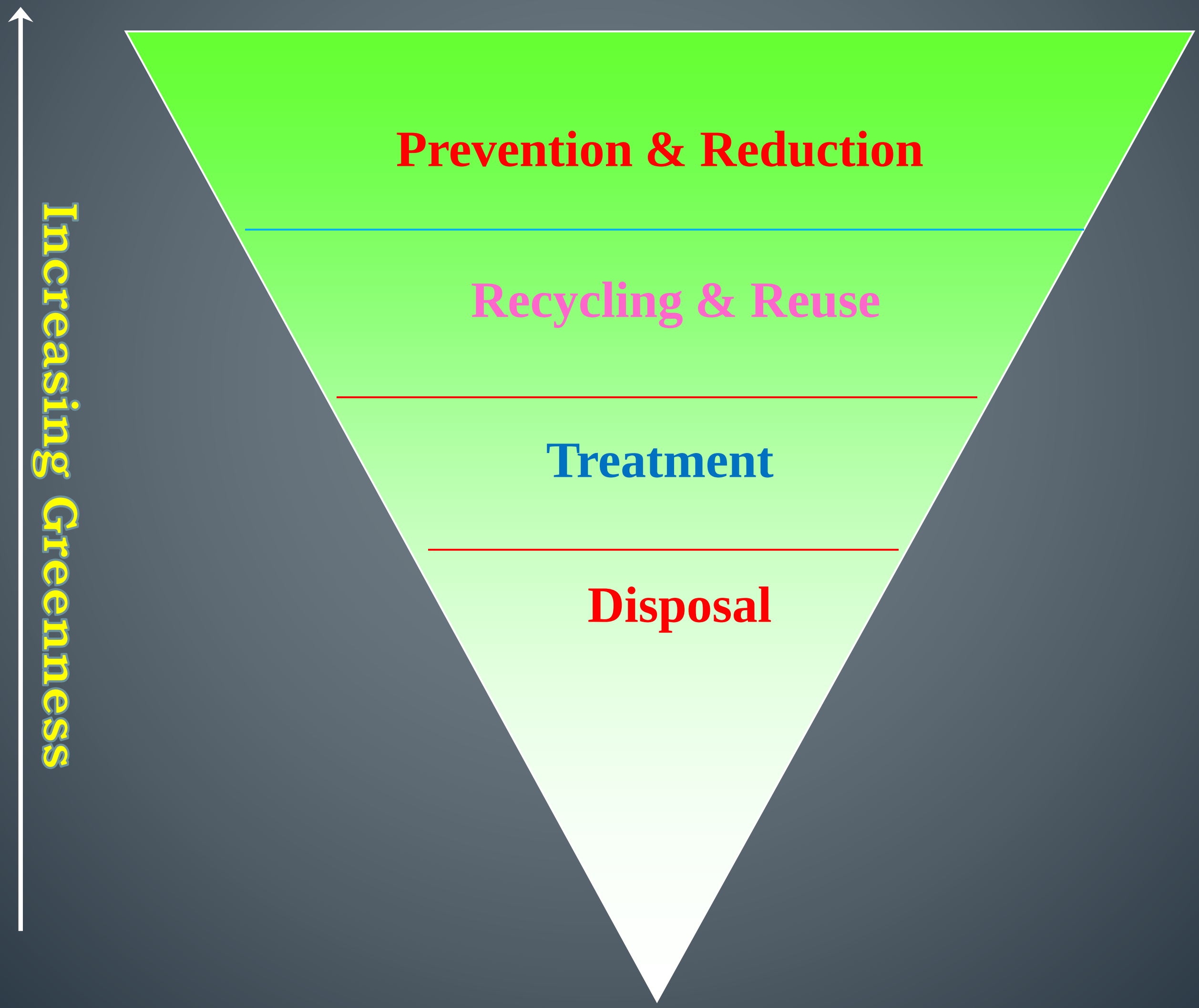
New Method: catalytic reaction between dimethyl urea & 1-naphthol, methyl amine is byproduct.



- **3.Synthesis of Ibuprofen:** Non steroidal **anti inflammatory** drug (pain killer-headche, toothache,etc.)
- **Traditional method**: 6 steps, poor atom economy, low yield(40%), $AlCl_3$ toxic & generates waste, more energy requirement.
- **New method:** only 3 steps **i)Acylation of isobutyl benzene**
- **ii) Reduction iii) Carboxylation**
- Yield- ***77%***, **HF catalyst recyclable**, **Raney Ni & CO-Pd can be recovered & reused**
- Less energy requirement, very high atom economy, reduces waste.

Isobutyl benzene

Pollution Prevention Hierarchy



Conclusion

Green chemistry **Not** a solution to all environmental problems **But** the most fundamental approach to preventing pollution.


THANK YOU
FOR YOUR ATTENTION!

QUESTIONS ?????