Title : GREEN CHEMISTRY

Date:23/3/2020

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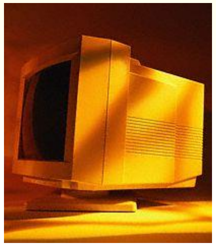
Lecture No : 2

Source of information : Green Chemistry

Benefits of the Chemical Industry



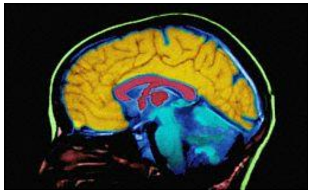






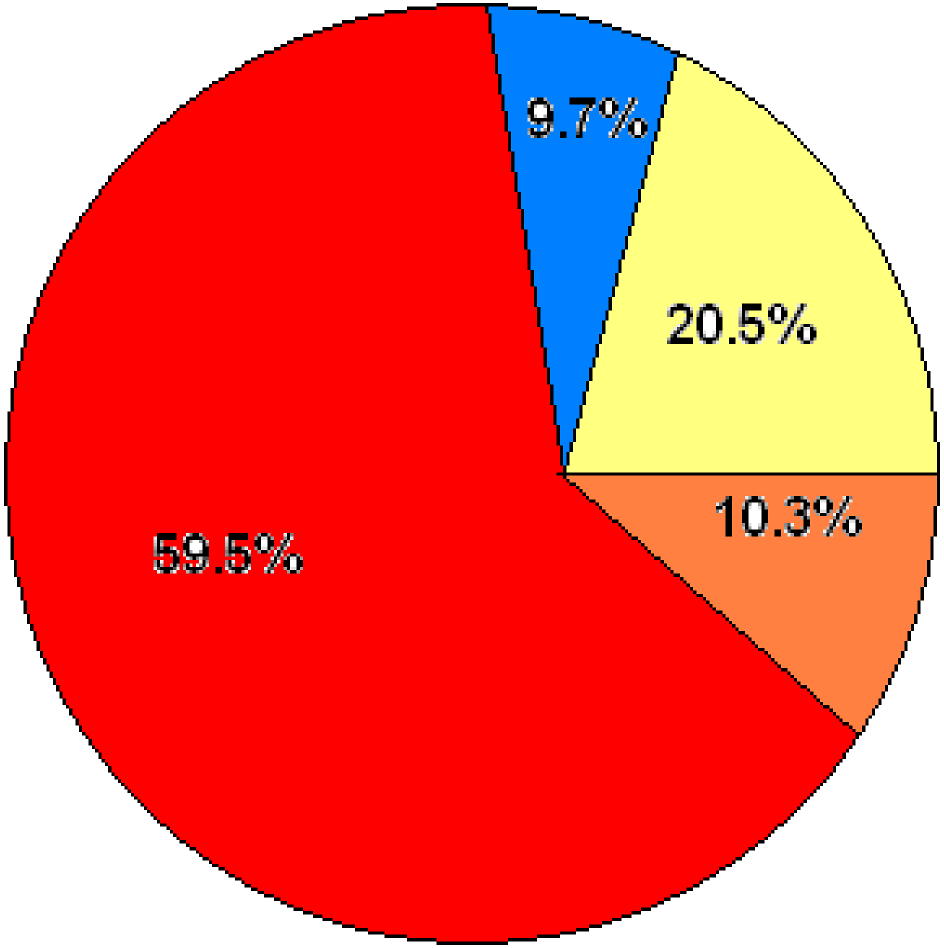






DEFINATION OF CHEMICAL INDUSTRY

Chemical industry is the most responsible source of pollutants and wastes to the environment. The general perception of the chemical industry is that, it has been responsible for an array of *environmental and health related problems*.



Chemical Release to the environment

59.5% - AIR

20.5% - Underground injection

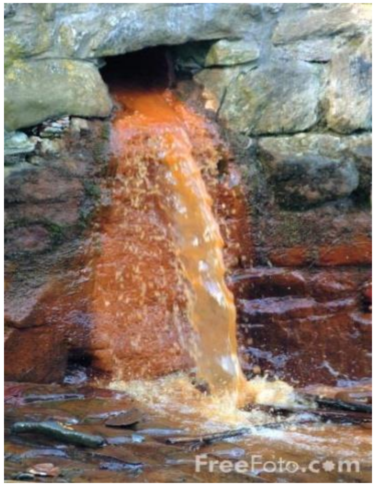
10.3 - Land

9.7% - Surface Water

Green Chemistry

Hazardous chemicals

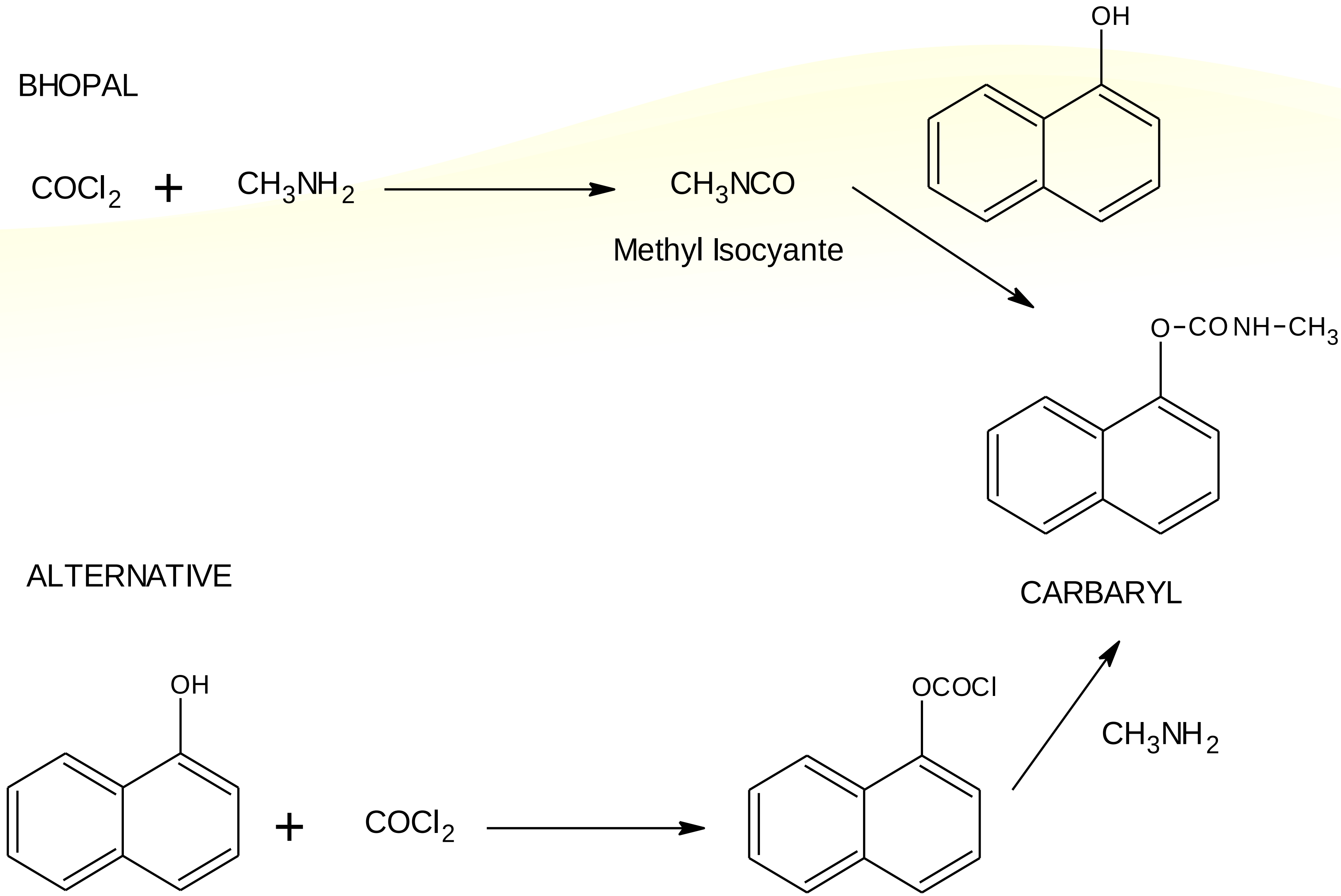
Chemical products	Chemical by-products	Exhaust gases	*Organic solvents*
Fertilizers, Pesticides	(Chemical wastes)	CO_2, SO_2, NO_2	Chlorinated solvents



BHOPAL TRAGEDY

More than three thousand people lost their lives and estimated more than two lacs were seriously injured.

The accident at Bhopal resulted due to ingress of water into large storage tank of methyl isocyanate (MIC). This cause pressure build up. The explosion covered the nearby town with toxic gases. MIC was responsible for Bhopal tragedy and its use could have been avoided by using and alternative synthetic path.


BHOPAL
COCl2 + CH3NH2
CH3NCO
Methyl Isocyante
OH
O-CONH-CH3
CARBARYL
ALTERNATIVE
OH
+ COCl2
OCOCl
CH3NH2

It is Essential that Chemists Place a Major Focus on the Environmental Consequences of Chemical Products and the Processes by which these Products are Made

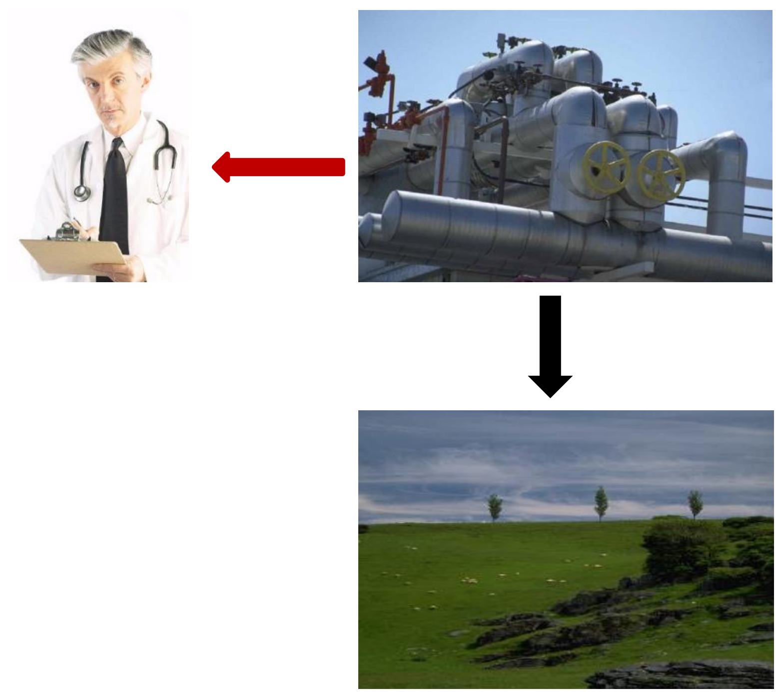
What is Green Chemistry ?

“The design of chemical processes, products and technologies that reduces or eliminates the use and generation of hazardous substances”

Green Chemistry

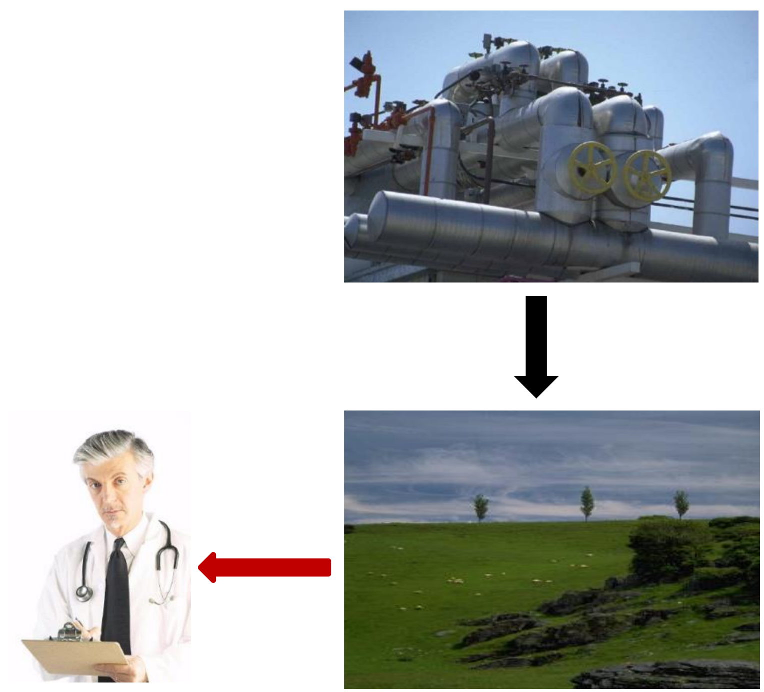
Green chemistry

Preventing the pollution at its source
With emphasizing on minimizing the hazard, and maximizing the efficiency of any chemical process



Environmental chemistry

Studying the effect of the pollutants on the environment, and the remediation processes



- Green chemistry is a mix of organic chemistry, inorganic chemistry, biochemistry and analytical chemistry.

- Its main goal is to develop methods that help **avoid dangerous chemical waste.**

GREEN CHEMISTRY

- *Green Chemistry or environmentally good chemistry is the design of chemical products and processes that reduce of eliminate the use and generation of hazardous substances*
- **Minimize: waste, energy use and resource use (maximize efficiency;**
- **utilize renewable resources).**

The Twelve Principles of GREEN CHEMISTRY (Anastas and Warner 1998)

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

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

3. Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. Chemical products should be designed to preserve efficacy of function while reducing toxicity.

5. The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary whenever possible and, innocuous when used.

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

7. A raw material feedstock should be renewable rather than depleting whenever technically and economically practical.

8. Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.

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

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

11. 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. Substances and the form of a substance used in a chemical process should chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

ATOM ECONOMY

"Because an Atom is a Terrible Thing to Waste"

- How many of the atoms of the reactant are incorporated into the final product and how many are wasted? *Infusing green chemistry into organic.*

Atom economy

- One of the key ideas of green chemistry is that of atom economy.
- This considers how much of the reactants in a chemical reaction end up in the final-useful product.
- Ideally all the atoms of the reactants would end up into useful products, no waste at all.

Reaction between ethyl propionate and methylamine to form N-methyl propionamide and ethanol.

$$CH_3CH_2COOCH_2CH_3 + CH_3NH_2 \text{ -----> } CH_3CH_2CONHCH_3 + C_2H_5OH$$

1 mol	1 mol	1 mol	1 mol
118 g	31 g	103 g	46 g

- 149 g of. starting materials (118 g + 31 g) yet the mass of the required
  product 103 g. The rest, 46 g of ethanol, is wasted.
- We have lost 2 atoms of carbon, 6 of hydrogen and one of oxy

$$\% \text{ Atom economy} = \frac{\text{mass of desired product}}{\text{mass of desired products plus waste products}} \times 100\%$$

$$\text{In the example above, the atom economy} = \frac{103}{149} \times 100\% = 69.1\%$$

Imagine we has done a similar reaction but starting with methyl propionate rather than ethyl propionate.

$CH_3CH_2COOCH_3$ + CH_3NH_2 -------> $CH_3CH_2CONHCH_3$ + CH3OH

1 mol	1 mol	1 mol	1 mol
104 g	31 g	103 g	32 g

$$\text{The atom economy} = \frac{103}{135} \times 100\% = 76.3\%$$

- In this case a molecule of methanol (mass 32 g mol-1) is being thrown away rather than a molecule of ethanol (mass 46 g mol-1).

Reaction type and atom economy

Chemical reactions are often classified as addition, elimination, substitution and rearrangement.

Addition

$$\underset{28}{CH_2{=}CH_2} + \underset{160}{Br_2} \text{ -------> } \underset{188}{CH_2BrCH_2Br}$$

$$\text{The atom economy} = \frac{188}{(28+160)} \times 100\% = 100\%$$

Atom economy of all addition reactions is 100%.

Elimination

$$C_2H_5OH \text{ ------> } CH_2{=}CH_2 + H_2O$$

46   28   18

$$\text{The atom economy} = \frac{28}{46} \times 100\% = 60.9\%$$

- The atom economy of an elimination reaction can never be 100% because there is always a molecule wasted.

Substitution Reaction

$CH_3COCl + C_2H_5OH$ -------> $CH_3COOC_2H_5$ +HCl

78.5	46	88	36.5

$$\text{the atom economy} = \frac{88}{124.5} \times 100\% = 70.7\%$$

Substitution reaction must always be less than 100% because there is always a molecule wasted.

Re-arrangement

$$CH_3CH_2CH_2OH \text{ ------> } CH_3CHOHCH_3$$

60 60

$$\text{the atom economy} = \frac{60}{60} \times 100\% = 100\%$$

The atom economy of all re-arrangement reactions is 100 % as nothing is lost.

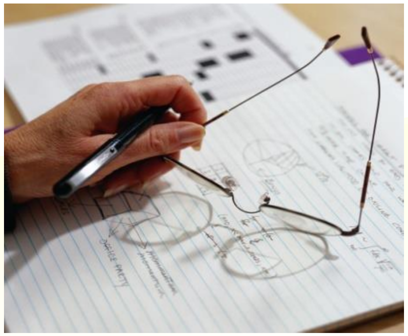
Organic solvents:

❖ Out of the top 10 chemicals disposed of by the chemical industry in the mid-1990s, five were solvents: *methanol, methylethyl ketone, tolouene, hexane and methylene chloride.*

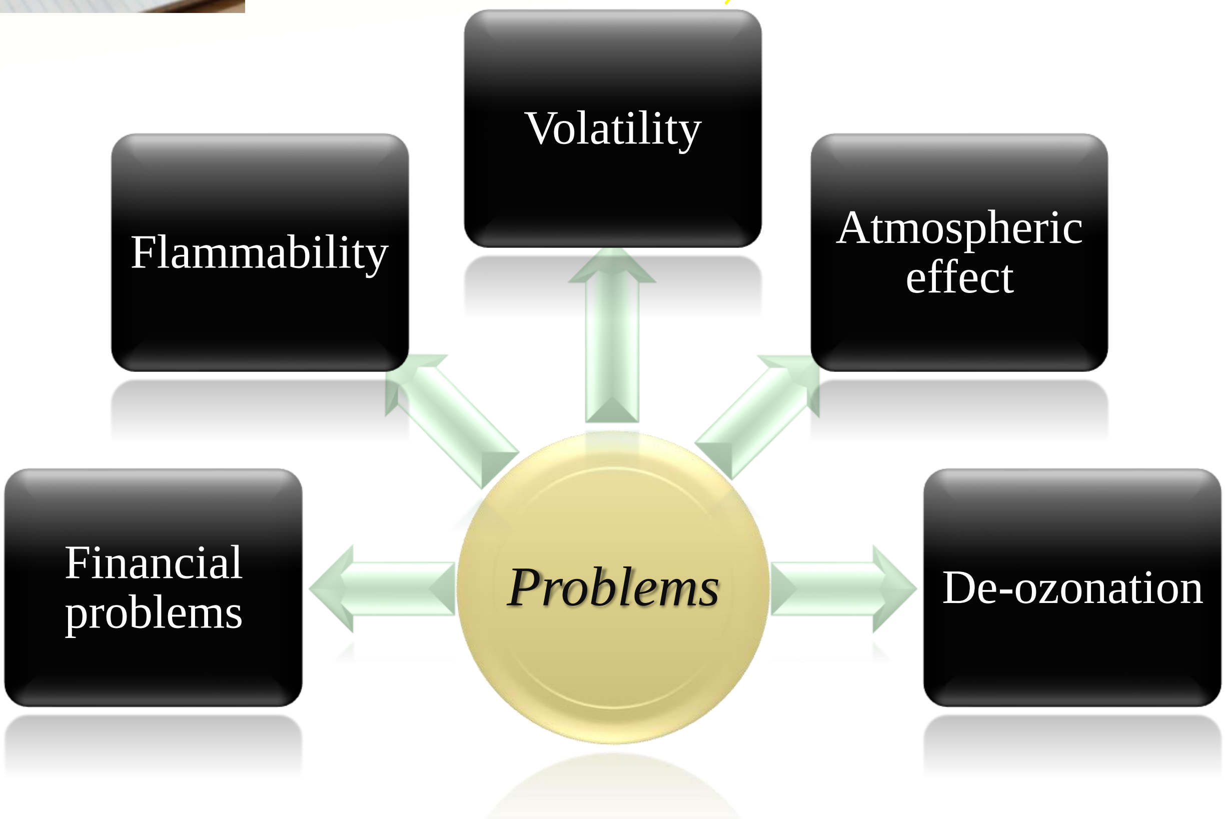
.

- They escape into the environment through evaporation and leakage, threatening the living beings due to ***their high stability and non-biodegredability.***
- They often have complex negative effects on the environment , they have been one of the source of ***ozone depletion, global climate change and smog formation .***

Green Chemistry



- Dangerous to the workers.
- Working under high pressure, combustion hazard.
- Escape to the atmosphere through evaporation.



Problems with Traditional solvents

- Direct
  - **Varying toxicity** depending on nature of VOC, exposure method and duration.
    - E.g. DMF (teratogenic), $CHCl_3$ (suspect carcinogen)
  - **Flammability** (fire hazards)
  - **Peroxide formation** (usually ethers)
- Indirect
  - **Ozone depletion**
    - Chlorofluorocarbons (CFC's) now phased out
      - E.g. CF_3Cl, lifetime in atmosphere 640 years, GWP 14,000
      - CCl_4 – now much more limited use (35yrs, GWP 1400)
  - **Global warming potential** (GWP)
    - E.g. HFC134a (CH_2FCF_3) used in refrigerants and air conditioning units, 14yrs, GWP 1300
  - **Environmental persistence**
- Use of less volatile solvents may improve environment as long as they do not lead to problems elsewhere.

Green Solvents Defination.

- The commonly used solvents like Benzene. Toluene, Methylene Chloride etc. For Organic Synthesis particularly in Industrial Production are known to cause health and environmental problems. In view of this, search for alternatives to the damaging solvents is of highest priority.This is particulary important as solvents are used in huge amounts in Industrial production and these are mostly volatile liquids which are difficult to store.

Green Solvent

- The Solvents which can eliminate or decrease the mentioned problems are generally known as Green Solvents.

Few of the green solvents are:

- ✓ Solventless.
- ✓ $ScCO_2$
- ✓ Water
- ✓ Ionic Liquids

Strategies of solvent replacement

- Avoid or minimise solvents in beginning of reaction.
- Use less toxic solvents
- Use renewable solvents (not derived from petrochemicals)
- Avoid VOC's – solvents with low vapour pressure / high boiling points may be preferable as long as this does not lead to other complications.

Various Green Solvents.

- Solventless
- Water
- Carbon dioxide
- Ionic liquids

All have advantages and disadvantages which need to be considered when assessing suitability for replacement

Solventless Chemistry

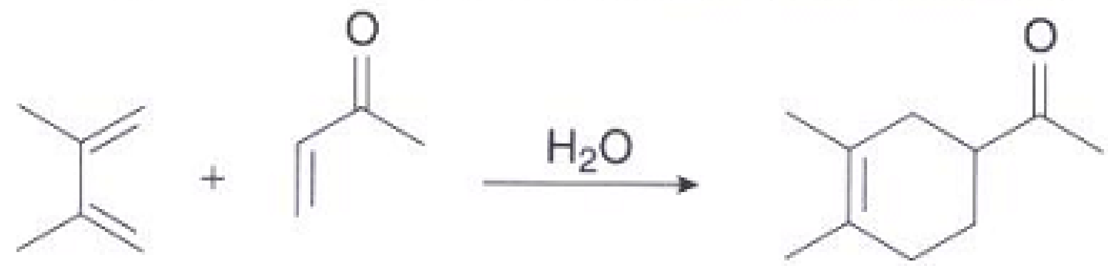
Advantage

- No harmful waste liquid.
- Economic reaction.
- Save time.

Disadvantage

- Not many reactions amenable to solventless approach, particularly on large scale
- Exothermic reactions can be dangerous on large scale. Solvents are better heat sinks.
- Efficient mixing can be a problem, particularly when have solid reagents or products
- Solvents still often required for extraction, separation and purification of products

Aqueous Conditions for the Diels-Alder Reaction



When water is used as a solvent for certain Diels-Alder reaction, rates can be accelerated

Voc alternatives

Most solvents used today are volatile organic compounds (VOCs). VOCs readily escape to the atmosphere when used causing a substantial fraction of all air pollution. Eliminating VOCs is environmentally desirable but requires that practical and economical VOC solvent alternatives be developed.

Supercritical water and supercritical carbon dioxide (CO_2) continue to provide successful green approaches for replacing VOCs in chemical processes such as decaffeinating coffee, dry cleaning and demanding chemical reactions.

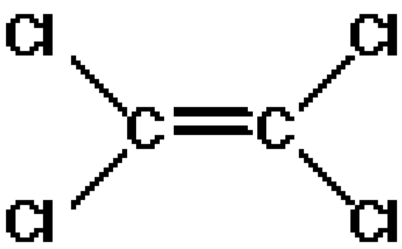
R. Rogers and others have developed a new class of solvents called room-temperature ionic liquids (RTILs). Many RTILs are based on chloroaluminate anions or alkyl imidoazolium cations. Most RTILs exhibit a low melting point, a high boiling point, and a high viscosity.

As solvents, RTILs have extremely low vapor pressures, an important green feature for replacing VOCs and decreasing atmospheric pollution. Many of the chemical properties of ionic liquids such as tunable polarity, good dissolving power for organic molecule, and easy drying are identical to those of VOCs. The major hurdles for commercialization of RTILs are cost limited toxicological data.

A technique that uses soap and water to degrease silicon wafer, thereby avoiding the use of chlorinatedfluorocarbons(CFCs or freons)during semiconductor manufacturing. Another CFC-free wafer-cleaning technology has been developed by J.DeSimone that uses surfactant and supercritical CO_2 as the solvent.

GREEN CHEMISTRY

- Dry Cleaning



  - Initially gasoline and kerosene were used
  - Chlorinated solvents are now used, such as perc

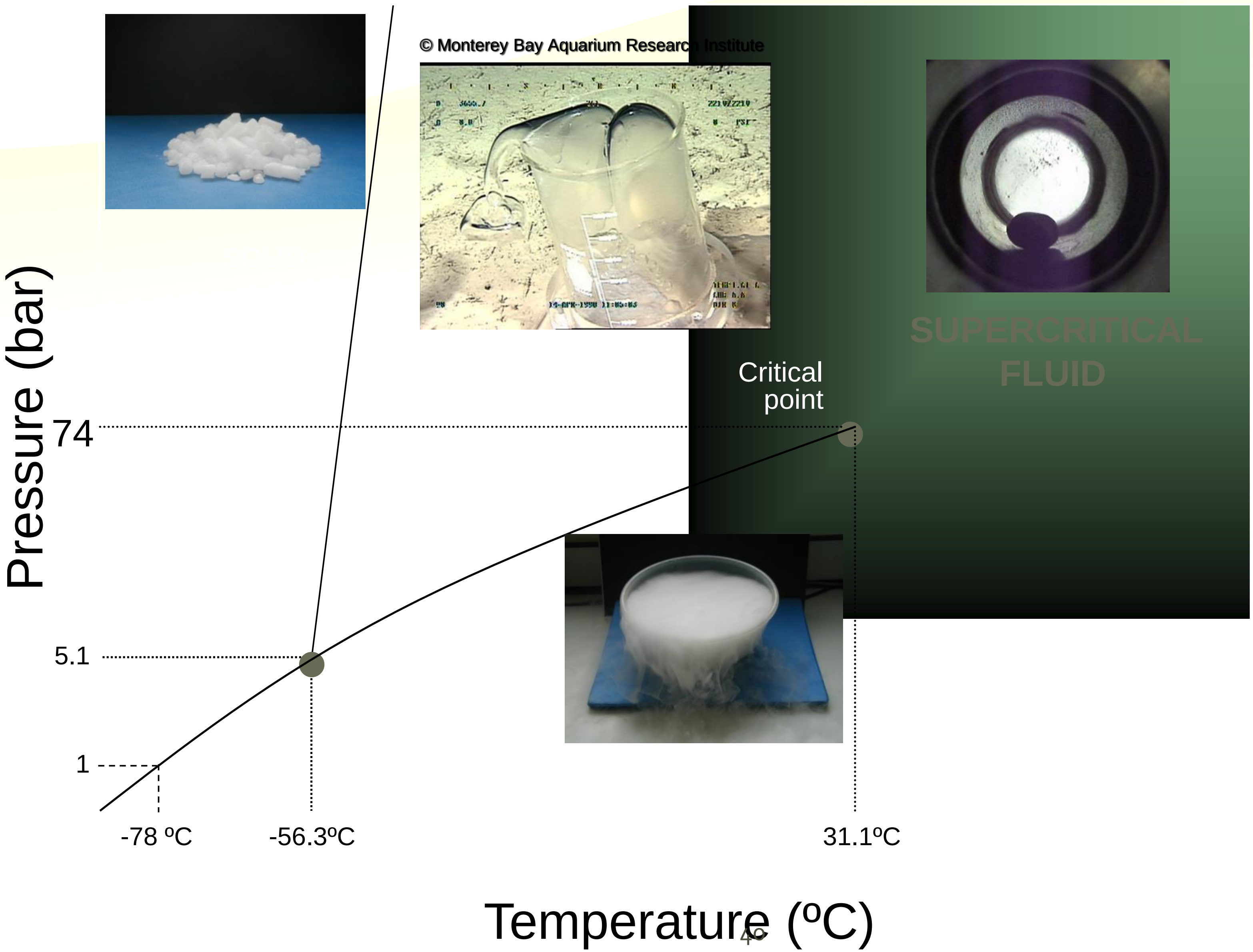
  - Supercritical/liquid carbon dioxide (CO_2); *infusing green chemistry into general chemistry*

Carbon Dioxide

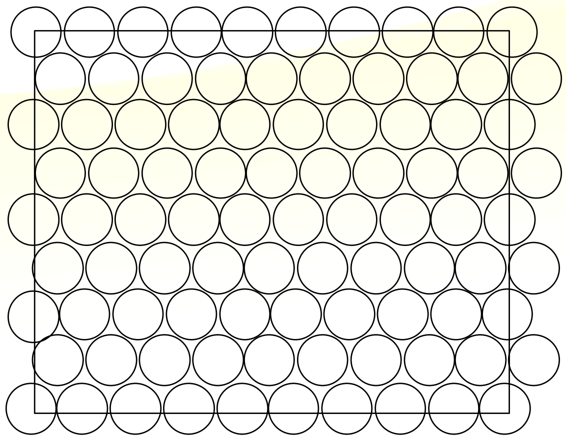
Advantage

- Natural, cheap, plentiful
- Available in >99.9% pure form.
- By-product of brewing, ammonia synthesis, combustion
- Already being adopted in a variety of commercial processes
- Non-toxic and properties well understood.
- Easily removed and recycled and can be disposed of with no net increase in global CO_2. Simple product isolation by evaporation, to 100% dryness.
- No solvent effluent
- Potential for product processing (extraction, particle formation, chromatography etc.)

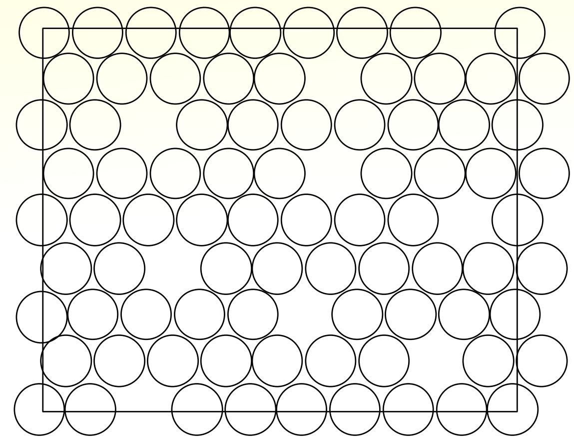
Phase diagram for pure CO_2



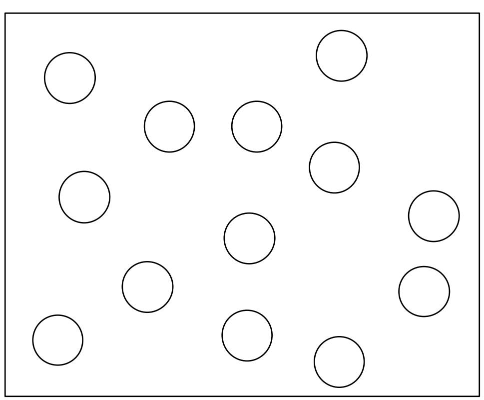
Super Critical Fluids are intermediate between liquids and gases



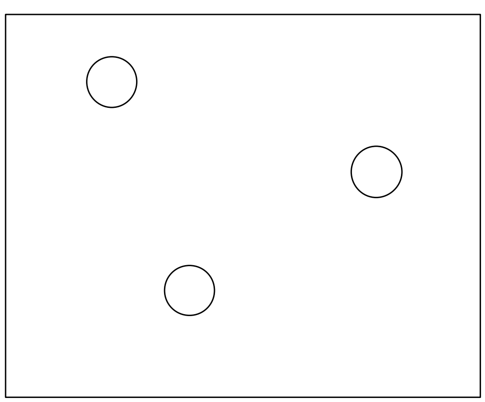
Solid



Liquid



Supercritical Fluid



Gas

Other advantages of $scCO_2$

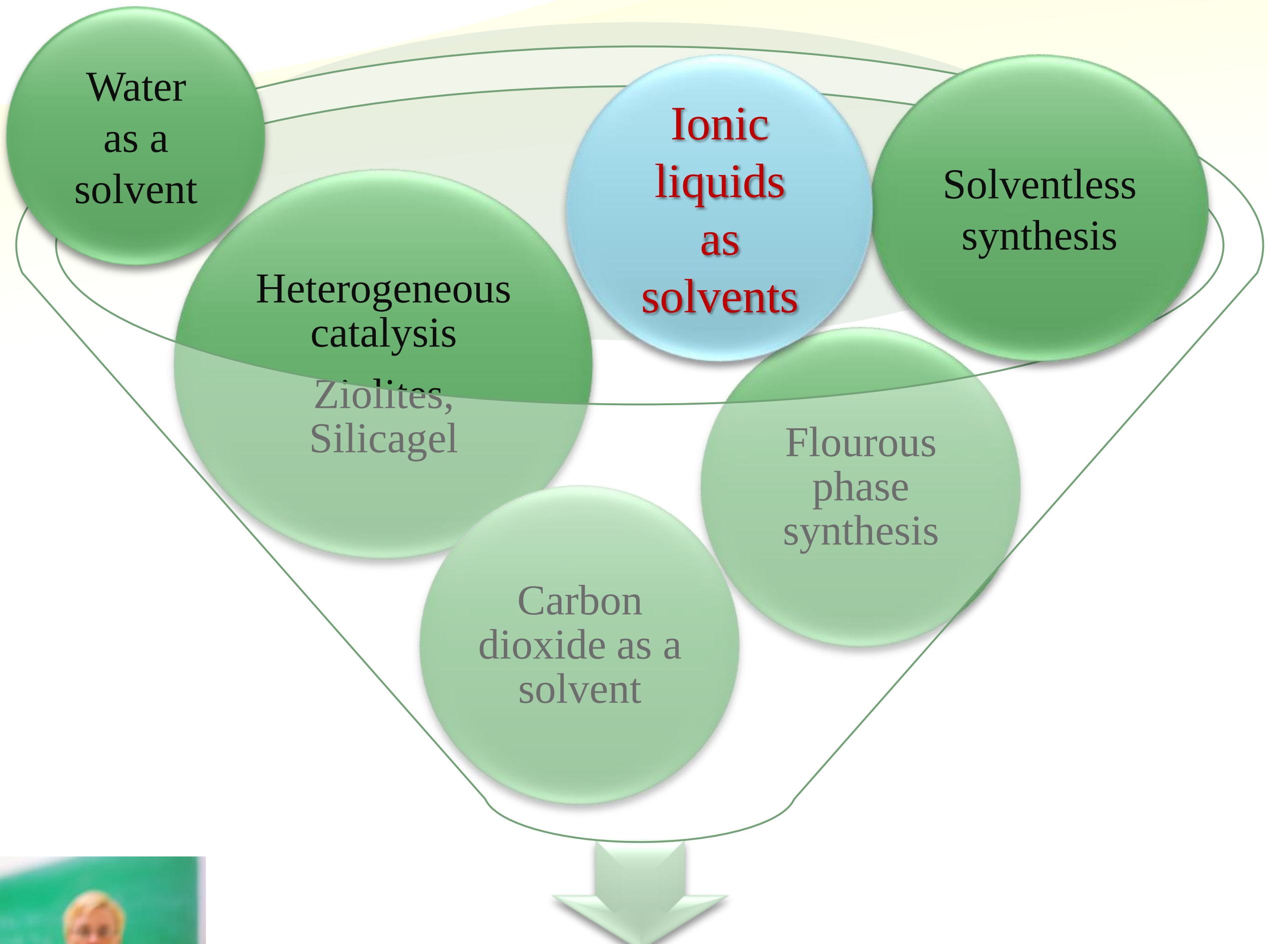
- **High compressibility**
  - Large change in solvent properties for relatively small change in pressure – infinite range of solvent properties available
  - Ability to tune solvent to favour a particular reaction pathway simply by optimising temperature or pressure
- Small amounts of **cosolvents can further modify solvent properties**
- **High diffusion rates** offer potential for increased reaction rates.
- Potential for homogeneous catalytic processes.
  - High solubility of light gases, some catalysts and substrates; bring all together in single homogeneous phase
- Inert to oxidation; resistant to reduction
  - Excellent medium for oxidation and reduction reactions.

Problems using $scCO_2$

- **Moderate pressures required**
  - Standard HPLC apparatus used in lab, reactors made of stainless steel, many commercially available.
  - Can be expensive for large scale work
- **Weak solvent**
  - Relatively non-polar, but high quadrupole moment. Use of co-solvents (MeOH, MeCN, THF, toluene)
  - Simple modification of reagents to improve solubility
- **Energy considerations**
  - Compression of CO_2 requires energy
  - Energy consumption reduced minimal decompression and recycling
- **Reacts in the presence of good nucleophiles**
  - Often reversible, can be exploited synthetically

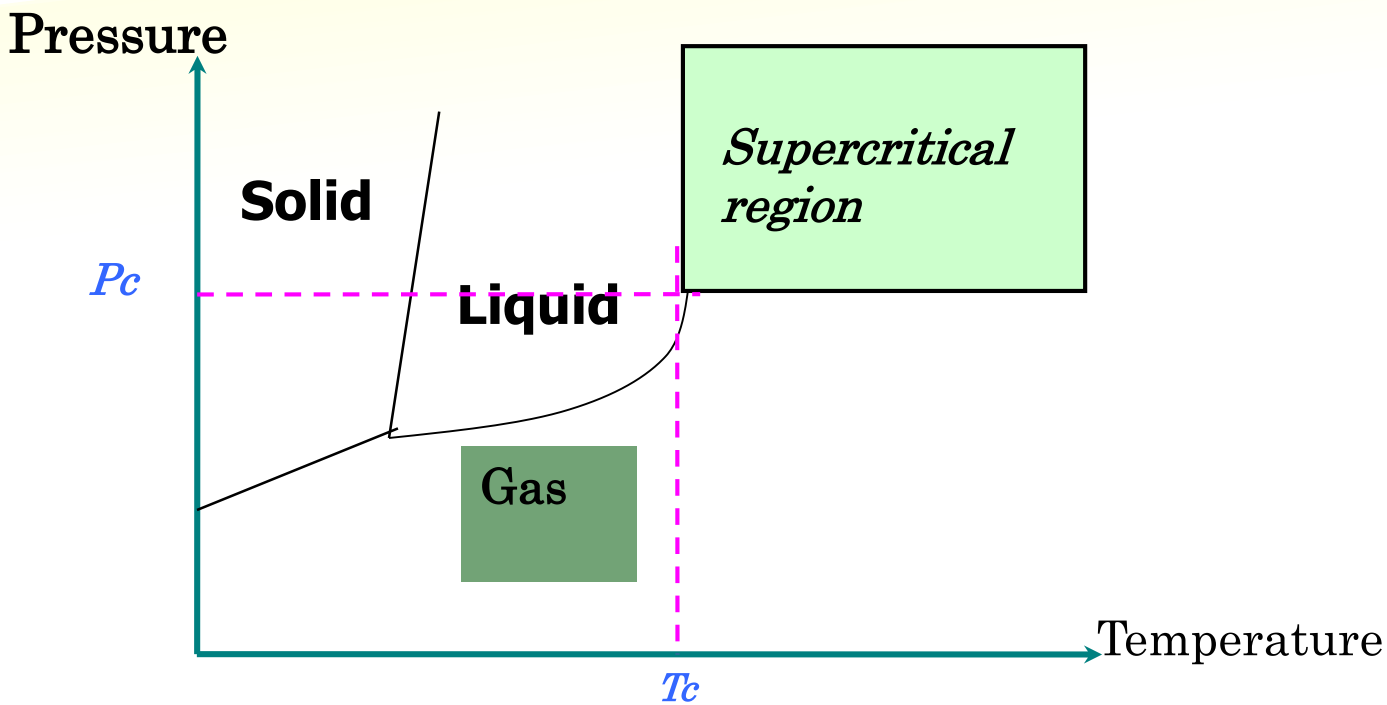
Green Chemistry

IONIC LIQUIDS



Green processes suggested by green chemistry

Supercritical fluids



Fluid	Tc (°C)	Pc (atm)
CO_2	31.0	78.8
H_2O	374.2	218

Carbon dioxide & water

Environmental fluids

Unique Properties

High density
Low viscosity
High solubility
Unique catalysis

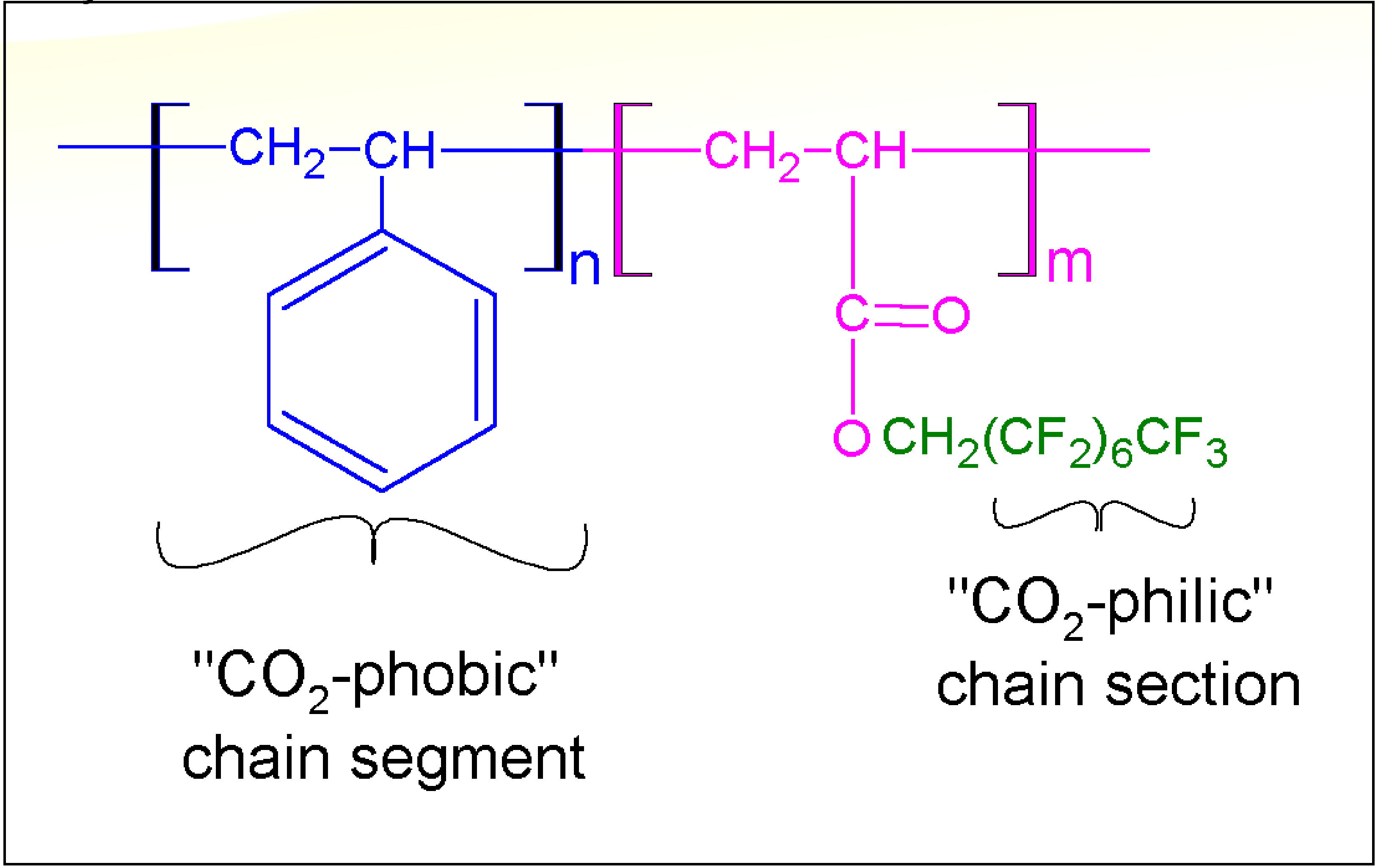
New Media for Green Chemistry
Processes for Chemical Transformations

Liquid Carbon Dioxide as a solvent

It may seem strange at first to think of CO_2 as a solvent. You are probably familiar with .CO_2 as either a gas in the air we exhale, or as a solid called dry ice.

Carbondioxide freezes at-78.4°C. If dry ice is touched it freezes skin rapidly, destroying the skin tissue. Because the resulting damage looks like a burn, some people have the misconception that dry ice will 'burn' you.

Joseph of the University of North Carolina surfactant polymers to have a "CO2-philic" end, which is attracted to liquid CO2, and a ‘CO2-phobic' end, which is not attracted to CO2 but to fats. greases and oils.
Allow CO2 to replace PERC as a dry cleaning solvent, in green chemistry.



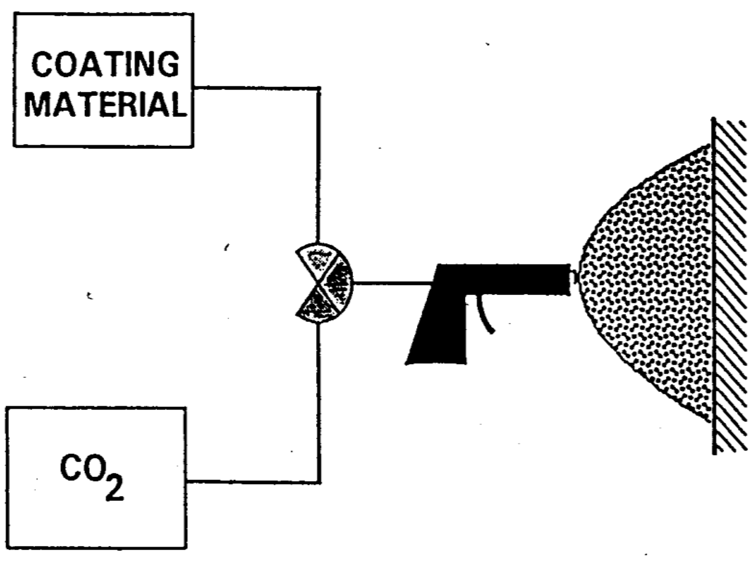
Environmental/Economic Advantages of Liquid CO_2

- Using CO_2 eliminates hazardous waste generation of Perchloroethylene (PERC).
- CO_2 does not pose the environmental and human health risks associated with PERC (used by 34,000 dry cleaners in US).
- Using the Hangers CO_2 process lowers energy consumption.
- Using CO_2 reduces environmental regulatory burdens for Hangers operators.
- Uses waste CO_2 from other processes.

A New Process Using Supercritical Carbondioxide to Replace Traditional Paint Solvents

A new process for spraying paints and other coatings has been developed which reduces atmospheric emissions of environmentally harmful volatile organic compounds (VOCs). The liquid solvents of conventional coatings have been replaced by supercritical Carbondioxide. The carbon dioxide not only reduces viscosity, but provides additional benefits. The resulting coatings have uniform thickness and excellent coalescence

Volatile organic compounds (VOCs) are a class of air pollutants. Every year, American industries spray 1.5 billion liters of coatings and paints, which release an average of 550 grams of VOC solvents for each liter sprayed. As many VOC solvents are hazardous a



Advantages and Disadvantages of using scCO2 as a solvent

Advantages: -

Non-toxic

Easily removed

Potentially recyclable

Non-inflammable

Disadvantages: -

Relatively high pressure equipment

Equipment can be capital intensive

Why Supercritical CO_2

- For pharmaceutical applications, SC-CO_2 is an ideal processing medium
- Relatively mild T_c (304.1 K), hence operation at near T_c (< 308 K) can be performed, though P_c is high (73.8 bar)
- CO_2 is non-toxic, non-flammable and relatively inexpensive ($ 0.06/ lb), eco-friendly and recyclable
- Remarkable in synthesis of polymers of controlled particle size (DeSimone et al, Science, 265, 356, 1994)
- High solubility of gaseous reactants (e.g. H_2)

  - H_2 in SC-CO_2 = 13.0 M vs. in THF = 0.4 M

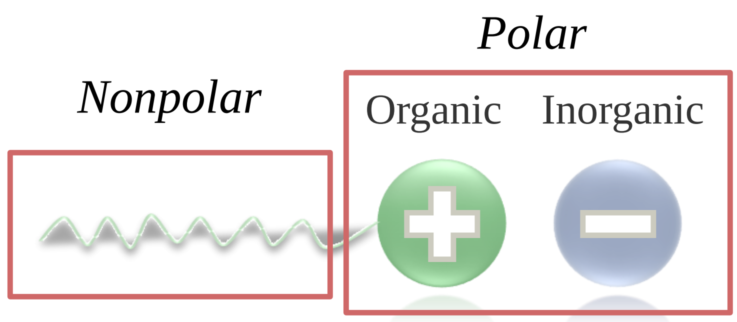
Reaction conditions

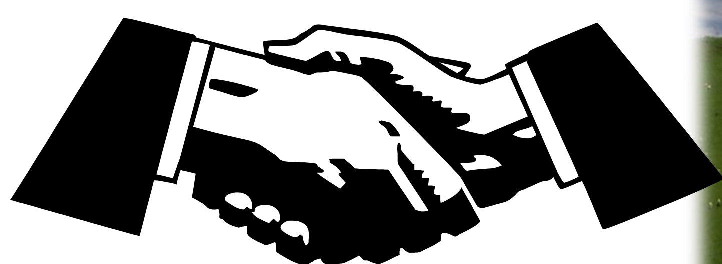
- Catalyst: $RuCl_2[P(CH_3)_3]_4$
- Solvent: Supercritical CO_2
- Temperature: 100 °C
- Pressure: 210 bar

IONIC LIQUIDS

Salts of *<u>Organic cations and polyatomic Inorganic anions</u>*, which have a melting point less than 100 c.

Dual character





Ionic Liquids

Is it a liquid at room temperature ?

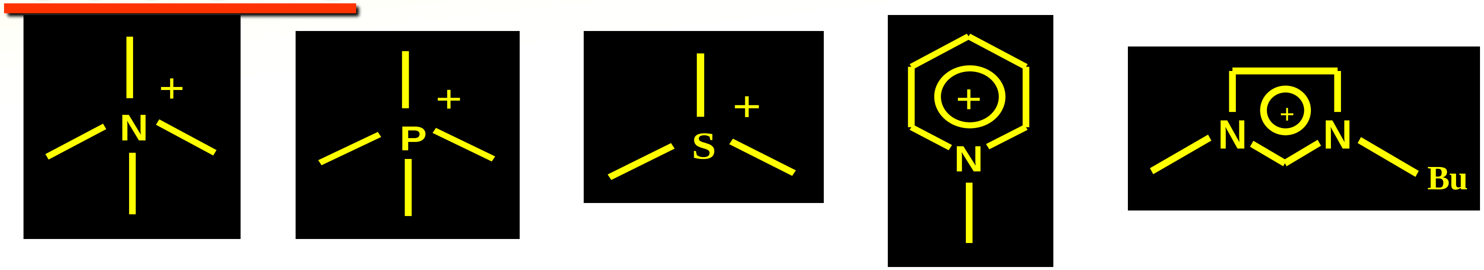
Can it be a solvent ?

Can it be used in industries ?

Is it a green solvent ?

Ionic liquid

Cations



Anions

- $AlCl_4^-$, $FeCl_4^-$, $AuCl_4^-$, SbF_6^-, etc.
- BF_4^- , PF_6^- , SBF_6^- , $ZnCl_2^-$,

  $CF_3SO_3^-$, $CH_3SO_3^-$, etc.

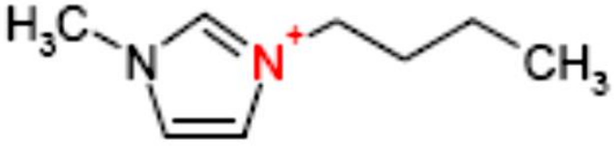
What are Ionic Liquids (ILs) ?

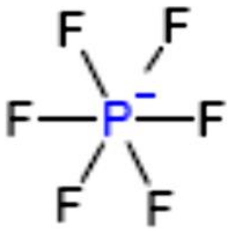
- *ILs are salts that melt below 100°C, composed wholly of ions.*
  - *CATIONS such as substituted imidazoliums, substituted pyridiniums or others*
  - *ANIONS such as borates, phosphates and halides and others*

- *Naming examples and structures*

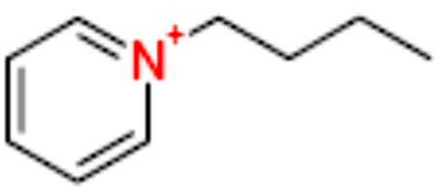
CATION **ANION**

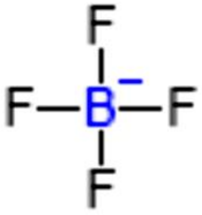
(1) 1-butyl-3-methylimidazolium hexafluorophosphate





(2) N-butylpyridinium tetrafluoroborate





Their non-measurable vapor pressure and non-flammability makes them attractive candidates for the implementation of safer process so that they are reared as eco-friendly alternative to volatile organic compounds(VOCs)

Ionic liquids have high thermal stabilities , allowing higher reaction temperatures. They also permit a range of separation techniques such as distillation or sublimation which are sometimes not possible using traditional organic solvents.

Ionic liquids have the following advantageous properties.

- No measurable vapour pressure
- Non-flammable below their decomposition temperature
- Tunable properties
- Excellent salvation properties for a variety of organic and inorganic compounds
- High electric conductivities
- High thermal stabilities
- Wide liquids range

The use of ionic liquids as “Green Solvents” or “Designer solvents” for chemical reactions has been the subject of many publications over the past decade.

Currently about 350 materials are commercially available and many more are described in the current literature.

Chemists from a broad range of disciplines are continually demonstrating that ionic liquids can be used as “high Performance Solvents” in a variety of chemical reactions.

Ionic Liquids, or molten salts, are defined as materials containing only ionic species without any neutral molecules and having a low melting point (usually less than 100°C).

Rika Hagiwara and Yasuhiko Ito
***Journal of Fluorine Chemistry* 105 (2000) 221-227.**

An Invitation to Innovate

- Ionic Liquids could have a major impact on the future of chemical industry.
- They represent an innovation in the way chemistry is carried out.

WHY?

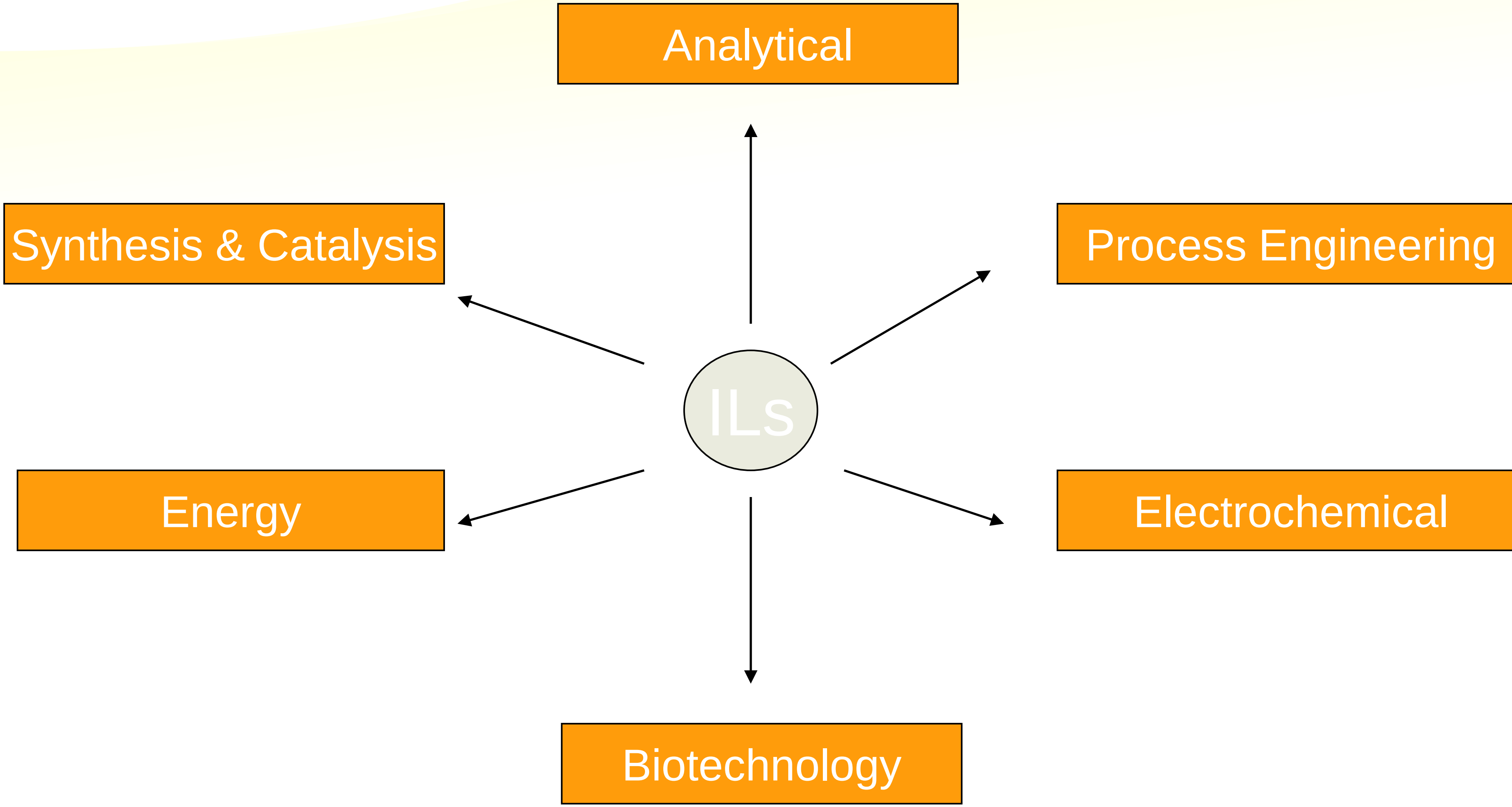
The **properties** of Ionic Liquids.

The **variety** of Ionic Liquids.

Desirable Properties

- Negligible vapour pressure
- Non-volatile
- Non-flammable
- High thermal, chemical and electrochemical stability
- Liquid over a wide temperature range
- Dissolution of many organic and inorganic compounds
- Variable miscibility with water and organic solvents

Ionic Liquid Applications



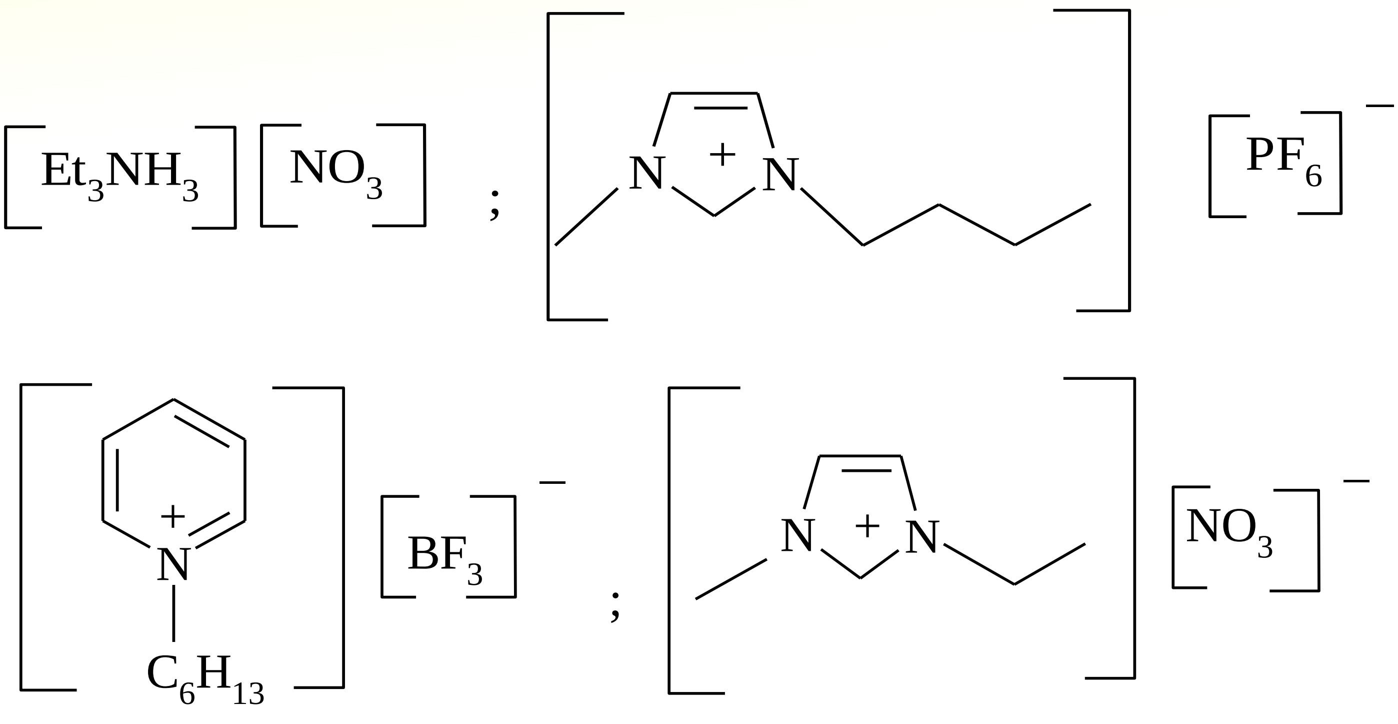
- The Ionic liquids comprising entirely of Ions were mainly of interest to **electrochemists**.
- It is possible by careful choice of starting materials to **prepare ionic liquids that are liquid at and below room temperature**.
- **The first ionic liquid** $[EtNH_3][NO_3]$

  M.P 12°C, was discover in 1914.

A solidified ionic liquid

- Broadly speaking Ionic Liquids are of two types:

1. Simple Salts: Made up of single Anion and Cation.



2. Binary Ionic Liquids: They are salts where an **equilibrium is involved .**

- An example of Binary Ionic Liquid system is a **mixture** of **Aluminium[III] Chloride and 1,3-Dialkylimidazolium Chloride.**
- It contains several different Ionic Spicies and their melting point and properties depend upon the Mole fraction of $AlCl_3$ and 1,3-Dialkylimidazolium Chloride present.

- For **Aluminium[III] Chloride** and **1,3-Dialkylimidazolium Chloride** Binary systems, the melting point depends upon the composition and is designated as **[emin]Cl-AlCl3.**

- where **$[emin]^+$ is 1ethyl 3methyl imidazolium.**

- The above Binary system **[emin]Cl-AlCl3**, can be basic,acidic or neutral in nature.

- The composition of binary ionic liquid is described the apparent mole fraction of $AlCl_3$[X($AlCl_3$)] present.

- Ionic Liquids with X[$AlCl_3$]< 0.5 contain an excess of Cl^- ions over $[Al_2Cl_7]^-$ ions are called **"Basic"**.

- On the other hand, those with X[$AlCl_3$] > 0.5 contain an excess of $(Al_2Cl_7)^-$ ions over Cl^- and are called **"Acidic".**

- Mixtures with $X[AlCl_3] = 0.5$ are called **"Neutral".**

- These **Ionic Liquids Basic , Acidic , Neutral** are used in different types of reactions.

- Thus the properties such as melting point , viscosity and Hydrophobicity and Misicibility with water can be varied by changing the structure and composition of the ions.

- The most common salts in use are those with alkyl ammonium , alkyl phosphonium, N-Alkyl pyridinium and N,N'Dialkyl Imidazolium cation.

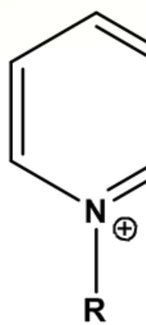
- The reactions in Ionic Liquids are easy to perform and need no special apparatus and methodologies.

- Also the ionic liquids can be recycled and this leads to reduction of the costs of the processes.

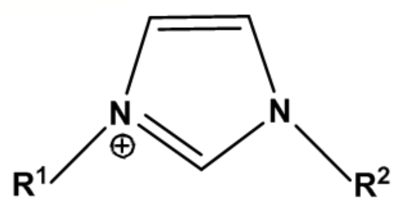
IONIC LIQUIDS

Kinds of ionic liquids

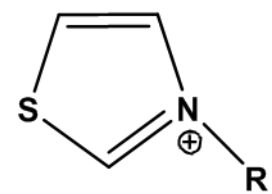
Cations



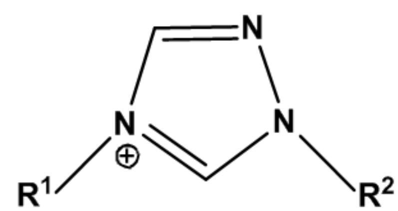
Pyridinium



Imidazolium



Thiazolium



Triazolium

$\overset{\oplus}{N}R_4$

Quaternary amines

$\overset{\oplus}{R}NH_3$

Ammonium

$\overset{\oplus}{P}R_4$

Phosphonium

$[P(OR)_4]^+$

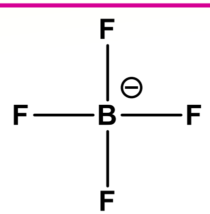
Phosphites

$[SR_3]^+$

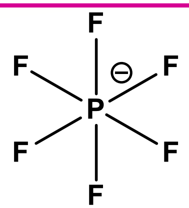
Sulfonium

Kinds of ionic liquids

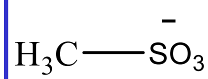
Anions



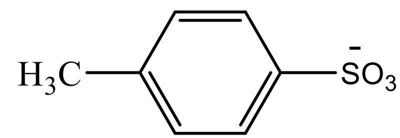
Tetrafluoroborte



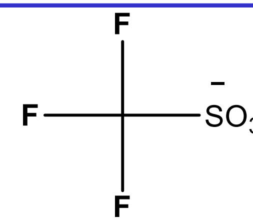
Hexafluorophosphate



Mesylate



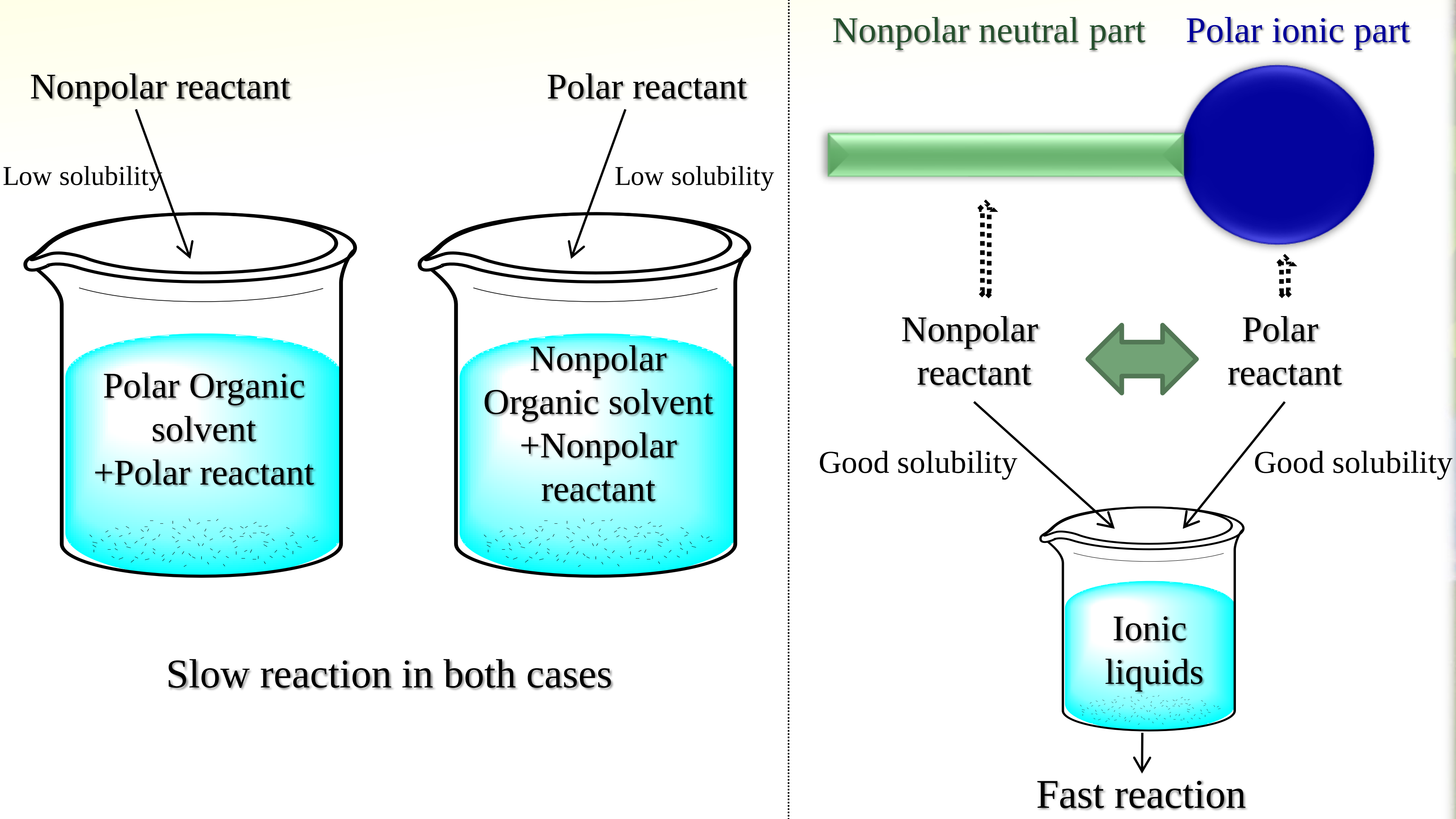
Tosylate



Triflate

Halogens	Lewis acids	Bases
F^- , Cl^- , Br^- , I^-	$Cl^-/AlCl_3$	OH^- , $RCOO^-$

Ionic liquids as alternative solvents for Organic synthesis

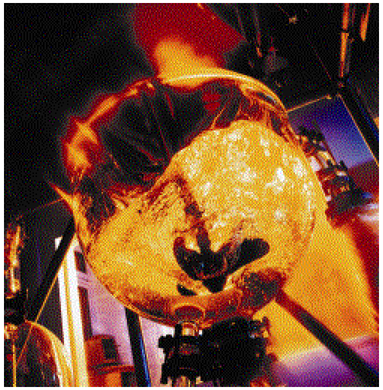


Ionic Liquids

✓ Synthesis & Catalysis

- CYCLOADDITION
- DIELS-ALDER CYCLOADDITION
- HECK COUPLING
- SUZUKI COUPLING
- STILLE COUPLING
- BAEYER-BILLINGER REARANGEMENT
- FRIEDEL-CRAFTS ALKYLATION
- FRIEDEL-CRAFTS ACYLATION
- WITTIG REACTION
- AROMATIC AMINATION

- OXIDATION
- NITRATION
- HALOGENATION
- EPOXIDATION
- ALKYLATION
- HYDROFORMYLATION
- HYDROGENATION



Green Chemistry Microwave-Induced Organic Reaction

- Rapid reaction rate
- Cleaner reaction condition
- Enhancements in chemical yields

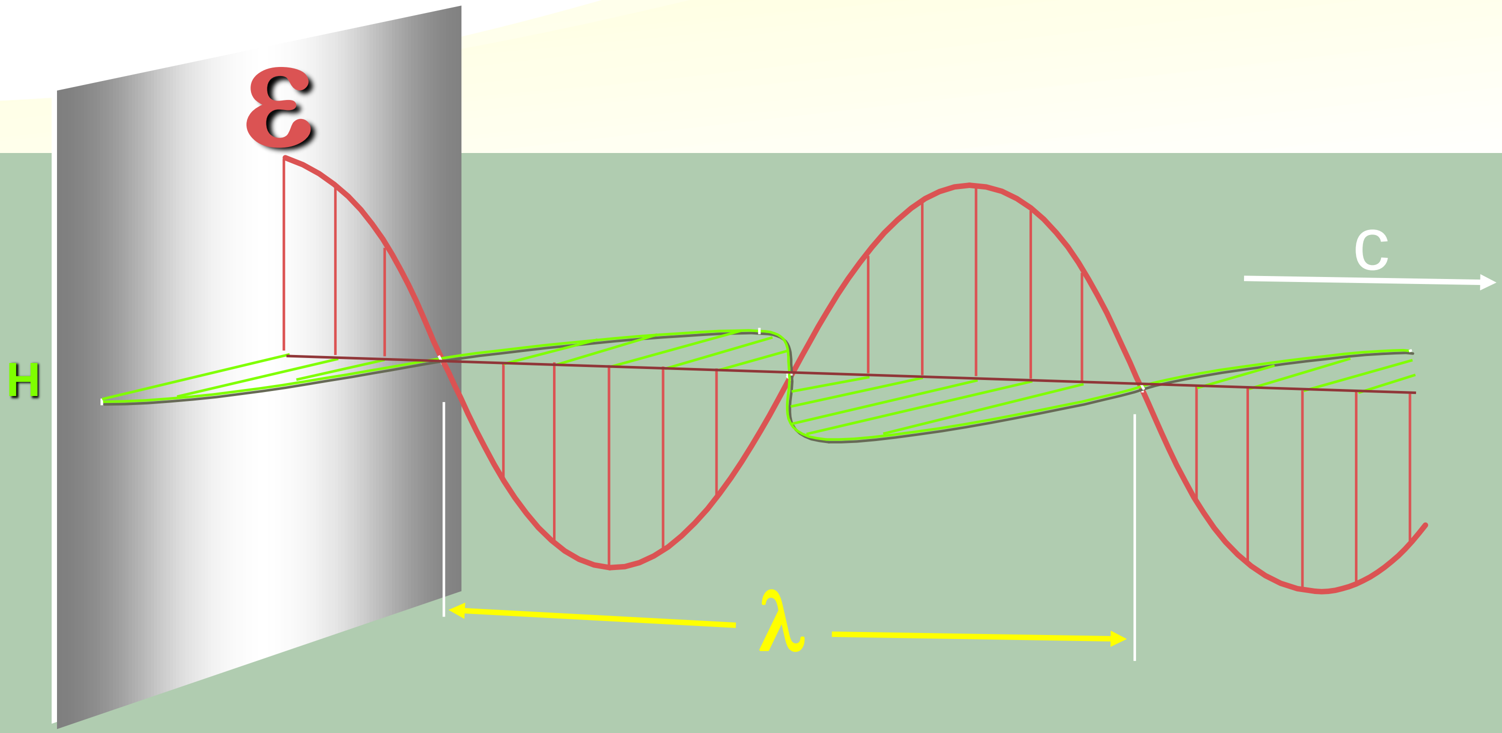
Q-Prom Microwave System

Q-Prom Microwave System

Q-Prom Microwave System Internal Temperature Gage

Q-Prom Microwave System

A Microwave



ε = electric field

H = magnetic field

λ = wavelength (12.2 cm for 2450 MHz)

= speed of light (300,000 km/s)

Electromagnetic spectrum

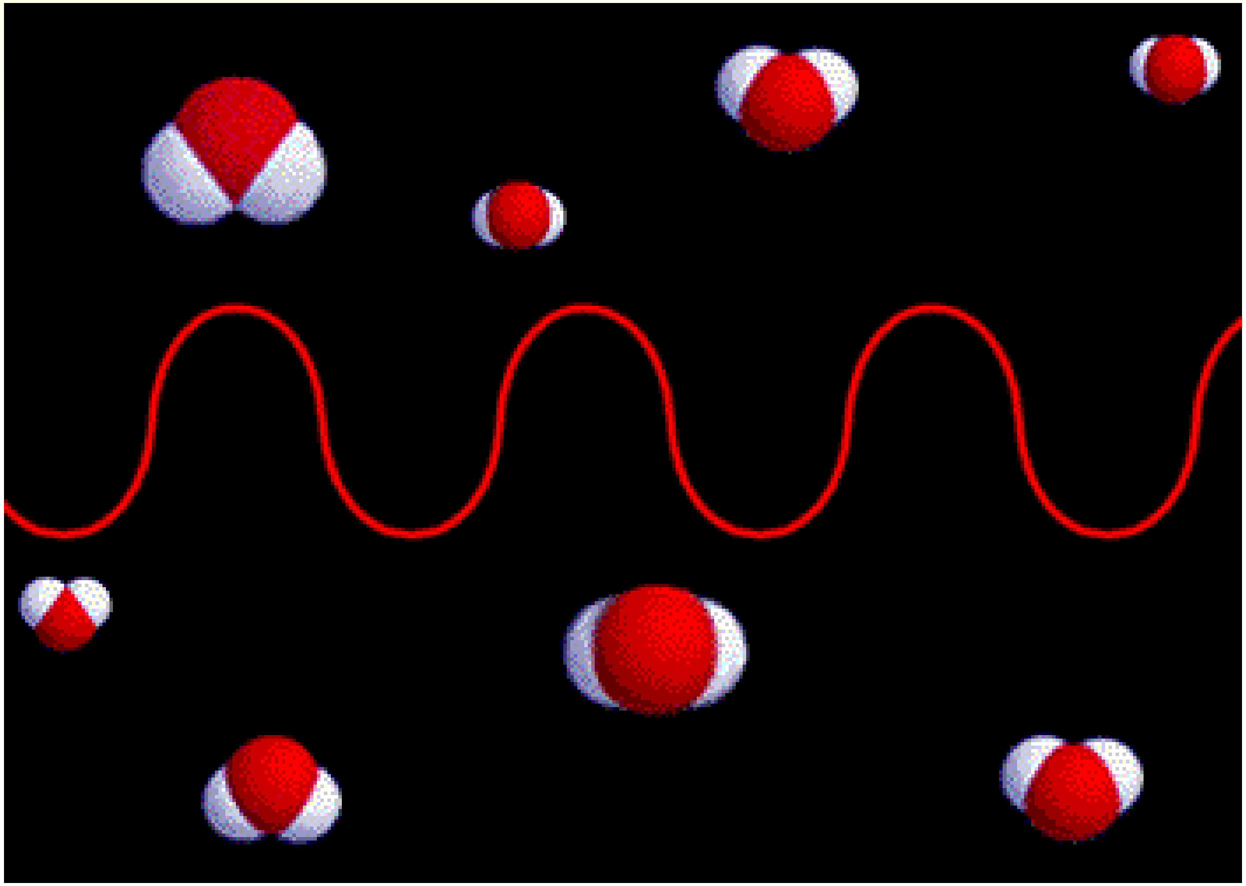
- X-rays-U.V.-Visible-IR MICROWAVE Radio waves
-
- Radarband
- Wavelength 1 cm 10 cm 1m 10m
-
- Frequency $3x10^{10}$ $3x10^{9}$ $3x10^{8}$

Absorption of microwave energy occurs by two mechanism

- Dipole Rotation
- Ionic Conduction

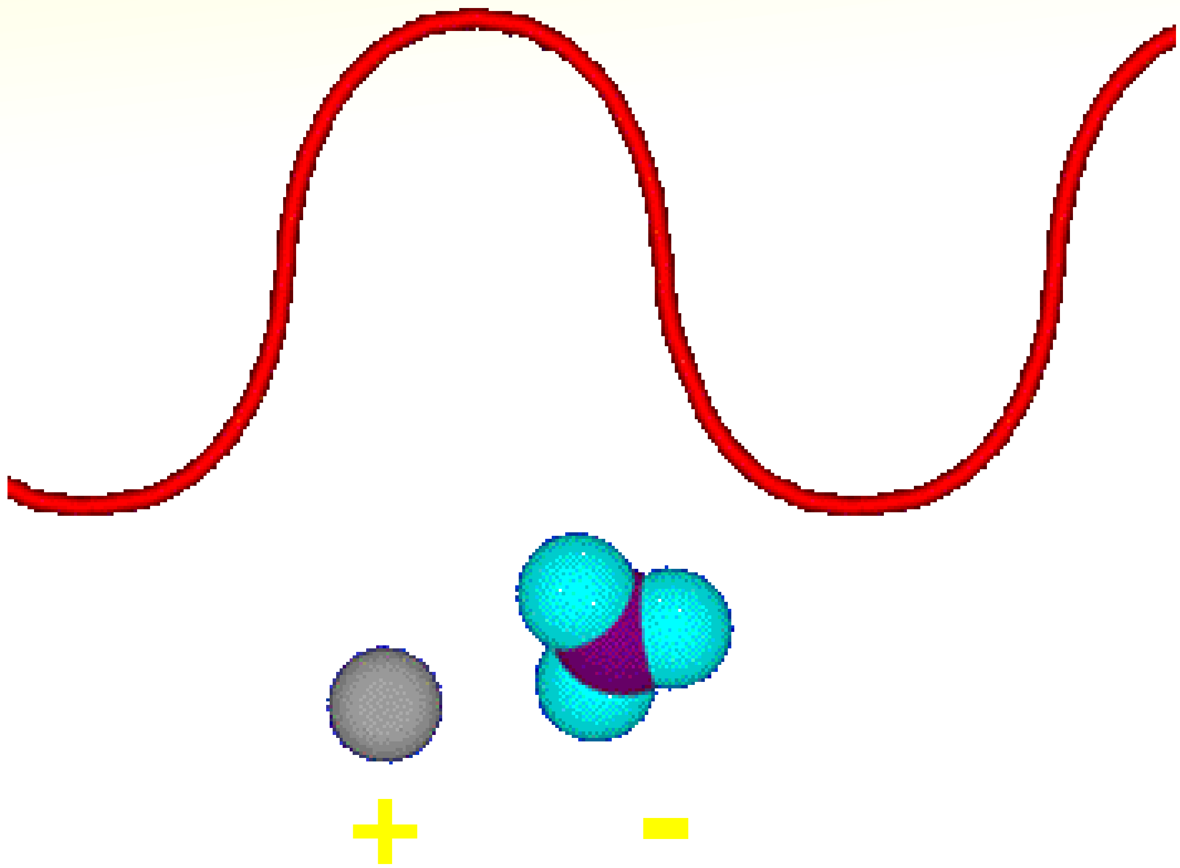
Dipole Rotation

(Microwave Electric Field Interaction with Water Molecule)



Ionic Conduction

(Microwave interaction with Calcium Carbonate)



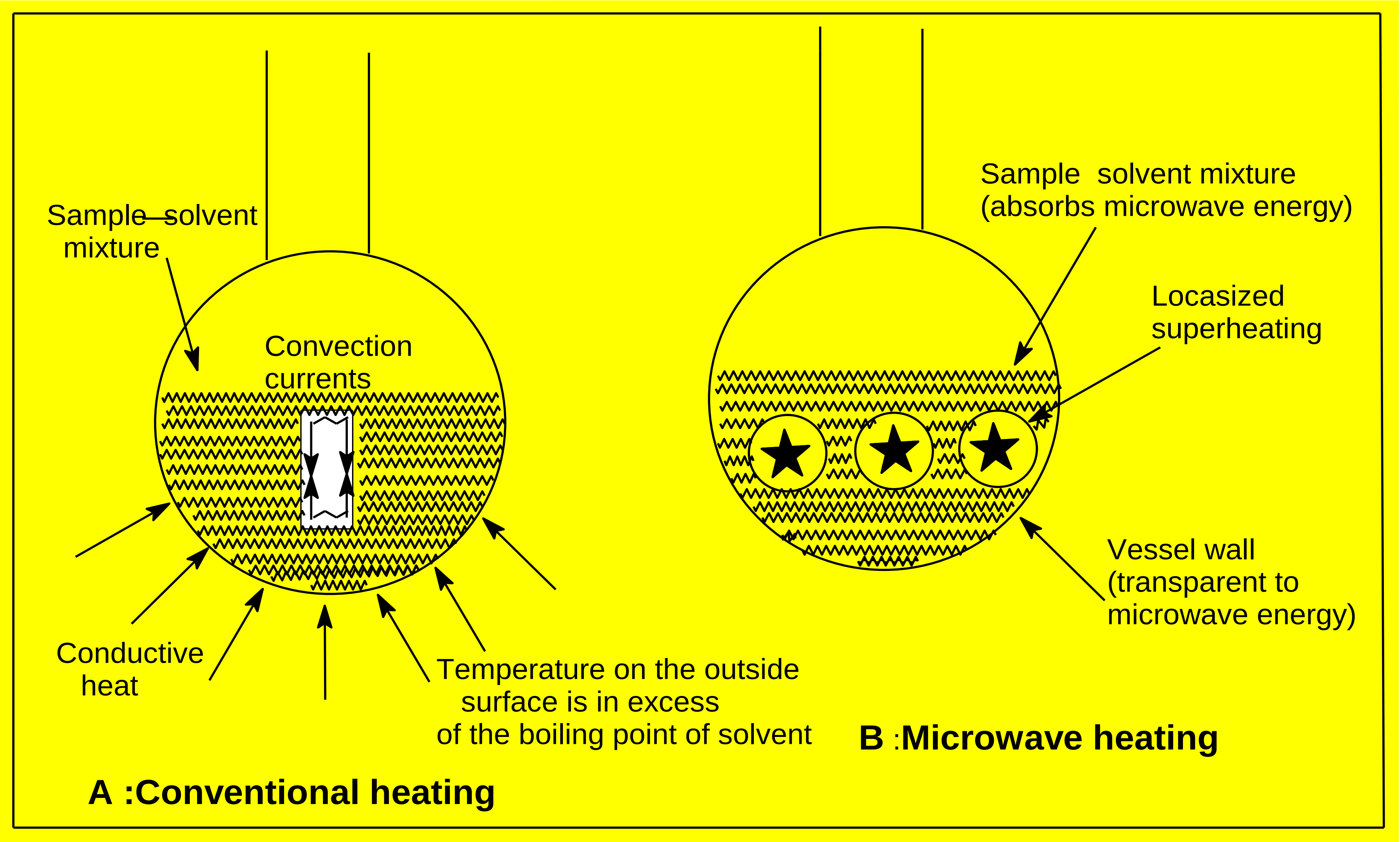
Q: What are the principle advantages of microwave –assisted organic synthesis over traditional methods?

A: One important advantage, which led to the initial adoption of microwave enhanced chemistry, is simply the **speed** with which synthetic reactions can be performed. Reactions that would take days with conventional methods can be completed in the minutes in the microwave, eliminating that bottleneck.

Q: How do the products generated by microwave synthesis compare to the products of traditional methods?

A: Microwave-enhanced synthesis actually generates **larger yields and purer products** than conventional techniques. Hot plates and Oil baths for example, heat the reaction mixture from the outside in, creating a hot vessel surface that can be the site of undesirable side reactions. Microwave energy, however, heats the entire sample at ones, eliminating the “hot spots” and reducing reaction time, all of which results in larger, purer yields.

Comparison between conventional heating & microwave heating



CONCLUSIONS

MICROWAVE + DRY MEDIA

Clean and Economic procedure

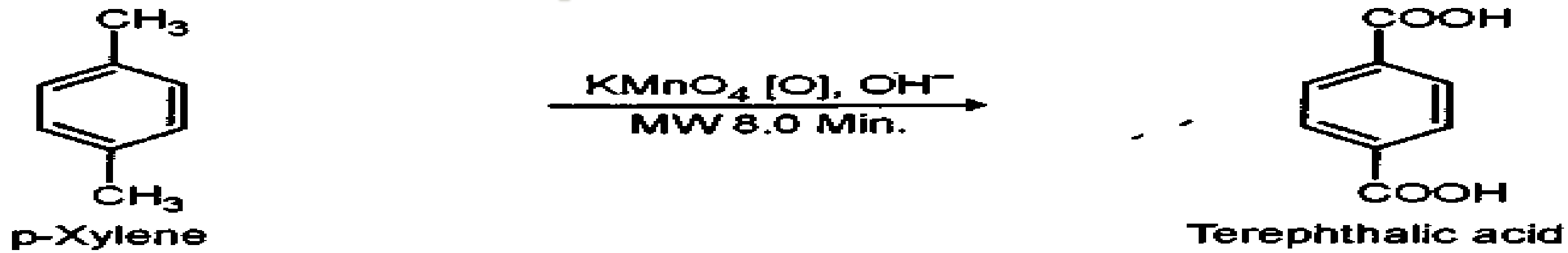
Serious Improvements and Simplifications/ Conventional Techniques

- Rapidity
- Higher yields
- Purity of products
-

To be avoided → Volatile & toxic solvents (+ Cost)
Corrosive mineral acids

<u>CLEAN, EFFICIENT & ECONOMIC TECHNOLOGY</u>

OXIDATION OF *p*-XYLENE



The same reactions was carried out by conventional method as well as Microwave method and comparative status is given below

	Microwave	**Conventional**
Reaction time (min)	8.0	60.0
Yield (%)	74.6	68.1

A mixture of 3.0 g of p-xylene, 5.0 g of KMnO4, 50.0 mL of water, and mL of 2N NaOH solution was taken in a conical flask. Then it was irradiated for 8.0 minutes in a microwave oven. The reaction mixture was cooled and product was filtered, washed with water and recrystallised from alcohol. **M.P.- >300°C**

Examples of Green Chemistry

Alternative biosynthetic pathway to adipic acid, using glucose

- Technologies to convert biomass into animal feed, industrial chemicals, and fuels
- New synthesis of 4-aminodiphenylamine avoiding the use of halogenated intermediates

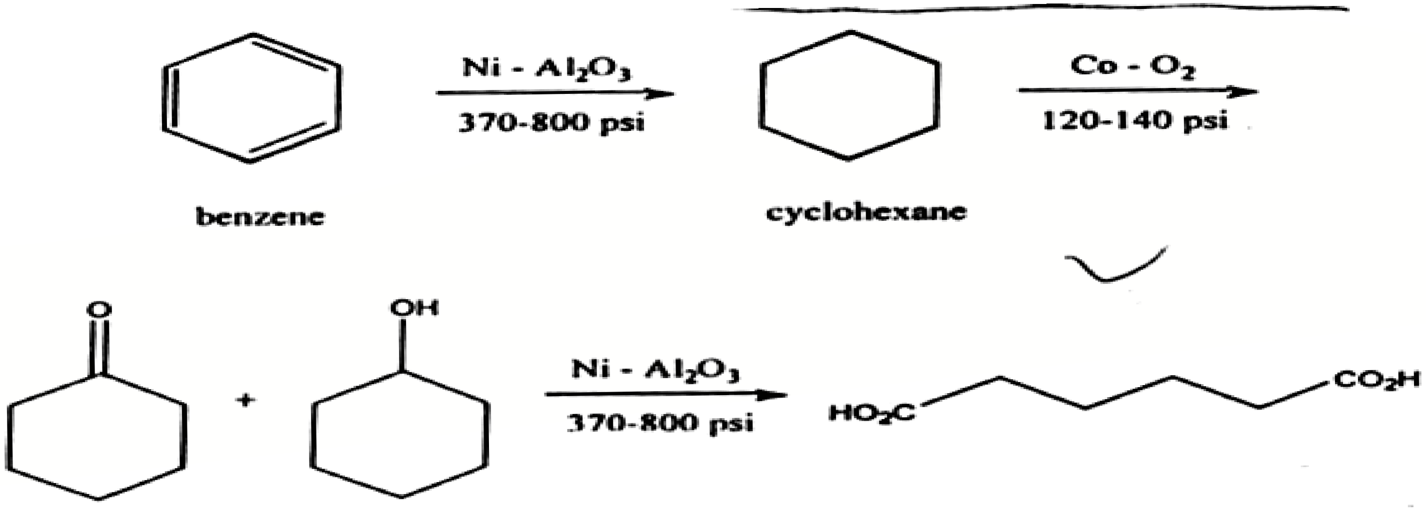
Alternative synthesis of DSIDA using a copper catalyst

Alternative synthesis of polyurethanes without using phosgene

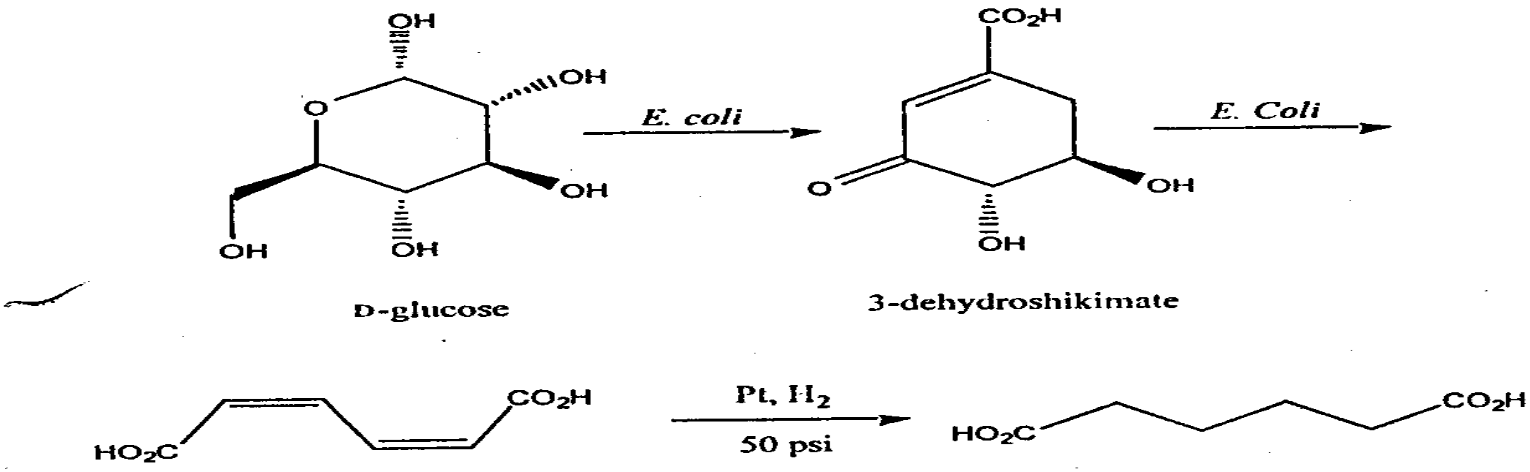
Synthesis of low molecular weight 'prepolymers'.

The photochemically mediated reaction of aldehydes with quino

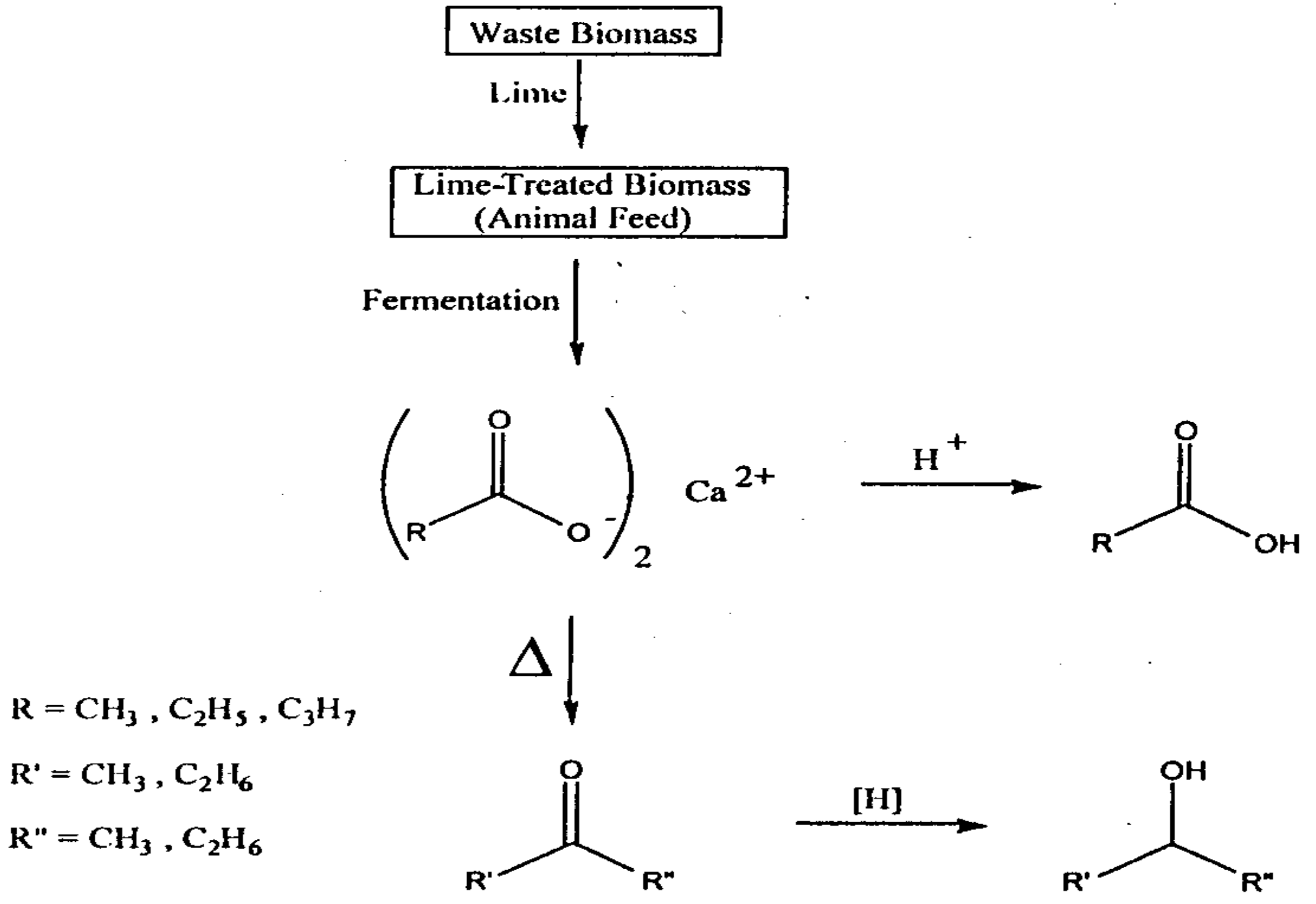
Traditional Synthesis of adipic acid, using Benzene



Alternative biosynthetic pathway to adipic acid, using glucose



Technologies to convert biomass into animal feed, industrial
chemicals, and fuels



Ultrasound Assisted Green Synthesis

Introduction :-

The word ‘ultrasound’ has become common knowledge due to the widespread use of ultrasound scanning equipments in medical applications. Ultrasound refers to sound waves having frequencies higher than those to which the human ear can respond (μ, > 16 KHz) (Hz = Hertz = cycles per second). High frequency ultrasound waves are used in medical equipments. The ultrasound frequencies of interest for chemical reactions (about 20-100 KHz) are much lower than those used for medical applications, but the power used is higher

The ultrasound is generated with the help of an instrument having an ultrasonic transducer, a device by which electrical or mechanical energy can be converted into sound energy. The most commonly used are the electromechanical transducer which converts energy into sound - they are mostly made of quartz and are commonly based on the piezoelectric effect.

The term ‘sonochemistry’ is used to describe the effect of ultrasound waves on chemical reactivity. A number of reviews on the chemical applications of ultrasound have been published.

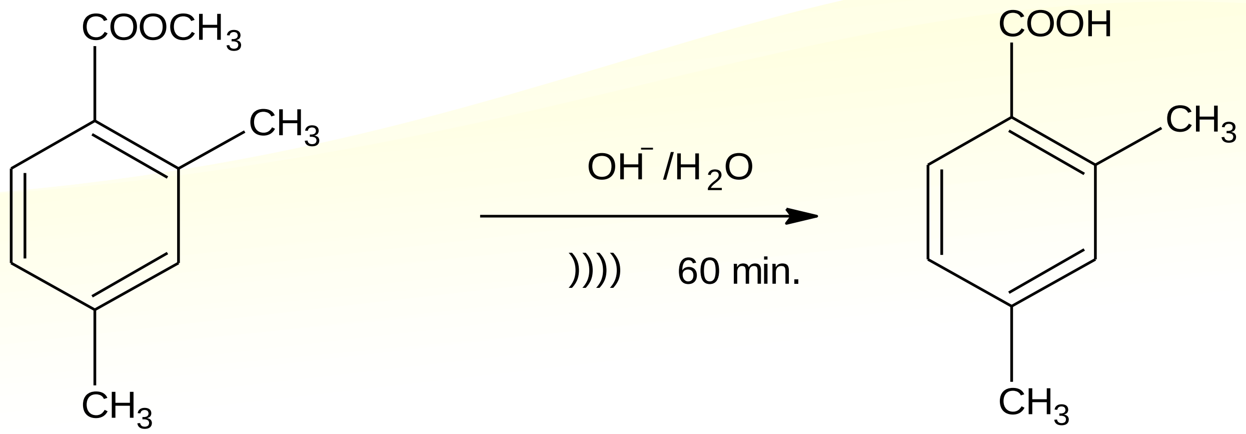
Applications of Ultrasound

Following are some of the important applications of ultrasound in chemical synthesis. Most of the reactions/synthesis reported are carried out at room temperature unless otherwise specified. The symbol)))) is used for reactions carried out on exposure to ultrasound.

Esterification: -

$$RCOOH + R'OH \xrightarrow[))))]{H_2SO_4,\ R.T.} RCOOR'$$

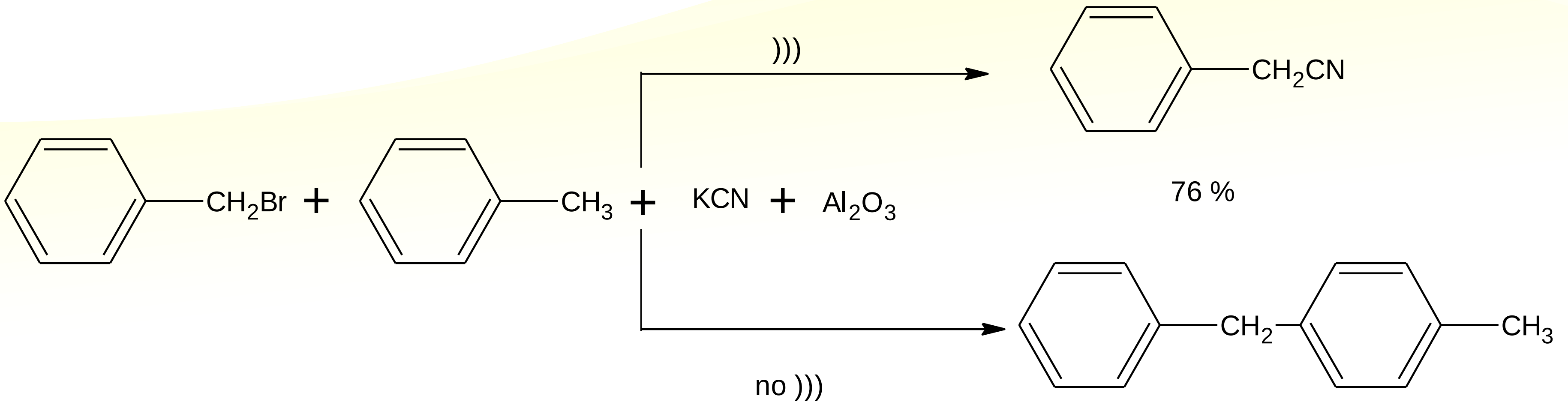
Saponification:



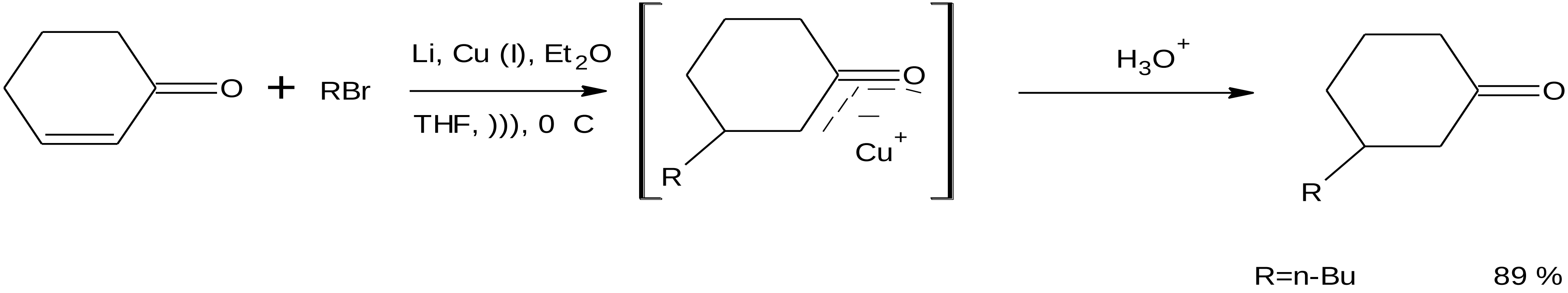
Hydrolysis:

$$\mathrm{ArCN} \xrightarrow[)))]{OH^- /H_2O} \mathrm{ArCOOH}$$

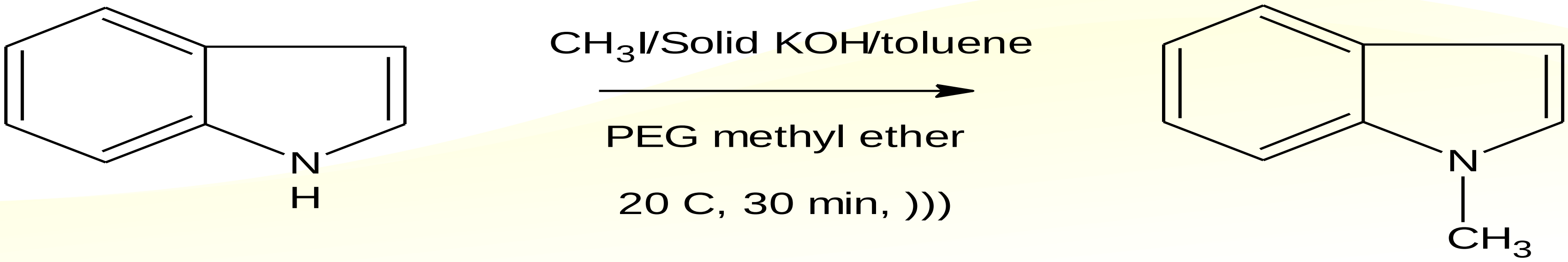
Substitution Reactions: -



Addition Reactions: -

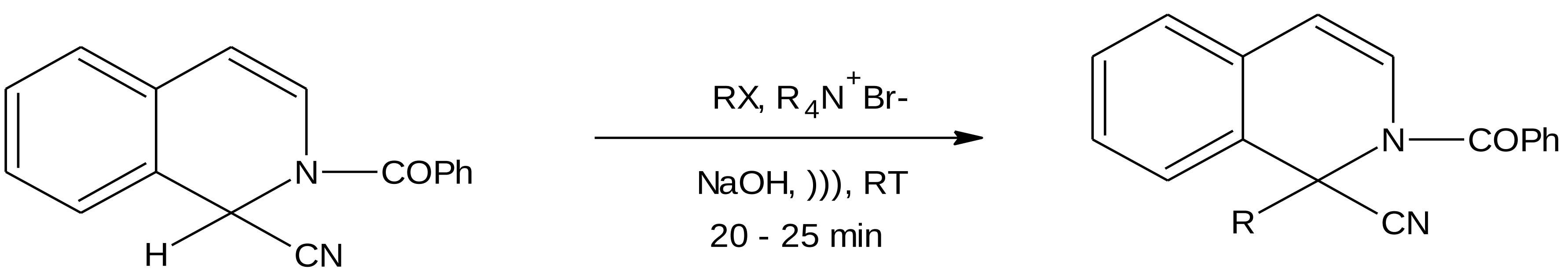


Alkylations:



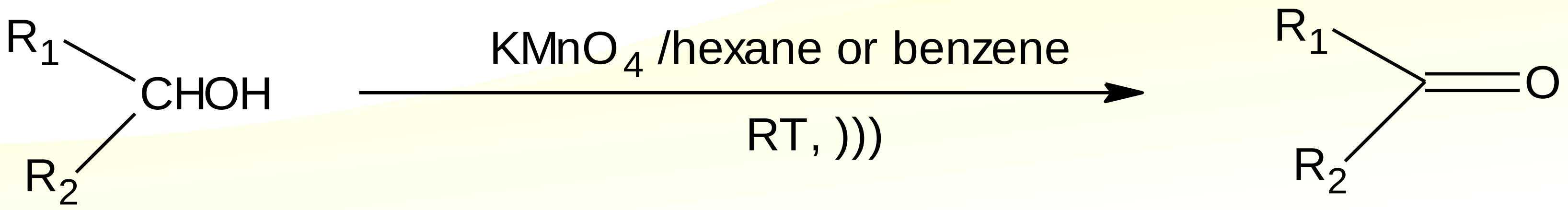
65 %

C-Alkylation of isoquinoline derivatives can be affected using sonication under PTC conditions .

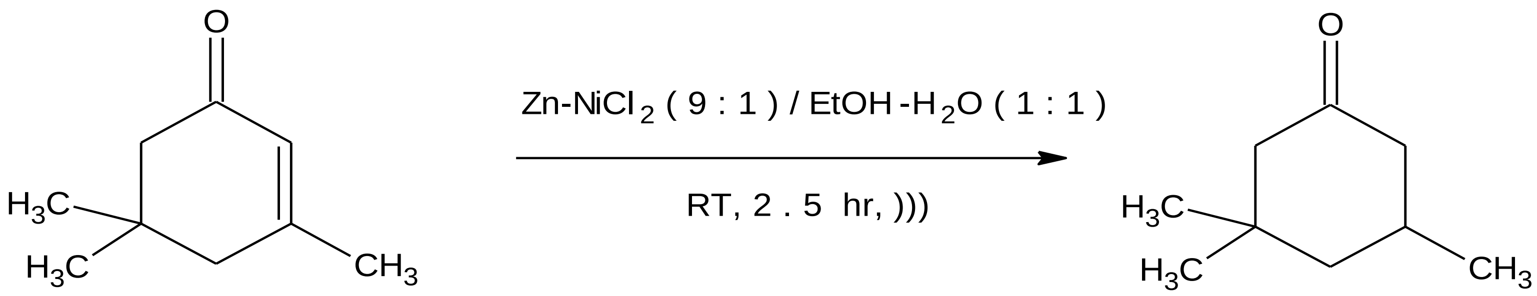


R = $PhCH_2$ 60%

Oxidation:

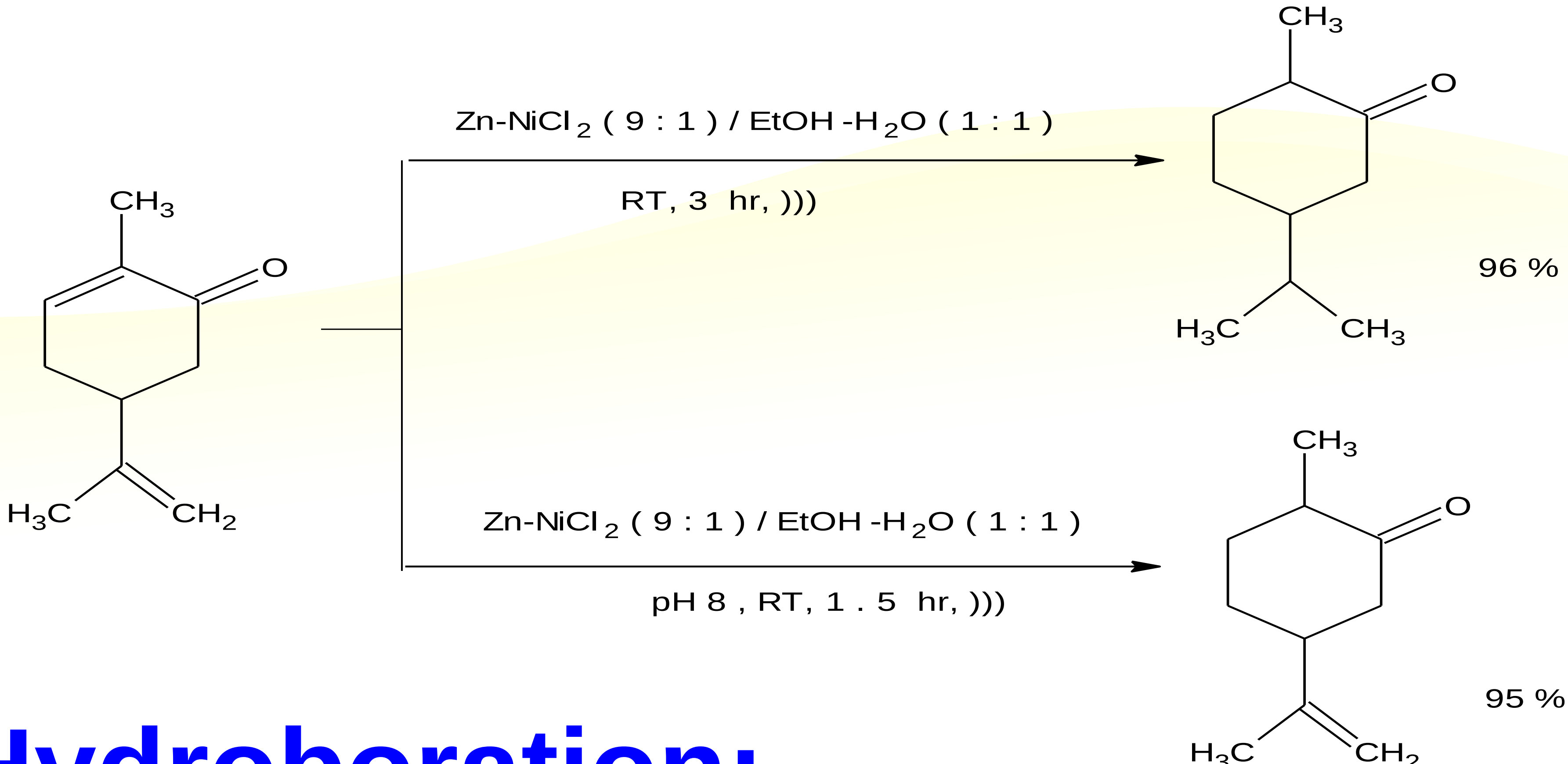


Reduction:

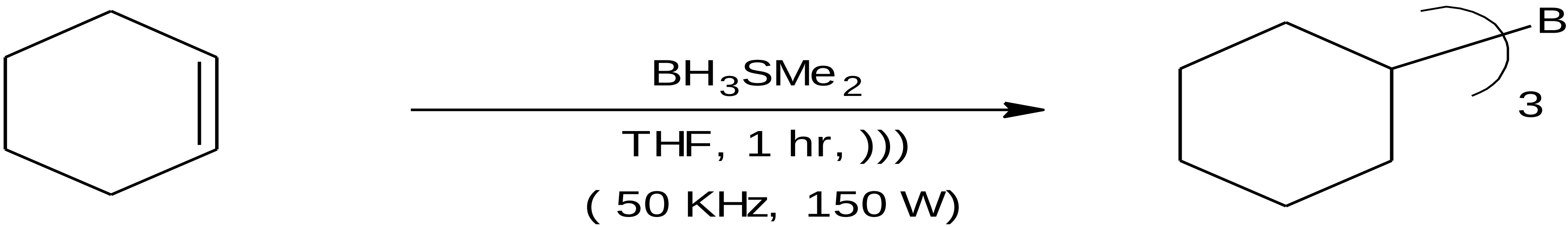


97 %

(the reaction takes 48 hr in the absence of ultrasound)

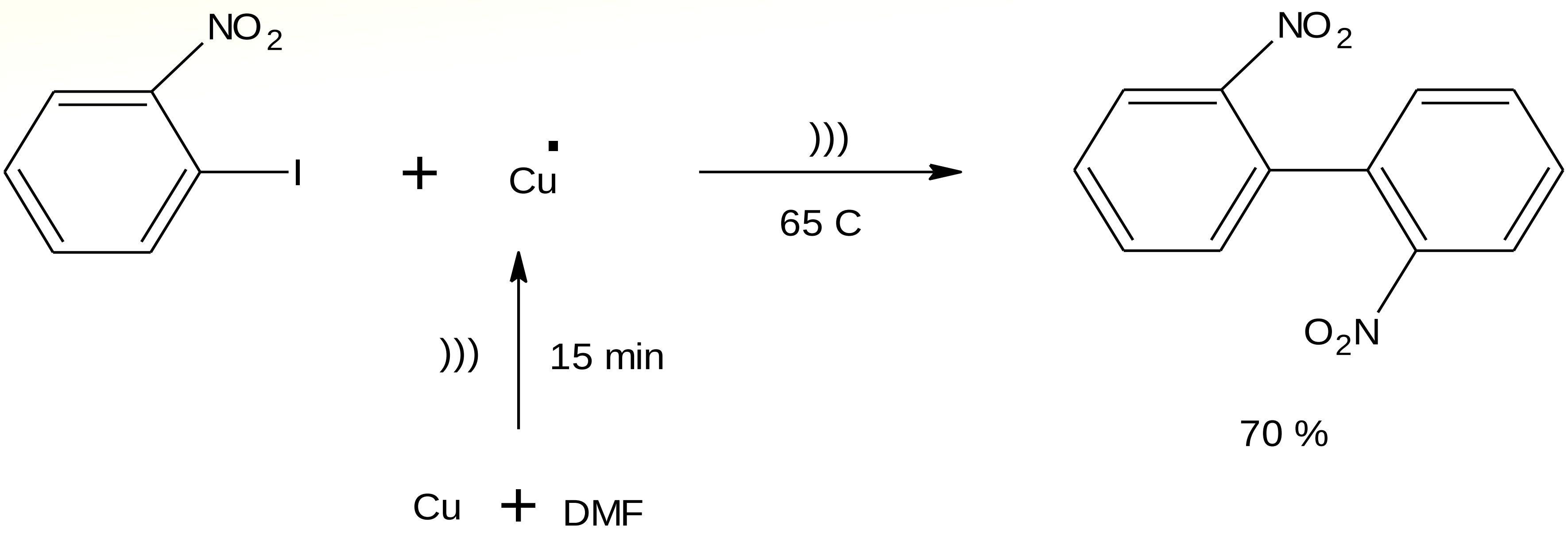


Hydroboration:



Coupling Reactions:

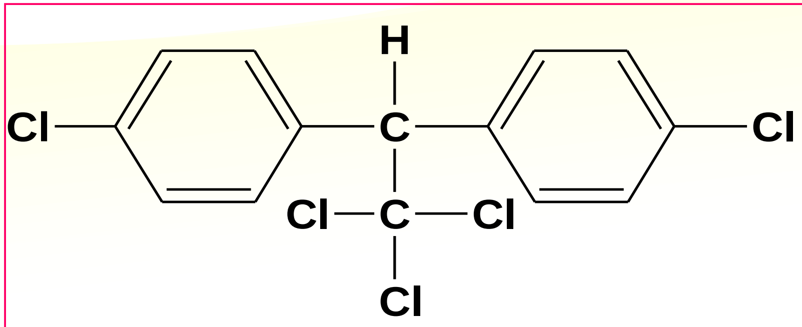
$$C_6H_5Br \xrightarrow[)))]{\text{Li, THF}} C_6H_5\text{-}C_6H_5$$



Smoking an Environmentally benign cigarette

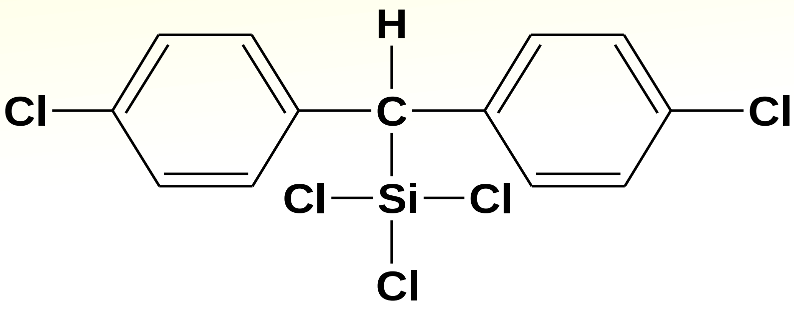
Research in china – Jina Hua Zhu and co-workers will make cigarette less damaging to health - used 3% CuO/NaY Zeolite adsorb 75% of common Volatile nitroso amine (VNA) which are carcinogenic cause cancer.

Eco-friendly Insecticide:



DDT

Dichloro-diphenyl-trichloroethane



Dichloro-diphenyl-trichlorosilicon ethane

It is prevent growth of plants insects.

It is harmful and mutagenic for cell growth of human being and animals

It is prevent growth of plants insects.
It is not harmful and not mutagenic for cell growth


सत्यम् ज्ञानम् अनन्तम्

THANK YOU