

Green Chemistry

		TREATMENT OF INDUSTRIAL WASTEWATER.		
2	Green Chemistry for Sustainable Engineering		08	CO2
	2.1	Principles and Concept of Green Chemistry: Definition and need for green chemistry in modern chemical industries, Twelve principles of green chemistry (Anastas and Warner), significance of each principle with respect to sustainability goals.		
	2.2	Green solvents: water, supercritical CO ₂ , ionic liquids, Comparison of traditional vs green chemical processes, Atom economy, waste minimization, and environmental metrics		
	2.3	Green Synthesis and Applications: Microwave- and ultrasound-assisted green synthesis, Case studies of industrial green chemistry practices		

- Our life depends on many useful chemical products like medicines, fabrics, insecticides, drugs, dyes, rubber, etc. Production of these chemical products causes severe pollution problems. All chemicals are toxic in varying extent. Hence it became necessary to review and modify all the chemical processes used for manufacture.
- Thus the design of harmless processes to produce various products has emerged a new branch of chemistry called as Green chemistry or environmentally benign chemistry.
- Green chemistry is highly effective approach to pollution prevention because it applies innovative scientific solutions to real world environmental situations.

Objectives of green chemistry

- 1) To minimize the environmental pollution caused due to chemical processes.
 - 2) To design harmless chemical processes w.r.t. chemicals used, products formed, byproducts generated, waste generated from the process and energy requirement.
 - 3) Sustainable development of chemical industry
 - 4) To reduce or eliminates the use or generation of hazardous substances in the manufacture.
- To achieve these objectives the green chemistry utilizes a set of principles, known as Twelve Principles of Green Chemistry, suggested by Paul Anastas and John Warner.

Twelve Principles of Green chemistry

1. Prevention of waste
2. Maximize % Atom economy
3. Non-hazardous chemical synthesis
4. Design safer chemicals and products
5. Auxiliary substances (Use safer solvents and reaction conditions)
6. Energy efficiency
7. Use of renewable feedstock
8. Avoid chemical derivatives
9. Use of catalysts, not stoichiometric reagents
10. Design chemicals and products to degrade after use (Design for degradation)
11. Use of new analytical methods (Real time monitoring)
12. Minimize the potential for accidents

Learn through the numerals:

1. Prevention of waste

- It is better to prevent waste than to treat or clean up waste after it is formed.
- It has been a common practice to dump waste on land or in water, which resulted in soil, water and air pollution.
- This made the legislation to be very stringent on industries and hence there was compulsion to have waste treatment and disposal units attached to the manufacturing plants. This increases the cost of process.
- Thus green chemistry involved to design chemical syntheses in such a way that the process involve pathway to give only products, leaving no byproducts to treat or clean up. i.e. Prevention is better than cure.

Nobel Prize 2005 in Chemistry

Dr. Yves Chauvin at the Institut Français du Pétrole, Rueil-Malmaison, France

Robert H. Grubbs, California Institute of Technology, Pasadena, California, USA and

Richard R. Schrock, Massachusetts Institute of Technology, Cambridge, Massachusetts, USA.

Metathesis reaction used mainly in the development of pharmaceuticals and of advanced plastic materials.

- more efficient (fewer reaction steps, fewer resources required, less wastage),
- simpler to use (stable in air, at normal temperatures and pressures) and
- environmentally friendlier (non-injurious solvents, less hazardous waste products).

Metathesis reducing potentially hazardous waste through smarter production.

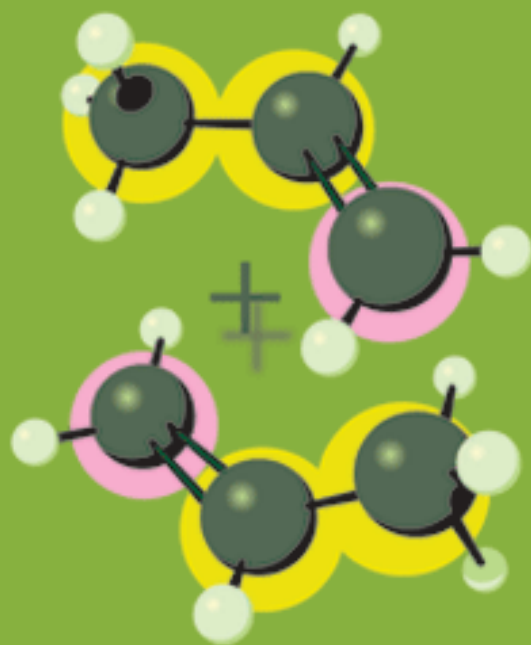
Metathesis is an example of how important basic science has been applied for the benefit of man, society and the environment.

It is best example of Green Chemistry

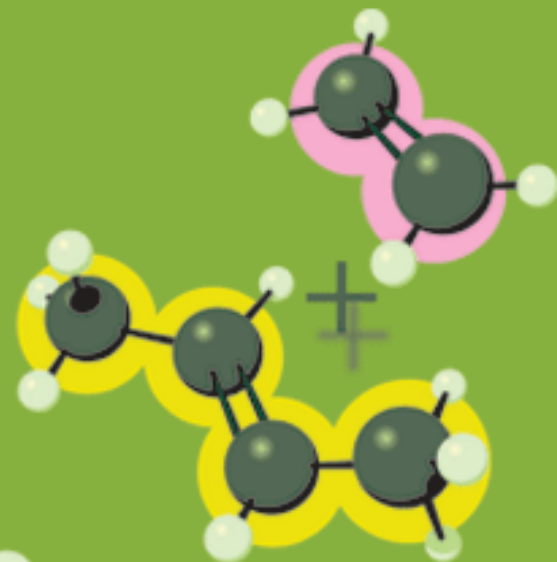
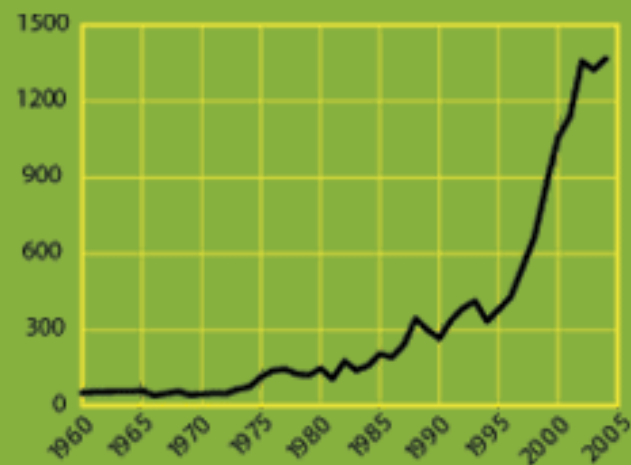
Metathesis – a change-your-partners dance

Metathesis means change places. In metathesis reactions, double bonds between carbon atoms are broken and re-formed in a way that causes atom groups to change places. This can be compared to a dance in which the couples change partners while the dance is going on.

Metathesis reactions do not occur in nature, but are a smart “short-cut” in organic synthesis when new molecules are being built. Metathesis does not take place by itself, but with the help of a catalyst. What the catalyst looked like and how it worked was long a mystery.

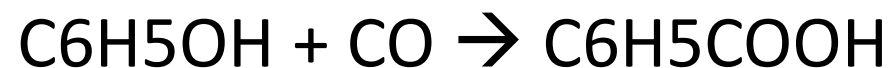


Metathesis marches on
Following the Laureates' discoveries, interest in metathesis has grown. The diagram shows the number of scientific papers per year since 1960 in which the word “metathesis” appears.



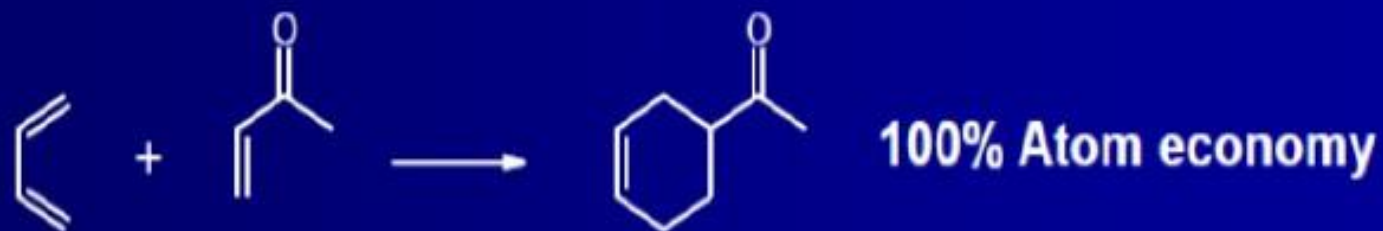
2. Maximize % atom economy

- Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
- Atom economy (atom efficiency) is the conversion efficiency of a chemical process in terms of all atoms involved and the desired products produced. Atom economy is an important concept of green chemistry philosophy.
- It is common observation that most of organic reactions release undesired products along with useful products of the reaction.
- Green chemistry requires that new processes should be designed such that the most of the starting material gets converted into product. This is called as Maximizing atom economy.

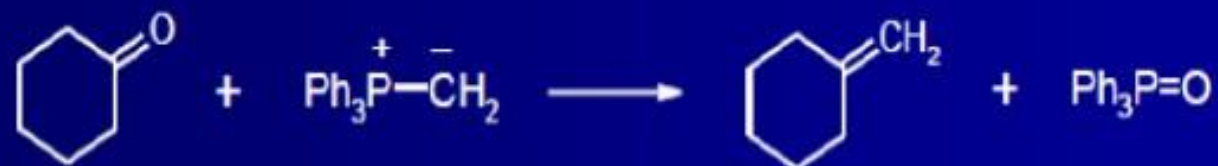


$$\text{Atom Economy} = \frac{\text{molecular weight of desired product}}{\text{molecular weight of all reactants}} \times 100\%$$

Diels-Alder Reaction



Wittig Reaction



35% Atom economy

The amount of **INPUT** is concerned! Different from **yield**!!

Atom Economy

The theoretical yield for every reaction can be calculated as,

$$\text{Theoretical yield} = \text{Stoichiometric ratio} \times \left[\frac{\text{Molecular weight of the desired product}}{\text{Molecular weight of limiting reagent}} \right] \times \text{weight of limiting reagent}$$

On conducting the reaction the experimental or actual yield of the process is obtained. From this percentage yield is calculated.

$$\text{Percentage yield} = \left[\frac{\text{Actual yield}}{\text{Theoretical yield}} \right] \times 100$$

e.g. Preparation of n-propyl bromide from n-propyl alcohol (0.6 g)



Thus 1 mole of reactant gives one mole of product

Hence

$$\begin{aligned}\text{Theoretical yield} &= \text{Stoichiometric ratio} \times \left[\frac{\text{Molecular weight of the desired product}}{\text{Molecular weight of limiting reagent}} \right] \\ &\quad \times \text{Weight of limiting reagent} \\ &= \frac{1}{1} \times \left[\frac{123}{60} \right] \times 0.6 \\ &= 1.23 \text{ gms}\end{aligned}$$

But actually yield of the above reaction is found to be 0.99 gms

$$\begin{aligned}\text{Hence percentage yield} &= \frac{0.99}{1.23} \times 100 \\ &= 80.49\%\end{aligned}$$

Atom economy can be calculated by using following formula,

$$\% \text{ Atom economy} = \frac{\text{Molecular weight of product}}{\text{Total molecular weight of reactants}} \times 100$$

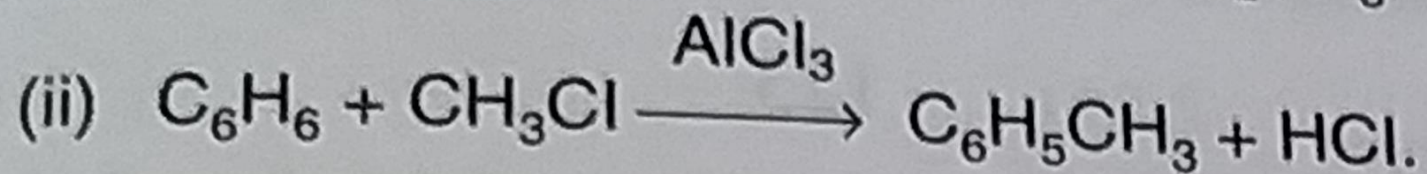
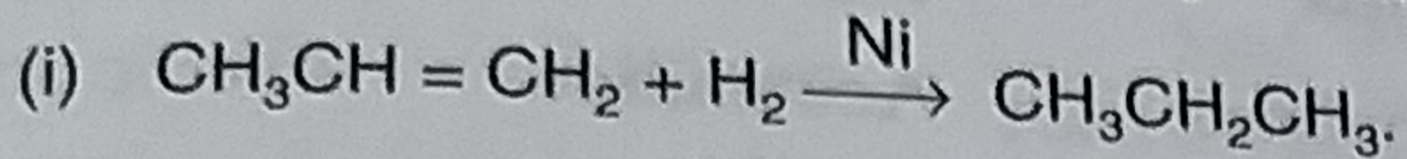
∴ In above reaction, % atom economy can be calculated as,

$$\begin{aligned}\% \text{ Atom economy} &= \frac{\text{Molecular weight of n-propyl bromide}}{\text{Molecular weight of (n-propanol + NaBr)}} \times 100 \\ &= \frac{123}{60 + 103} \times 100 \\ &= \frac{123}{163} \times 100 \\ &= 75.5\%\end{aligned}$$

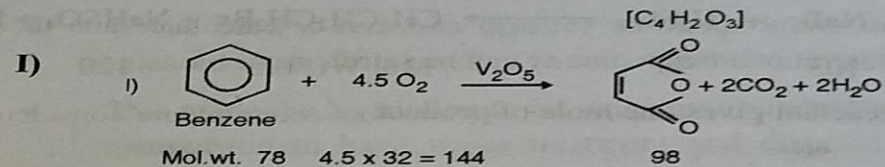
Other examples for understanding the efficiency of reaction is given here,

(May 2011, 4 Marks)

Calculate the percent atom economy for the following reactions –



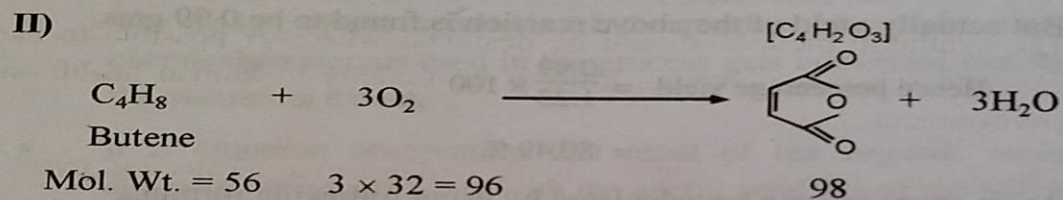
$$78 + 50.5 \rightarrow 92 \quad \% \text{Atom Economy} = 92 / (78 + 50.5) = 71.595\%$$



$$\% \text{ Atom economy} = \frac{98}{78 + 144} \times 100$$

$$= \frac{98}{222} \times 100$$

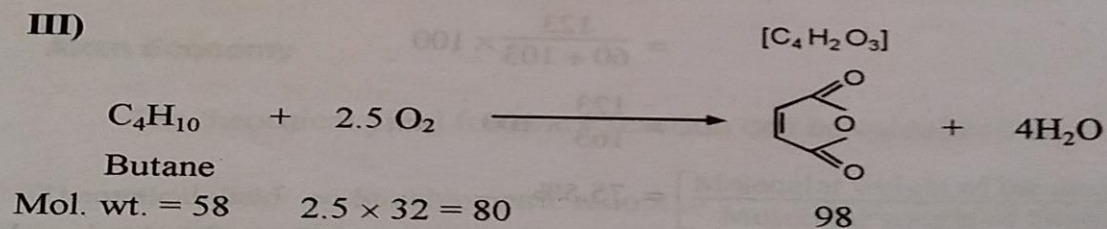
$$\therefore \% \text{ Atom economy} = 44.1\%$$



$$\% \text{ Atom economy} = \frac{98}{56 + 96} \times 100$$

$$= \frac{98}{152} \times 100$$

$$\therefore \% \text{ Atom economy} = 64.5 \%$$



$$\% \text{ Atom economy} = \frac{98}{58 + 80} \times 100$$

$$= \frac{98}{138} \times 100$$

$$\therefore \% \text{ Atom economy} = 71.0 \%$$

Numerical 1

- $\text{C}_6\text{H}_6 + \text{CH}_3\text{COCl} \rightarrow \text{C}_6\text{H}_5\text{COCH}_3 + \text{HCl}$
- Benzene + Acetyl chloride \rightarrow Acetophenone
- 78 + 78.5 120

$$\% \text{AE} = 76.677\%$$

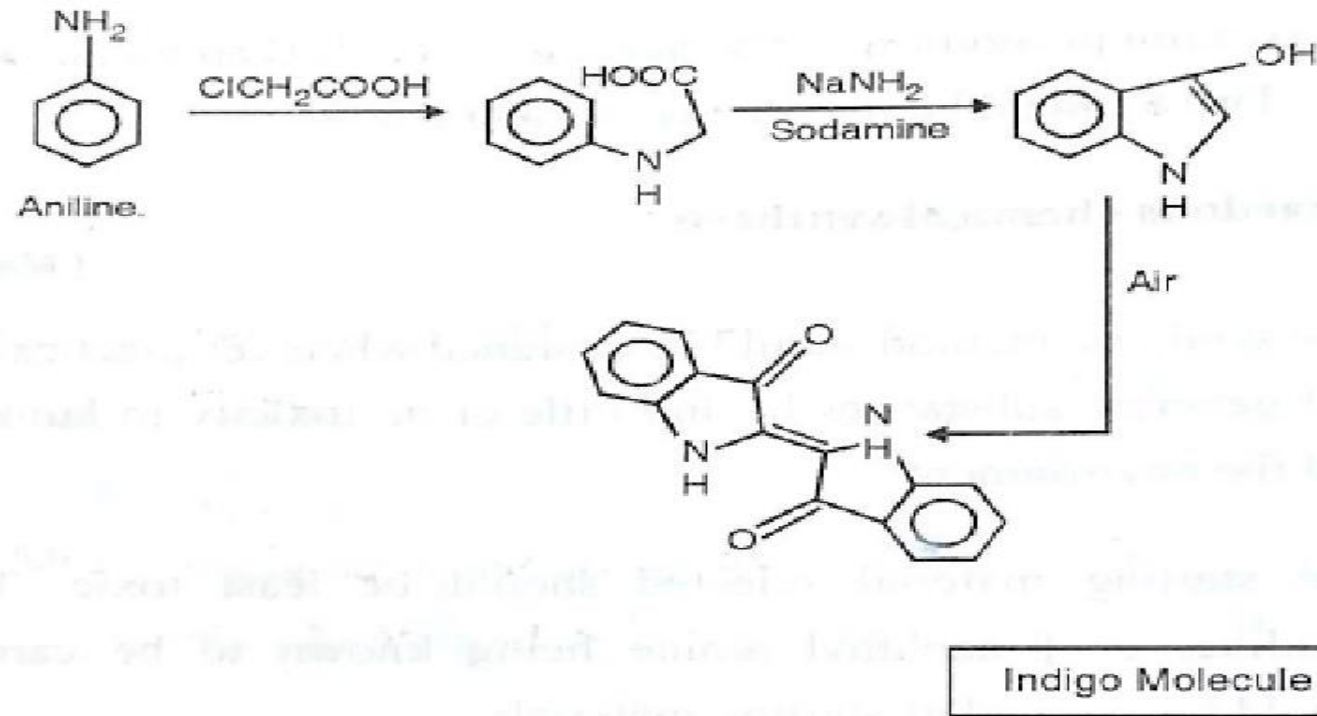
- Numerical 2
- $\text{C}_6\text{H}_5\text{NH}_2 + (\text{CH}_3\text{CO})_2\text{O} \rightarrow \text{C}_6\text{H}_5\text{NHCOCH}_3 + \text{CH}_3\text{COOH}$
- Aniline + Acetic anhydride \rightarrow Acetanilide + acetic acid
- $93 + [(43 \times 2) + 16] = 102 \rightarrow 135$

3. Non-hazardous chemical synthesis

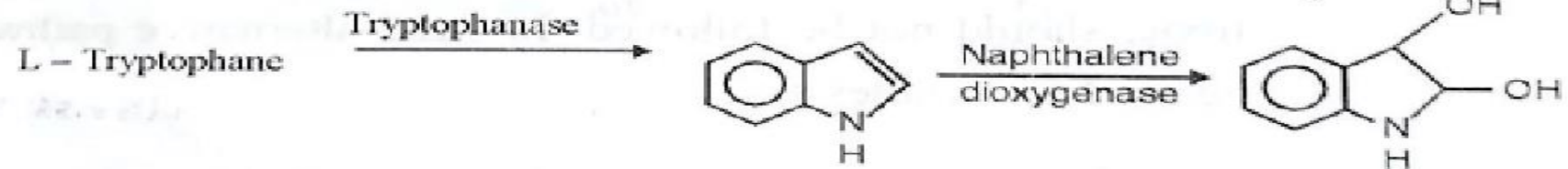
- The synthetic method should be designed to generate substances having little or no toxicity to human health and the environment.
- The starting material selected should be least toxic. E.g. pyridine or α -naphthylamine being carcinogenic should be avoided as starting materials.
- The reactions in which intermediates or reagents or products are toxic should be avoided, instead alternative pathways should be developed.
- E.g. Bhopal gas tragedy was caused due to leakage of Methyl isocyanate (MIC) gas, an intermediate in the manufacture of pesticides and was known to be highly poisonous.
- Hence green chemistry recommends the design of synthesis to use and generate the substances with little or no toxicity to humans and the environment.

Synthesis of Indigo

(A) Conventional Route using hazardous Aniline

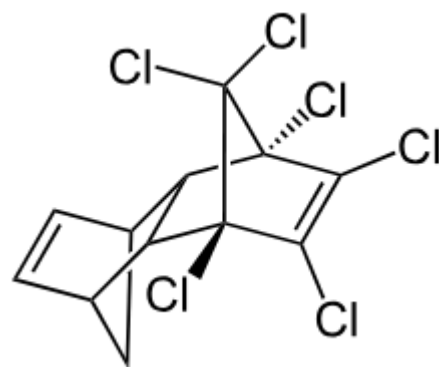
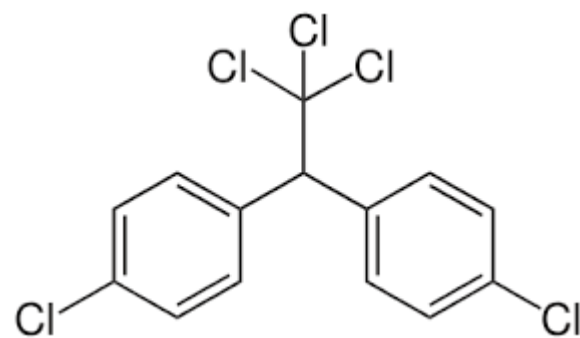
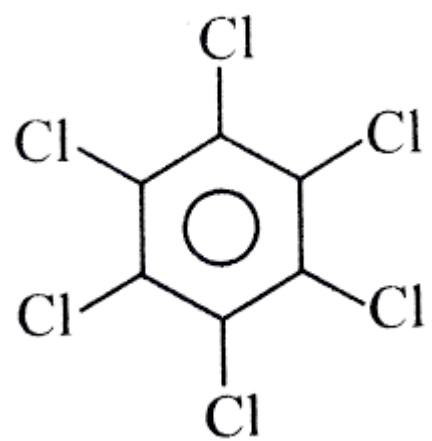


(B) Greener Route : Using enzyme



4. Design safer chemicals and products

- The chemical products should be designed to preserve the efficiency of desired function while reducing toxicity.
- When any new drug formulations are to be put in market, they are put first on clinical trials to check their toxic effects on humans.
- If found toxic then alternatives are prepared keeping in consideration of medicinal properties but only toxicity reduced.
- Many insecticides like DDT (Dichlorodiphenyltrichloroethane), gamaxane, aldrin etc. are found to be toxic to humans, use of these should be avoided and alternatively biological pesticides should be used.



5. Auxiliary substances (Use of safe solvents)

- The use of auxiliary substances like solvents, separating reagents etc should be avoided in the synthesis.
- Avoid using carcinogenic solvents, separating reagents or other auxiliary chemicals, instead use safer chemicals.
- The solvents such as acetone, benzene, ether being highly inflammable should be avoided.
- Other chemicals such CCl_4 , CHCl_3 causes ozone depletion hence should be avoided.
- If a solvent is necessary, water is a universal solvent which is safer to use.
- For dry cleaning of the fabrics, the toxic solvents like perchloroethylene was used, which is replaced during recent years by liquid CO_2 .

6. Energy Efficiency (Energy efficient chemical processes)

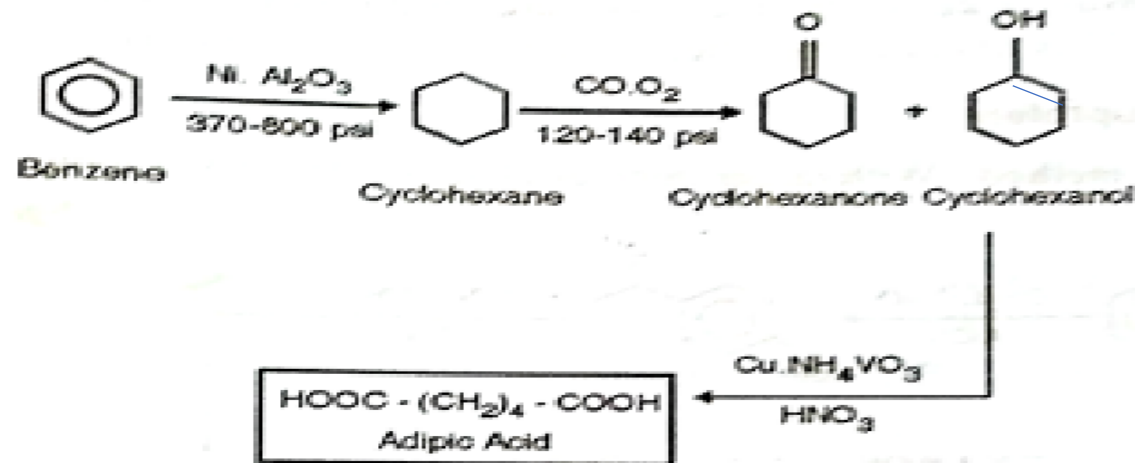
- The energy requirements of chemical processes should be minimized considering their environmental and economic impacts. The synthetic methods should be carried at ambient temperature and pressures.
- The main aim of green chemistry is to increase energy efficiency.
- This can be achieved by **use of catalysts** and by stopping use of fossil gaseous fuels which cause pollution.
- The energy efficiency of the process can be increased by proper heat transfer and minimal wastage of energy during the process.
- Wherever found suitable microwave radiations and ultra sound methods can be used.
- Use fermentation process for chemical synthesis where energy requirement is low and products are less harmful.

7. Use of renewable feedstock

- The raw materials used should be renewable rather than depleting, wherever feasible economically and experimentally.
- Renewable feedstock is often made from agricultural products or of waste products of other processes.
- Example, Adipic acid was earlier synthesized from benzene, which is carcinogenic. A new method is developed to prepare adipic acid from glucose obtained from corn starch or cellulose. This is a green process.

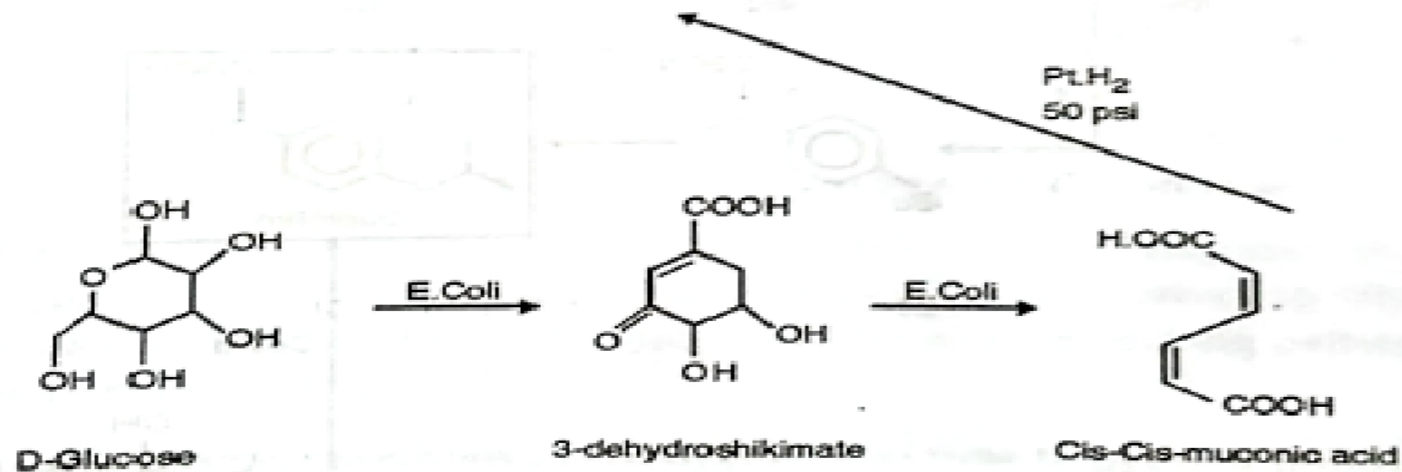
Synthesis of Adipic Acid

(A) Traditional pathway : Using Benzene (Carcinogenic solvent)



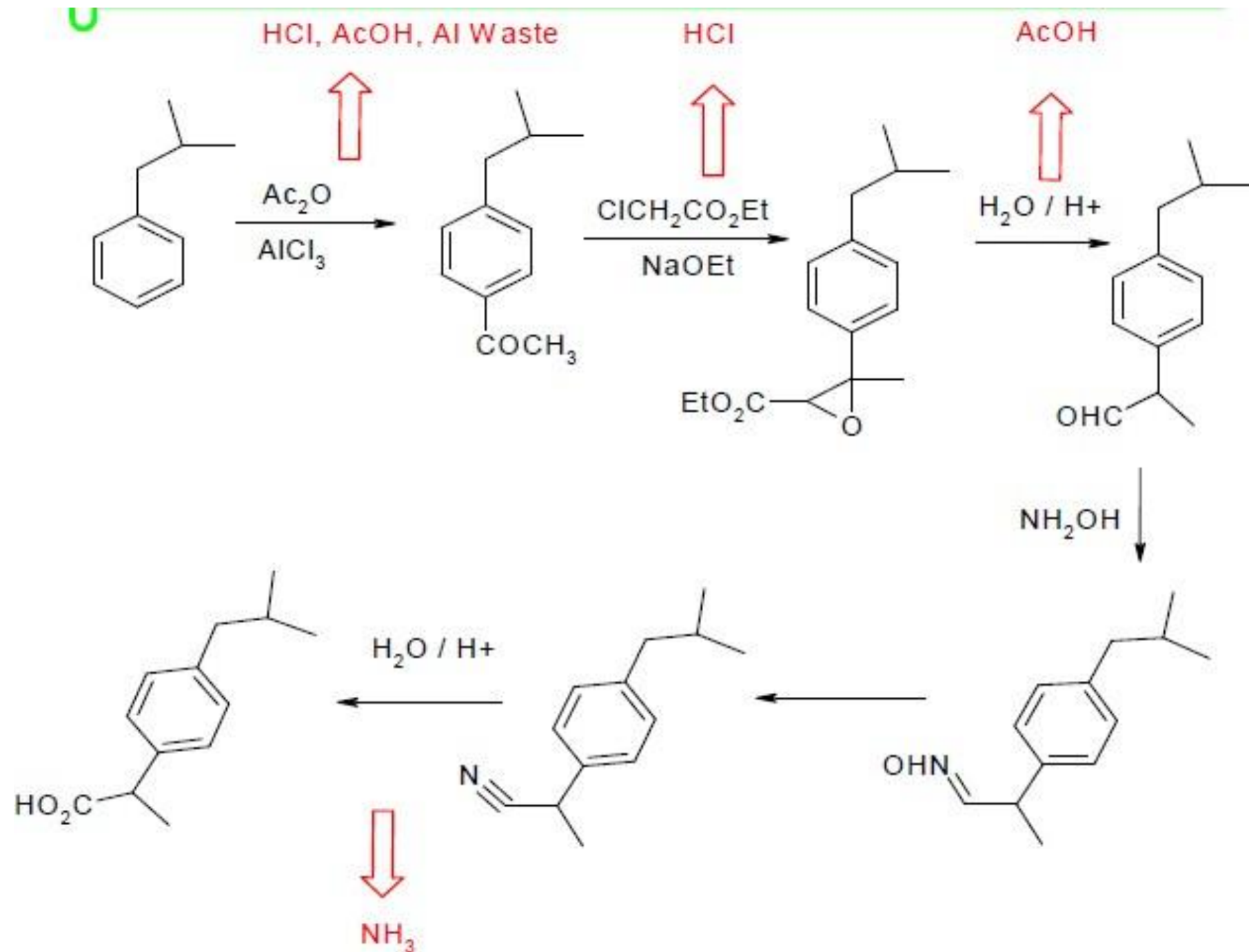
(B) Greener pathway

Using glucose (absolutely safe)



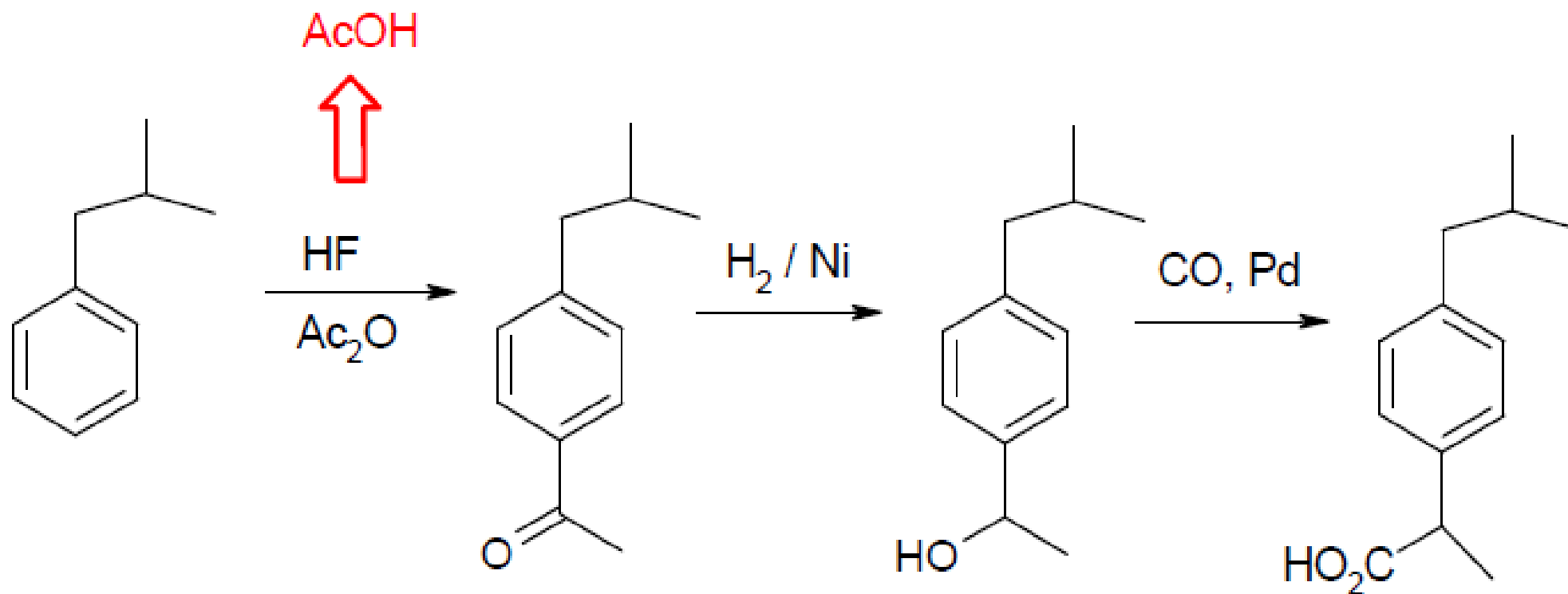
8. Avoid chemical derivatives

- During the synthesis unnecessary derivatization such as protecting groups or any temporary modifications should be avoided if possible.
- The use of derivatives increases the steps of the process.
- The additional reagent required and it also generates more waste products.
- To avoid these effects alternative reagents are to be used which are more selective.
- Example, synthesis of ibuprofen is as given below. A traditional synthesis involves large number of steps and atom economy is low (40%). An alternative method increases the atom economy to 77%.



BHC Company – Greener Commercial Synthesis

- Consist of three steps
- Atom economy 77 %



9. Use of catalysts

- The catalyst as we know facilitates transformation without being consumed or without being incorporated into the final product.
- Catalysts are selective in their action in that the degree of reaction that takes place is controlled, e.g. mono addition v/s multiple addition.
- A typical example is that reduction of triple bond to a double bond or single bond.
- In addition to the benefits of yield and atom economy, the catalysts are helpful in reducing consumption of energy.
- Catalysts carry out thousands of transformation before being exhausted.
- Catalytic reactions are faster and hence require less energy. They are preferable to stoichiometric reagents, which are used in excess and work only once.
- In recent years many processes have been developed which use non-toxic recoverable catalysts and also biocatalysts.

10. Design chemicals and products to degrade after use

- 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.
- It is extremely important that the products designed to be synthesized should be biodegradable.
- They should not be persistent chemicals or persistent bio accumulators.
- It is now possible to place functional groups in a molecule that will facilitate its biodegradation.
- Functional groups which are susceptible to hydrolysis, photolysis or other cleavage have been used to ensure that products will be biodegradable.
- It is also important that degradation products do not possess any toxicity and detrimental effects to the environment. Plastic, Pesticides (organic halogen based) are examples which pose to environment.
- Example, DDT when used as pesticide, its residues remains in soil for many years causing pollution. The alternative to this is biological insecticides.

11. New Analytical methods

- Analytical methodologies need to be further developed to allow for real time, in process monitoring and control prior to the formation of hazardous substances.
- Methods and technologies should be developed so that the prevention or minimization of generation of hazardous waste is achieved.
- It is necessary to have accurate and reliable reasons, monitors and other analytical methodologies to assess the hazardous that may be present in the process stream.
- These can prevent any accidents which may occur in chemical plants.
- Example, preparation of ethylene glycol, in which if reaction conditions are not monitored perfectly, toxic substances are produced at higher temperature.

12. Minimize the potential for accidents

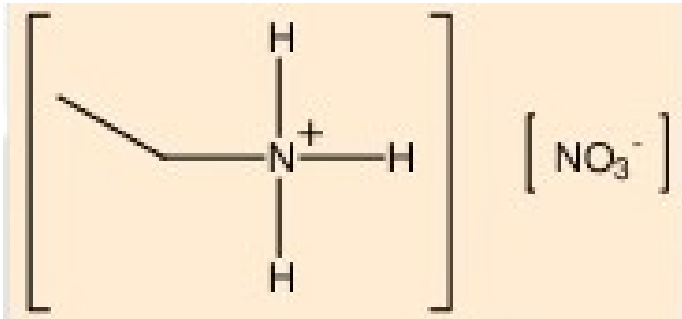
- Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions and fires.
- The occurrence of accidents in chemical industry must be avoided.
- It is well known that the incidents in Bhopal (India) and Seveso (Italy) and many others have resulted in the loss of thousands of life.
- It is possible sometimes to increase accidents potential inadvertently with a view to minimize the generation of waste in order to prevent pollution.
- It has been found that in an attempt to recycle solvents from a process (for economic reasons) increases the potential for a chemical accident or fire.
- The use of safer chemicals, minimizing temperature, pressure and using catalysts help in minimizing the potential of accidents which is desirable.

Green Solvents

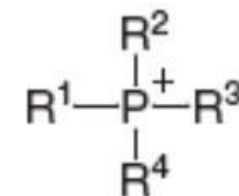
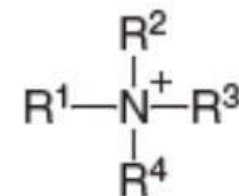
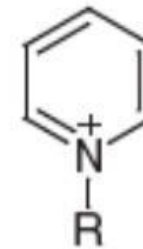
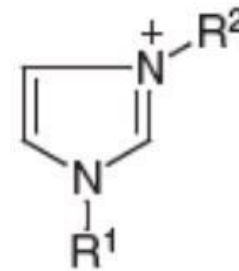
- Green solvents are environmentally friendly solvents, or biosolvents, which are derived from the processing of agricultural crops. The use of petrochemical solvents is the key to the majority of chemical processes but not without severe implications on the environment.
- Examples of biosolvents include ethyl lactate, derived from corn, and bio-based alcohols like ethanol and propanol.
- Green solvents were developed as a more environmentally friendly alternative to petrochemical solvents.
- There is no “ideal green solvent” suitable for all sorts of chemical transformations.

Ionic Liquid: Green Solvent

- Benzene, toluene, methylene chloride cause health and environmental problems
- Ionic liquids are highly polar and liquid at room temperature
- First ionic liquid: ethyl ammonium nitrate (1914, Paul Walden) m. p. 12 °C
- Ionic liquids use as green solvent



Cations



Anions



Characteristic Features of Ionic Liquid

- ☐ Almost no vapour pressure
 - ☐ Non-flammability
 - ☐ Non-combustibility
 - ☐ High thermal stability
 - ☐ Relatively low viscosity
 - ☐ Wide temperature ranges for being liquids
 - ☐ High Ionic conductivity.
-
- These ionic liquids are not only used as reaction solvents
 - Also exhibit Lewis acid or Lewis base properties, when the ratio of cations and anions is changed.

Paradigm Confirmed: The First Use of Ionic Liquids to Dramatically Influence the Outcome of Chemical Reactions

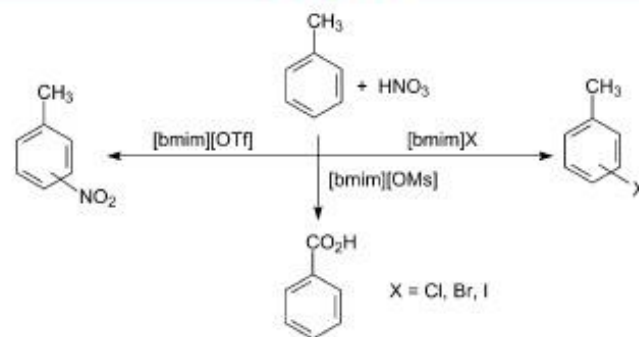
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ABSTRACT



It has been an unproven paradigm that the choice of which ionic liquid to use in a chemical reaction can have a dramatic effect on the outcome of that chemical reaction. We demonstrate, for the first time, that the reaction of toluene and nitric acid in three different ionic liquids gives rise to three completely different products in high yield. Furthermore, ionic liquids can catalyze these reactions with the only byproduct being water.

Supercritical fluids as green solvents

❑ Supercritical carbon dioxide (scCO₂)

- scCO₂ is a promising green solvent because of its **negligible toxicity** and **high solubility** window for different kind of solutes.
- It is also produced as a by-product in many large scale production of compounds. Its high diffusivity and variable density in the supercritical region replaced many conventional and toxic solvents.
- It provides a green pathway for the many chemical reactions. For example, in the Wacker oxidation of alkenes, it is used as heterogeneous catalyst to promote the oxidation.
- In some of the processes due to its low polarity nature, some entrainer like organic solvents are mixed in a particular ratio to increase the solubility of the polar solutes. For example, on addition of ethanol as entrainer, the extend of solubility and rate of extraction is increased tremendously in compare to pure scCO₂. In case of some metal nitrate salts like Pb(NO₃)₂, Co(NO₃)₂, and Al(NO₃)₃, scCO₂ cannot dissolve them properly.

2. Properties of Supercritical Fluids

- **Density:** Comparable to liquids → high solubilizing power.
- **Viscosity:** Comparable to gases → enhances mass transfer.
- **Diffusivity:** Higher than liquids → faster penetration into solid matrices.
- **Tunable Solvent Power:** Small changes in pressure/temperature significantly alter solubility, enabling selective extraction.
- **Environmentally Benign:** Non-flammable, recyclable, and often non-toxic (especially CO₂).

3. Common Supercritical Fluids Used as Green Solvents

- **Carbon dioxide (CO₂)**: Most widely used, mild critical conditions ($T_c = 31.1\text{ }^{\circ}\text{C}$, $P_c = 73.8\text{ bar}$), non-toxic, non-flammable.
- **Water (scH₂O)**: High critical point ($T_c = 374\text{ }^{\circ}\text{C}$, $P_c = 221\text{ bar}$), polar medium, useful for hydrolysis, oxidation, biomass conversion.
- **Other SCFs**: Ethanol, nitrous oxide, propane, ammonia (used selectively depending on polarity and safety).

4. Applications in Green Chemistry

- **Extraction**

- Supercritical CO₂ for decaffeination of coffee/tea.
- Extraction of essential oils, flavors, fragrances, and pharmaceuticals.
- Avoids toxic organic solvents.

- **Chemical Reactions**

- Polymerization, hydrogenation, oxidation, and enzymatic reactions.
- scCO₂ as a medium enhances reaction selectivity and product purity.

- **Material Processing**

- Particle formation (e.g., drug nanoparticles by supercritical antisolvent technique).
- Cleaning of precision instruments (microelectronics, medical devices).

- **Waste Treatment & Cleaner Production**

- Supercritical water oxidation (SCWO) for destroying hazardous organic waste.
- scH₂O for converting biomass into biofuels.

❑ Advantages of Supercritical Fluids as Green Solvents

- **Non-toxic, non-flammable, safe (esp. CO₂).**
- **Easily recoverable:** Simply depressurize to remove SCF without solvent residues.
- **Reduced VOC emissions** compared to conventional solvents.
- **Tunability** allows selective extractions and cleaner processes.
- **Compatible with Green Chemistry Principles** (prevention of waste, safer solvents, design for energy efficiency, use of renewable feedstocks).

Limitations

- High-pressure equipment required → costly.
- Energy-intensive compression for CO₂ and heating for water.
- Not all compounds are soluble in scCO₂ (polar solutes require co-solvents like ethanol).
- Scale-up challenges in industrial processes.

Microwave Induced Green Synthesis

- Conventional heating usually involves the use of a furnace or oil bath, which heats the walls of the reactor by convection or conduction.
- The core of the sample takes much longer to achieve the target temperature, e.g. when heating a large sample of ceramic bricks.
- microwave absorption is able to heat the target compounds without heating the entire furnace or oil bath, which saves time and energy.



Microwave Induced Green Synthesis

- In microwave induced organic reactions, the reactions can be carried out in a solvent medium or on a solid support
- The solvent to be used must have a dipole moment so as to absorb microwaves and a boiling point at least 20-30 °C higher than the desired Reaction temperature.
- An excellent solvent in domestic microwave oven is DMF (b. p. 160 °C dielectric constant 6.7)
- Hydrocarbons e.g. hexane, benzene, toluene, xylene are unsuitable because of less dipole moment and also these solvents absorb microwave radiations poorly.
- Due to High polarity and non volatility, ionic liquids might be ideal for carrying out high temperature reactions

COMPARISON



CONVENTIONAL HEATING

- Vessel gets heated first
- Both gas and solution phase get heated
- Too high pressure -> Explosion



MICROWAVE HEATING

- Only Solution gets heated



DEMERITS OF MW-ASSISTED SYNTHESIS

Heat Force controlled is difficult.

Water Evaporation.

Closed container is dangerous because it can blast.



Applicable Microwave Instrumentation

Multimode Batch Reactors



Domestic MW Oven



Mars-S



MLS Ethos 1600

Single Mode Instruments



Emrys Liberator



Initiator



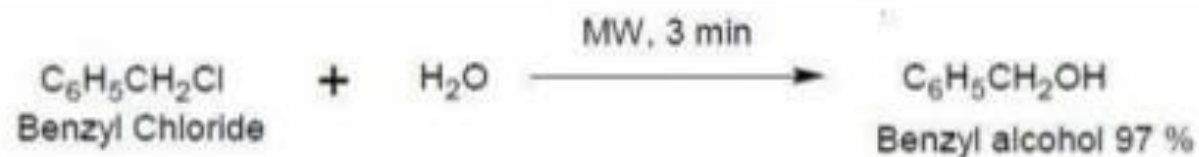
Discover

SOLVENTS

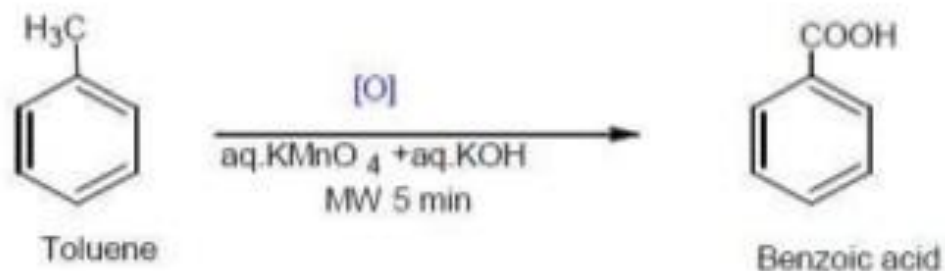
Energy Transfer Medium	Boiling Point	Dielectric Constant (20°/25°)
Acetone	56.6	20.70
Acetyl Acetone	140.6	25.70
Acetonitrile	82.0	37.50
Benzene	80.1	2.27
1-Butanol	117.7	17.80
Carbon Disulfide	46.3	2.64
Carbon Tetrachloride	76.7	2.23
Chlorobenzene	132.1	5.62
Chloroform	61.7	4.81
1,2-Dichloroethane	83.5	10.65
Diethyl Ether	34.6	4.34
Diethyl Glycol	244.8	31.70
Dimethyl Formamide	153.0	36.71
Dimethyl Sulfoxide	189.0	46.60

REACTIONS

HYDROLYSIS



OXIDATION

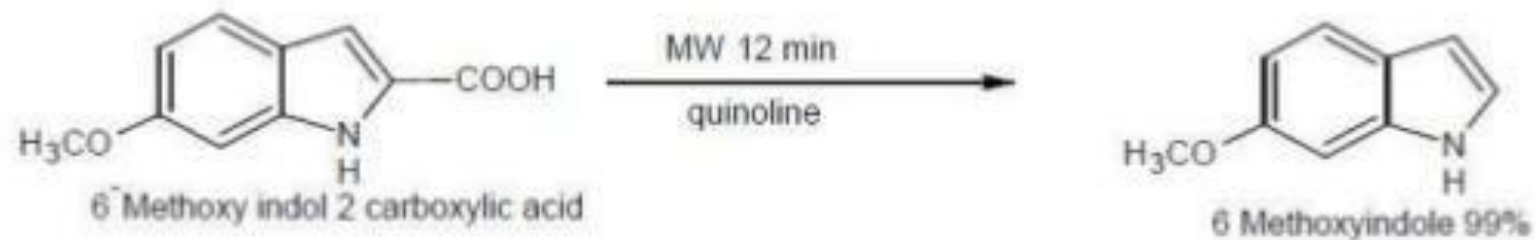


REACTIONS

ESTERIFICATION

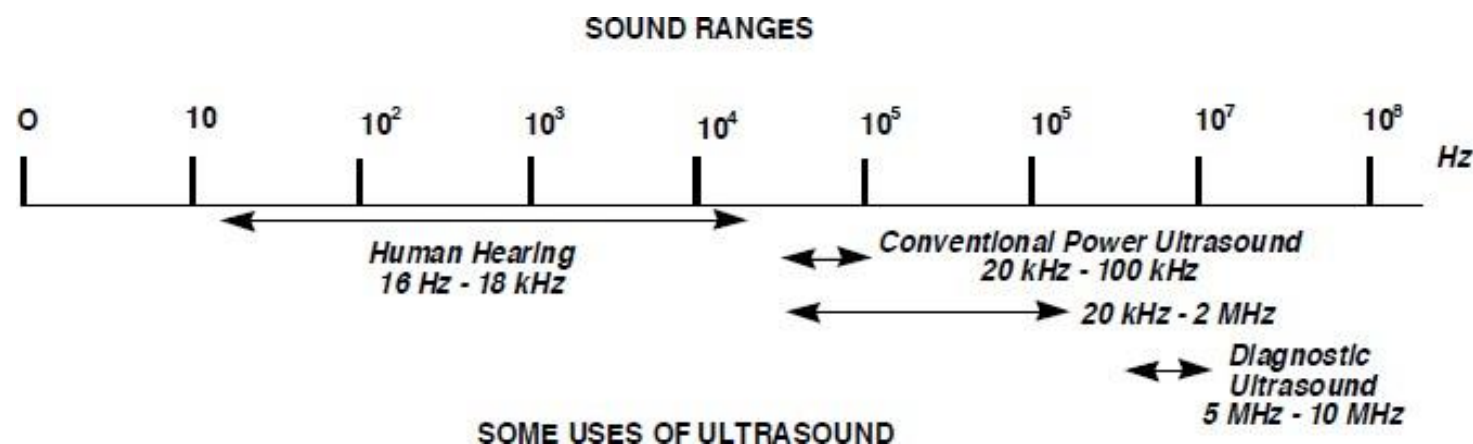


DECARBOXYLATION



ULTRASOUND APPLICATIONS IN ORGANIC SYNTHESIS

- Ultrasound refers sound waves having frequency higher than those to which human ear can respond ($>16\text{kHz}$).
- Ultrasound generated by ultrasonic transducer, a device which convert electrical energy into sound energy.
- “Sonochemistry” effect of ultrasound waves on chemical reactivity.
- Most of the reaction carried out at room temperature.



SONOCHEMISTRY is a field of chemistry that studies how ultrasonic waves are used to influence chemical reactions, often by causing acoustic cavitation. This process creates high-temperature, high-pressure "hot spots" within tiny, collapsing bubbles in a liquid, which can initiate or accelerate chemical processes like reduction, oxidation, and synthesis. It's considered a green method, offering benefits such as higher yields and shorter reaction times, and is applied in fields from material synthesis to environmental remediation.

How it Works

Ultrasonic Irradiation: High-intensity ultrasound (frequencies typically from 20 kHz to 10 MHz) is applied to a liquid.

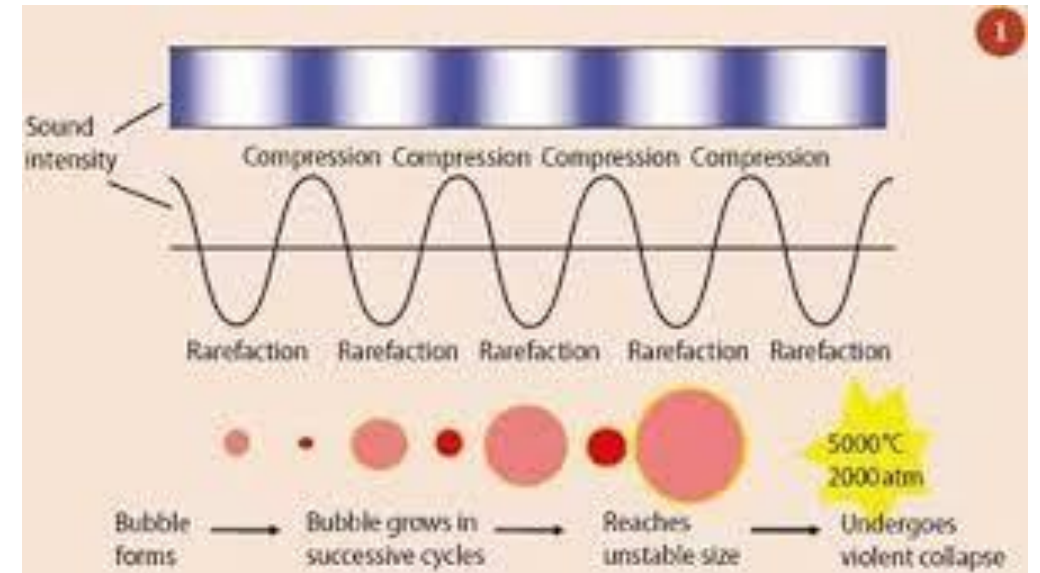
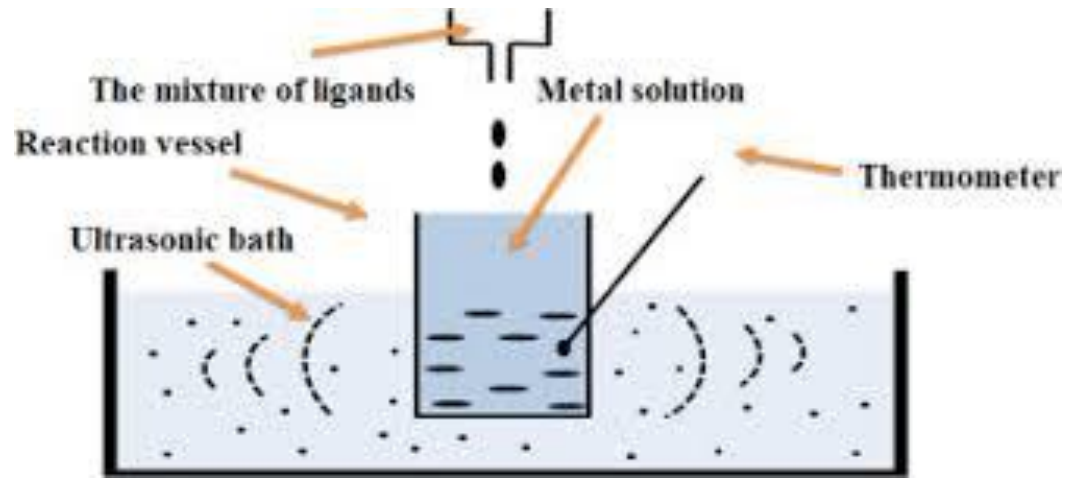
Acoustic Cavitation: The sound waves create cycles of compression and expansion in the liquid, leading to the formation and growth of small bubbles.

Bubble Collapse: When these bubbles reach an unstable size, they violently collapse.

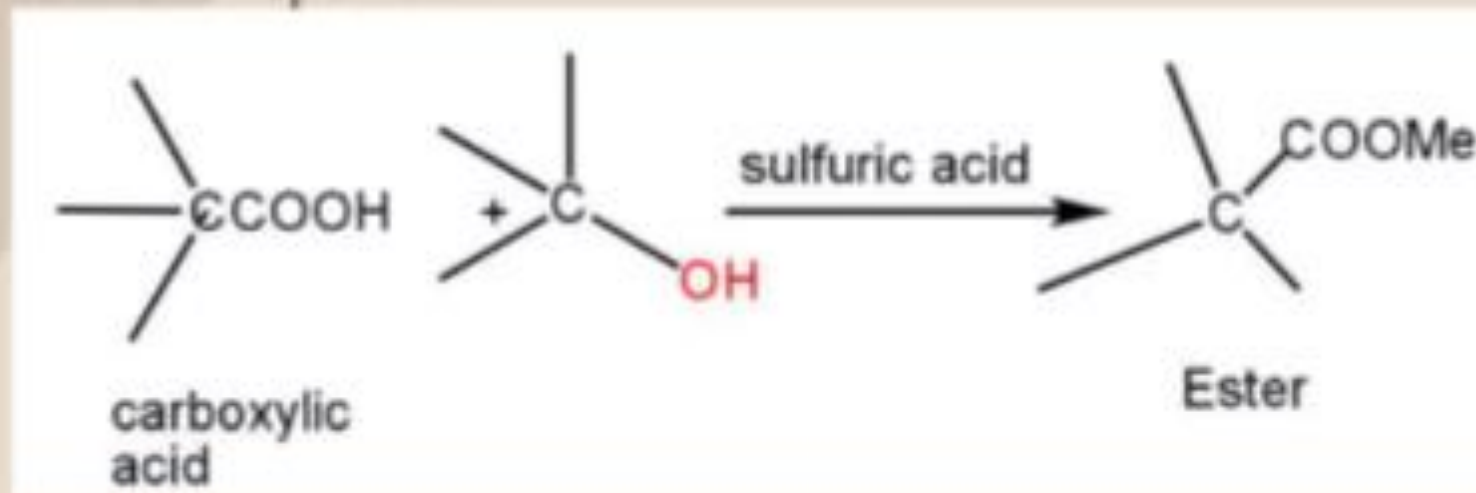
Hot Spots: This collapse generates localized "hot spots" with extremely high temperatures (around 5,000 K) and pressures (about 1,000 atm).

Chemical Activation: The energy from these hot spots drives chemical reactions.

SONOCHEMISTRY

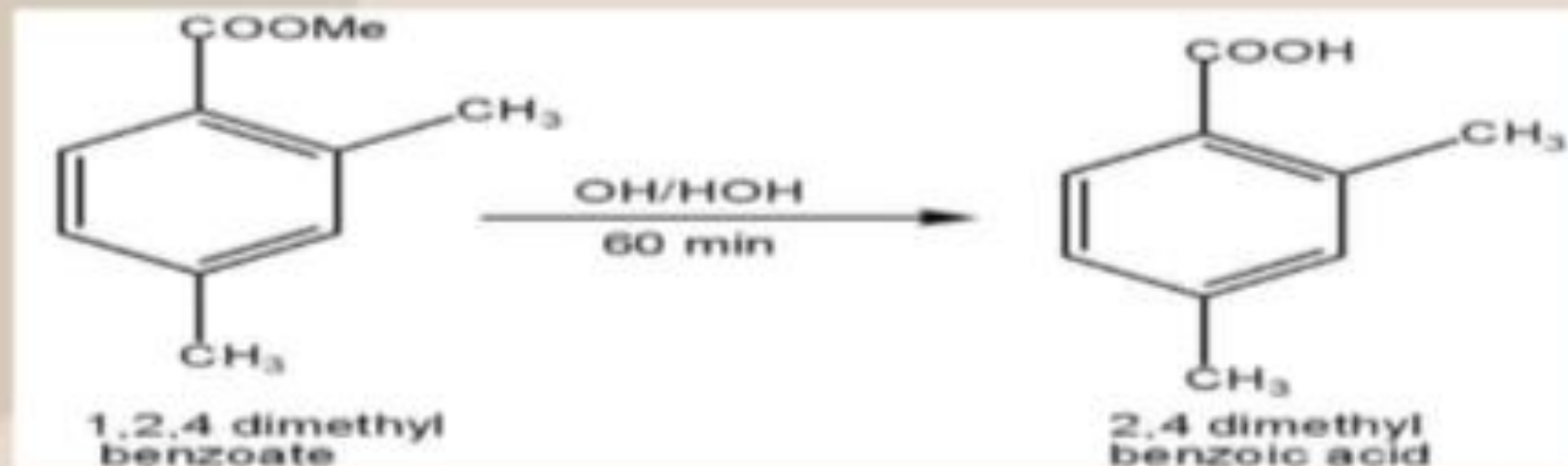


1. Esterification : The esterification is generally carried out in the presence of catalyst like sulphuric acid. Reaction requires longer time, and yields are very low. A simple procedure for the esterification of a variety of carboxylic acids with different alcohol at ambient temperature using ultrasound is reported.

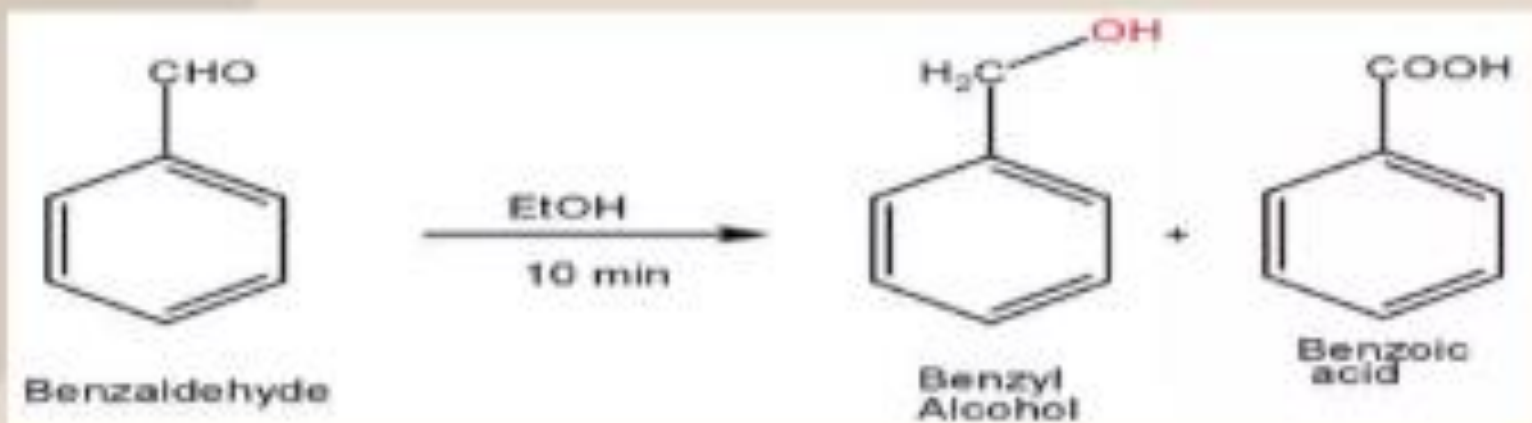


2 .Saponification: Ester hydrolysis is frequently affected under aggressive conditions. It can be conducted under milder condition when sonication is used.

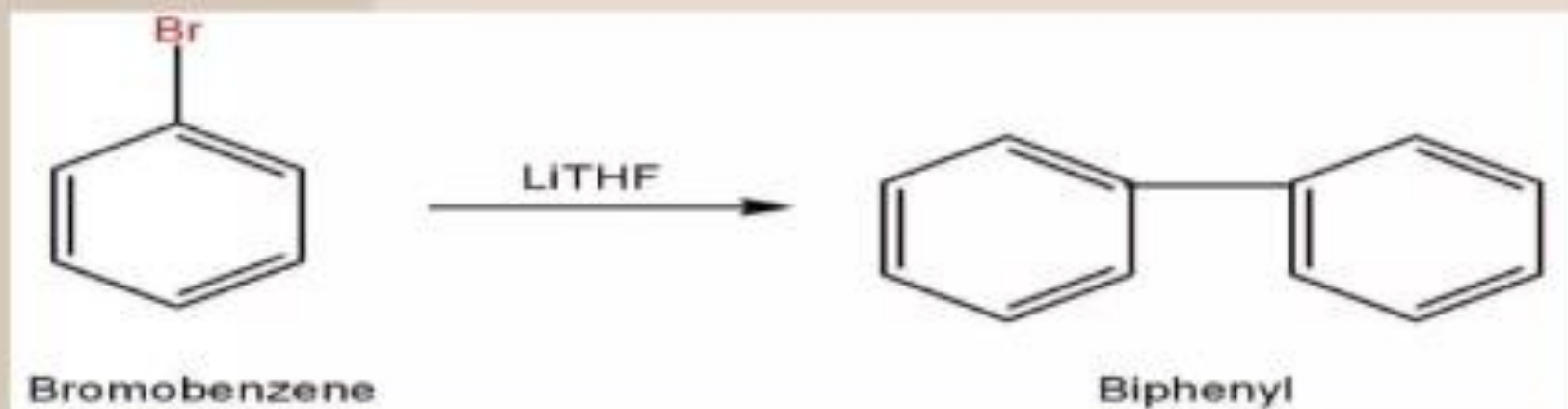
Ex : methyl 1-2,4-dimethylbenzoate on saponification (20KHz) gives 2,4 dimethyl benzoic acid 94% compared to 15% yield by normal process of heating with aqueous alkali (60 min).



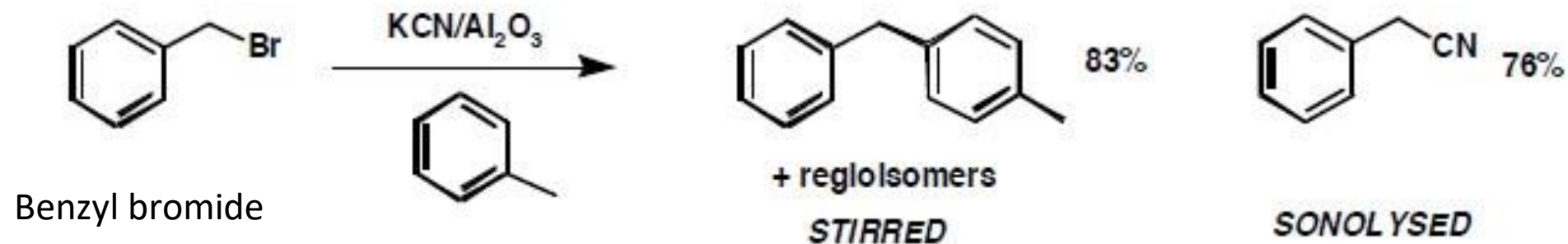
- Cannizzaro reaction: Under heterogeneous conditions catalyzed by barium hydroxide is considerably accelerated by low intensity ultrasound. The yield 100% after 10 min where as no reaction is observed without the use of ultrasound.



- Ullmann-type coupling reactions: The Ullmann-type coupling reaction occurs at a lower temperature and shorter time in almost quantitative yield with probe sonication.



A specific nature of sonochemistry is suggested *Ando et al JCSCC, 1984, p439*



Sonication seems to obey some rules of its own

Sonolsomerization

