4. GREEN CATALYSIS & GREEN SYNTHESIS

4.1 HETEROGENEOUS CATALYSIS (USE OF ZEOLITES, SILICA, ALUMINA SUPPORTED CATALYSIS)

The catalysis in which the phase of catalyst is different from phase of the reactants or products. The history of heterogeneous catalysis began with the synthesis of sulfuric acid in the 18th century, well before the word catalysis was coined and its concept defined. Generally heterogeneous catalysis involves gas–solid or liquid–solid systems in which catalyst is in solid phase and reactants are in fluid phase (gas or liquid). It is a surface phenomenon, and it involves adsorption of gaseous reactants on solid catalyst. The main advantage of it is relative ease of separation of reactants/products/catalysts. Further, the catalysts are more tolerant of extreme operating conditions than their homogeneous equivalents.

List of Heterogeneous Catalytic Reactions

Type of reaction	**Reactants**	**Catalysts**	**Products**
Ammonia synthesis (Haber Process)	$N_2 + H_2$	Fe promoted with Mo	NH_3
Ammonia oxidation	$NH_3 + O_2$	Pt-Rh	NO used in manufacture of HNO_3
Oxidation of sulfur oxide (Contact Process)	$SO_2 + O_2$	V_2O_5 or Pt	SO_3 used in manufacture of oleum & sulfuric acid
Hydrogenation of oils	Unsaturated oil + H_2	Ni	Saturated oil
Cracking	Various petroleum fractions	Silica, alumina, and combination with molecular sieves	Wide range of compounds
Polymerization	Ethylene	$AlR_3 + TiCl_4$	Polyethylene
Dehydrogenation	Ethylbenzene	Iron oxide or chromia alumina	Styrene

Mechanism of Heterogeneous Catalysis

A heterogeneous catalytic reaction involves the following processes:

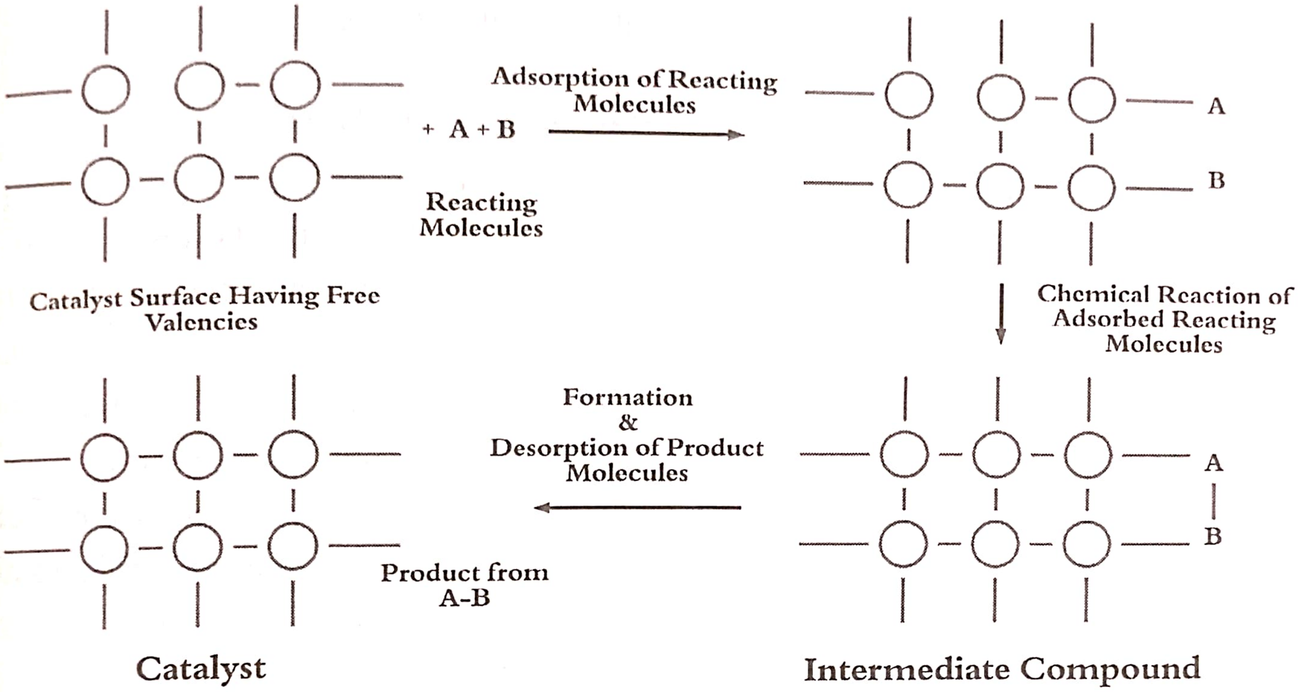
a) ***Diffusion*** of reactants from a fluid phase to solid surface.

b) Adsorption of reactants onto a solid surface (***physisorption***).

c) Surface reaction of adsorbed species (***chemisorption***).

d) ***Desorption*** of products from the solid surface.

e) ***Diffusion*** of products from the solid surface into the fluid phase.



Heterogeneous Catalysis in Green Chemistry

Heterogeneous catalysis offers many green chemistry benefits and addresses the goals of green chemistry by providing the following:

- Use of less toxic materials (Principle No. 3).
- Easy separation of product and catalyst.
- Lower energy requirements and energy saving (Principle No. 6).
- Eliminating the need for separation of products by distillation or extraction (Principle No. 8).
- Catalytic versus stoichiometric amounts of materials (Principle No. 9).
- Increased selectivity.
- Decreased use of processing and separation agents.

Applications of Heterogeneous Catalysis

In recent decades, the field of heterogeneous catalysis expanded rapidly. Now, heterogeneous catalysis has the applications in many fields. The applications are:

- Synthesis of bulk chemicals.
- Conversion of renewables to chemicals and materials.
- Oil refining process.
- Conversion of petroleum and natural gas into cleaner and more efficient fuels.
- Production of alternative fuels such as hydrogen and biofuels.
- Treatment of harmful gases and particles emitted into the atmosphere by human activities.
- Treatment of organic pollutants present in drinking water.

Zeolites, Mesoporous Silica and Alumina Supported Catalysis

Zeolites are microporous, three-dimensional crystalline solids of hydrated aluminosilicate minerals made from interlinked tetrahedra of alumina (AlO_4) and silica (SiO_4). Microporous zeolites (pore size < 2nm), mesoporous silica and alumina (pore size of 2 to 50 nm) are widely used as heterogeneous catalysts. These solids have been used as heterogeneous catalysts in the fields of petroleum refining, cracking, isomerization, synthesis of hydrocarbons, synthesis of fine chemicals and environmental remediation.

Zeolites are ideal heterogeneous catalysts for gas phase reactions conducted at temperature higher than 300 °C due to their unique structure, thermal and chemical stability. Zeolites, silica and alumina exhibit Lewis acidity due to containing bi-or trivalent cations in the framework, Bronsted acidity is due to containing protons and Lewis basicity is due to presence of oxygen on framework. Hence, these can act as solid acid and base catalysts and are used in acid-catalyzed and base-catalyzed reactions.

Use of Zeolites, Mesoporous Silica and Alumina Supported Catalysis

1. Acid-catalyzed reactions

- ***Alkylation Reactions:*** Gas phase alkylation of benzene and ethylene in presence of shape-selective acidic ZSM-5 zeolite forms styrene. Mesoporous silica and alumina are also used as catalysts in alkylation reactions.
- ***Fluid Catalytic Cracking (FCC):*** It is one of the most important processes in oil refining. Zeolites, silica and alumina are used in FCC in the production of gasoline from petroleum by cracking.
- ***Oligomerization Process:*** These catalysts play a crucial role in the oil refining industry in the production of oligomers such as liquid paraffins, plasticizers, and fuels.

- ***Friedel-Crafts Acylation:*** These are used in acylation due to their tuned acidity, shape selectivity, and high stability.
- ***Cycloaddition of CO_2 into Epoxides:*** These are used in cycloaddition of CO_2 with epoxide which forms five-membered cyclic carbonates.
- ***Ring Opening of Epoxides:*** These catalysts are used in ring opening of epoxides with nucleophiles such as amines and alcohols.

2. *Base-catalyzed Reactions*

In these catalysts, the protons and exchangeable sites are the acid sites. The oxygens of the framework are the basic sites. These are used in base catalyzed Knoevenagel condensation reaction of aldehyde with active methylene compounds.

3. *Oxidation Reactions*

These materials in their pure state can't perform oxidation reactions. The zeolites with transition metals on the framework have exhibited catalytic performance in oxidation of several organic compounds using H_2O_2 as an oxidizing agent. The redox property of porous materials is due to containing transition metal ions such as Ti^{4+}, V^{4+}, Sn^{4+}, Zr^{4+}, Fe^{3+}, Cu^{2+}, etc. on the framework.

4. *Hydrogenation*

These catalysts integrated with transition metals (Ni, Pd, Pt, Ru, Ir, etc.) into their framework are used in the hydrogenation of alkenes with molecular hydrogen.

4.2 BIOCATALYSIS

Biocatalysis is the use of natural substances to accelerate rate of the chemical reactions. The natural substances which speedup chemical reactions are called as biocatalysts. These are derived from renewable resources which are biocompatible, biodegradable, and non-hazardous. Biocatalysis fits very well with the principles of green chemistry and follows 10 out of 12 principles of green chemistry.

Advantages of Biocatalysis

- Most of the chemical reactions are carried out in aqueous medium at ambient temperature and pressure.

- The biocatalytic reactions generally take place in single step.
- No need of protection and deprotection of functional groups in biocatalytic reactions.
- The biocatalytic reactions are very fast.
- Biocatalytic reactions are stereospecific, chemoselective, regioselective and stereoselective.

Enzymes

The most commonly used biocatalysts are enzymes. Most of the enzymes are proteins that catalyze chemical reactions in our body. Enzymes are easily available natural substances and enzyme catalysis is an important tool in green synthesis.

Types of Enzymes

There are six main types of enzymes: Oxidoreductases, transferases, hydrolases, lyases, isomerases, and ligases.

1. ***Oxidoreductases:*** These enzymes catalyze oxidation-reduction reactions by direct oxidation with O_2 (**oxidases**) or by transferring hydrogen from one substrate to another substrate (**dehydrogenases**).
2. ***Transferases:*** This group of enzymes catalyze the transfer of a functional group from one substrate to another substrate.
3. ***Hydrolases:*** These enzymes catalyze hydrolysis of a compound.
4. ***Lyases:*** This class of enzymes catalyzes breakdown of a covalent bond without using water or oxidation. These can catalyze addition and elimination reaction.
5. ***Isomerases:*** These enzymes catalyze isomerization of reactants into structural or optical isomers.
6. ***Ligases:*** These enzymes catalyze the formation of covalent bond between two large molecules.

List of Biocatalytic Reactions

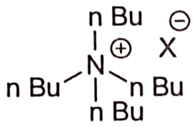
Main category	**Subcategory**	**Type of reaction catalyzed**
Oxidoreductase	Oxidases	Oxidation of substrate
	Reductases	Reduction of substrate
	Dehydrogenases	Removal of hydrogens
Transferases	Transaminases	Transfer amino group between substrates
	Kinases	Transfer phosphate group between substrates
Hydrolases	Lipases	Hydrolysis of ester linkages in lipids
	Proteases	Hydrolysis of amide linkages in proteins
	Nucleases	Hydrolysis of sugar-phosphate ester bonds in nucleic acids
	Carbohydrases	Hydrolysis of glycosidic bond in carbohydrates
	Phosphatases	Hydrolysis of phosphate-ester bonds
Lyases	Dehydratases	Removal of H_2O from substrate
	Decarboxylases	Removal of $CO_2$from substrate
	Deaminases	Removal of NH_3 from substrate
	Hydratases	Addition of H_2O to substrate
Isomerases	Racemases	Interconversion of enantiomers
	Mutases	Transfer of a functional group from one position to another in the same molecule
Ligases	Synthetases	Formation of a new bond between two substates
	Carboxylases	Formation of a new bond between a substate and CO_2

4.3 PHASE TRANSFER CATALYSIS

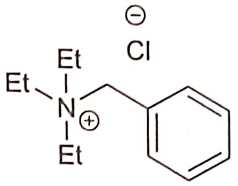
Phase transfer catalysis is a heterogeneous catalysis. A catalyst which accelerates rate of the reaction by facilitating migration of a reactant from one phase to another phase is called as phase transfer catalyst. The acceleration of a reaction by phase transfer catalyst is known as phase transfer catalysis (PTC).

Quaternary ammonium salts and **phosphonium salts** are PTCs for anionic reactants. **Crown ethers** and **cryptands** are PTCs for cationic reactants. The PTC-ion system has a hydrophilic interior containing the ion and a hydrophobic exterior. Among PTCs, the quaternary ammonium salts are the cheapest, hence widely used in the industry.

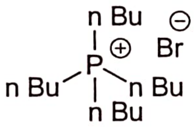
Typical PTCs



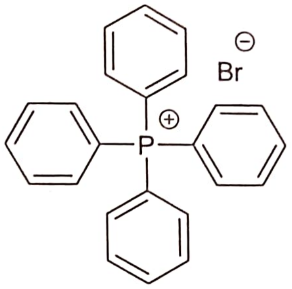
X = Br, Tetrabutylammonium bromide (TBAB)
X = F, Tetrabutylammonium fluoride (TBAF)
X = OH, Tetrabutylammonium hydroxide (TBAH)



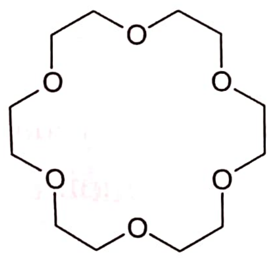
Benzyltriethylammonium (TEBA) chloride



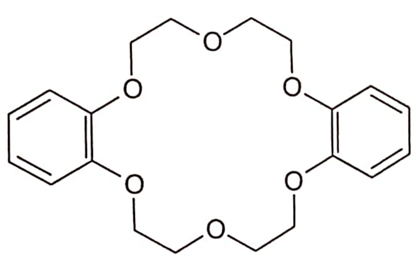
Tetrabutylphosphonium bromide



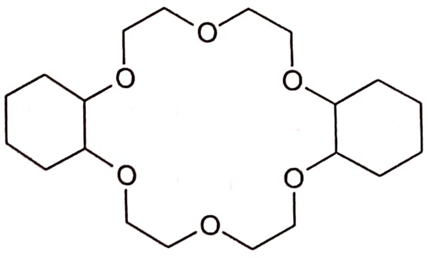
Tetraphenylphosphonium bromide



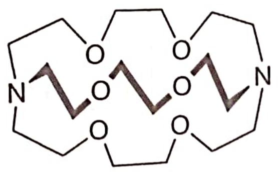
18-crown-6



Dibenzo-18-crown-6



Dicyclohexyl-18-crown-6



Polyether cryptand [2.2.2]

Mechanism of PTC

Phase transfer catalysis involves transfer of species from one phase to another phase by the catalyst and reaction of transferred species with reactants. The PTC mechanism contains the following steps:

1. The dissolved catalyst quaternary ammonium halide in the aqueous phase (Q^+X) undergoes anion exchange with the anion (Y^-) of the reactant dissolved in the aqueous solution.
2. The ion-pair formed (Q^+Y^-) can cross the liquid-liquid interface due to its lipophilic nature and diffuses into the organic phase (phase transfer).
3. The anion (Y^-) in the organic phase participates in nucleophilic substitution reaction with the organic reagent (RX) and forms desired product (RY).
4. Later, the catalyst (Q^+X^-) diffuses into the aqueous phase through the liquid phase boundary (phase transfer) and the cycle continues.

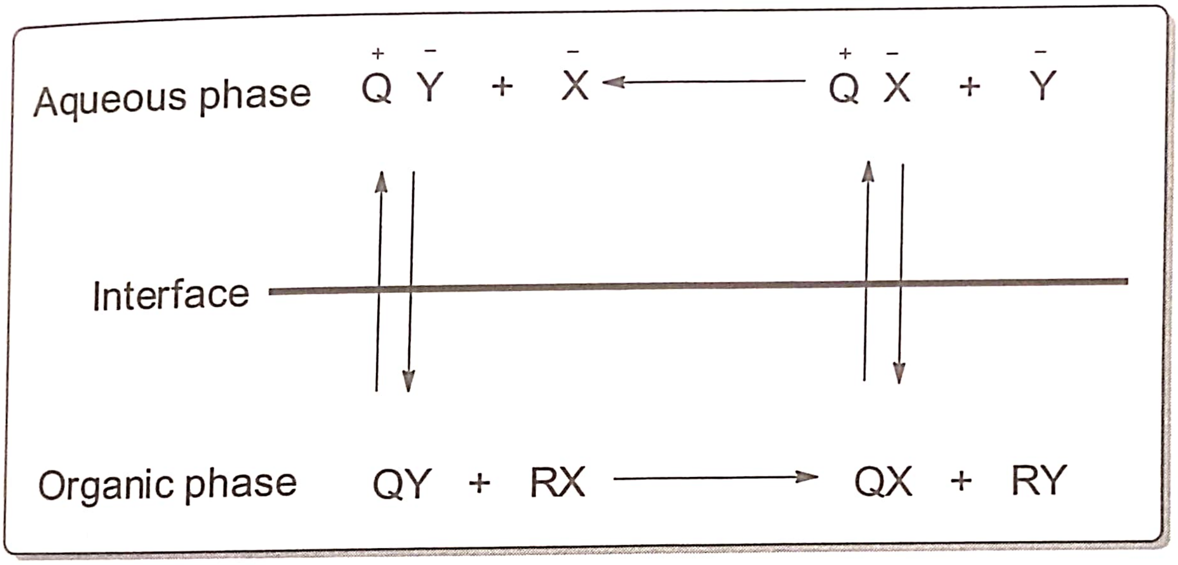


Fig. 4.3 Mechanism of phase transfer catalysis

Advantages of PTC

- It accelerates rate of the reaction and reduces reaction time.
- It improves yields of the reactions.
- Minimizes the formation of byproducts.
- Eliminates expensive and dangerous solvents.
- Eliminates the need of expensive raw materials and minimizes waste.
- Less side reactions.
- Solvent free synthesis is possible.
- It is useful in green chemistry .

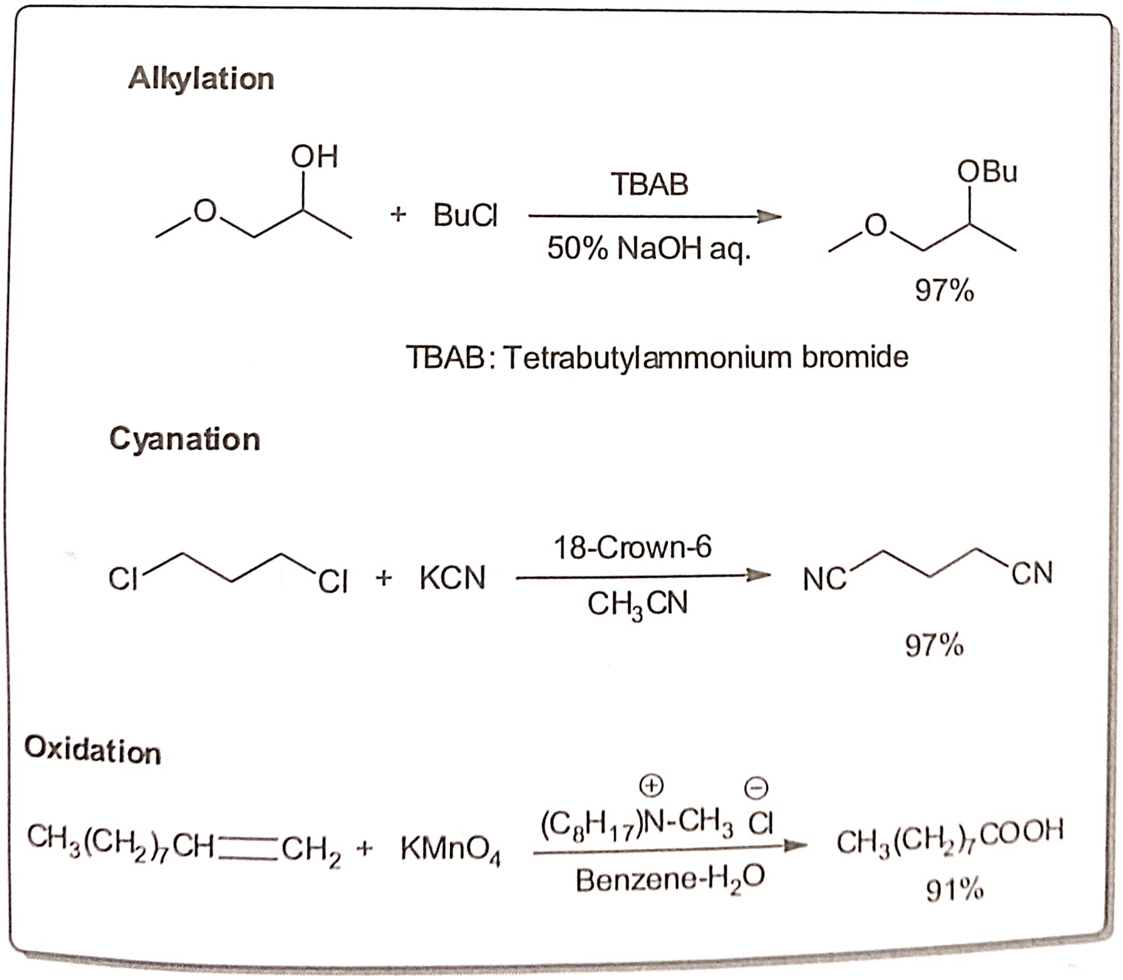
Disadvantages: The main disadvantage of PTC is the need to separate the catalyst from the product in organic phase.

PTC in Green Chemistry: The PTC involves use of less amount organic solvent, formation of less hazardous byproducts, good yield. The wide use of PTC in aqueous system allows more enhanced environment friendly green synthesis and solvent free synthesis.

Applications of PTC

PTC is particularly useful for reactions of organic anions with nonpolar organic reactants. It is also applicable for generating intermediates such as carbenes, nitrenes, and organometallic reagents. PTCs have synthetic application in the following reactions:

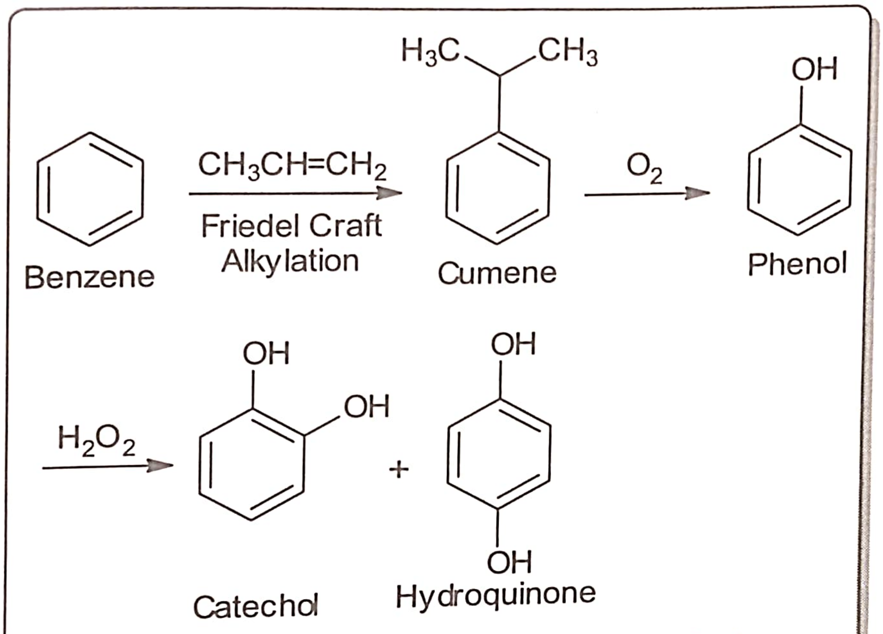
- ***Alkylations:*** The most common application of PTC is alkylations.
- Nucleophilic substitution reactions.
- Aldol and related condensations.
- Carbenes reactions.
- Oxidations and reductions.
- Organometallic transformations.



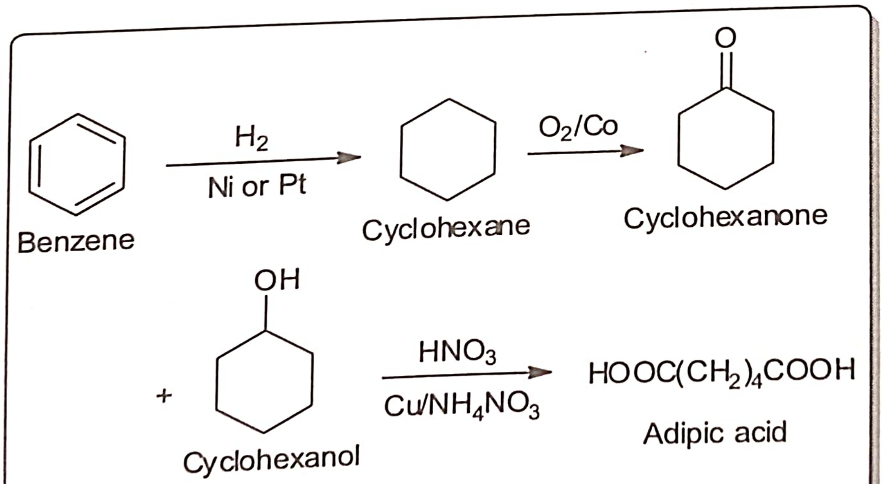
4.4 GREEN SYNTHESIS

4.4.1 Synthesis of Catechol and Adipic Acid

Conventional Synthesis: Both catechol and adipic acid are made conventionally from carcinogenic benzene which causes environmental and health problems. The non-renewable petrochemicals are the sources of benzene. The synthesis of adipic acid generates nitrous oxide (N_2O) as a by product, which is a potential greenhouse gas and ozone depletion substance.

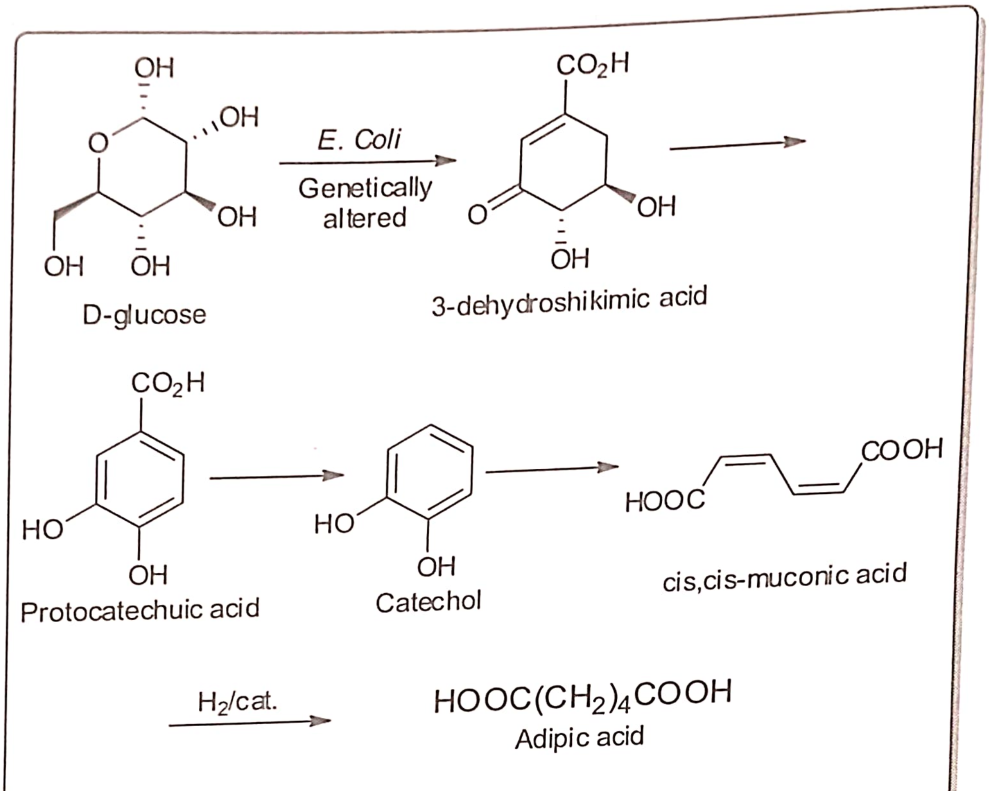


Conventional Synthesis of Catechol



Conventional Synthesis of Adipic acid

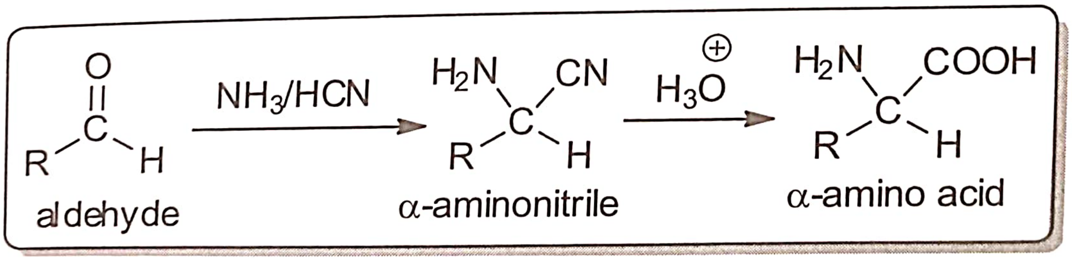
Green Synthesis: Both catechol and adipic acid are made environmentally benign synthesis using **D-glucose** as a starting material and a **biocatalyst** (genetically modified microbe, **Escherichia coli**). The starting material D-glucose is a non-toxic and a renewable resource. Further, it uses water as a solvent, which is a green solvent.



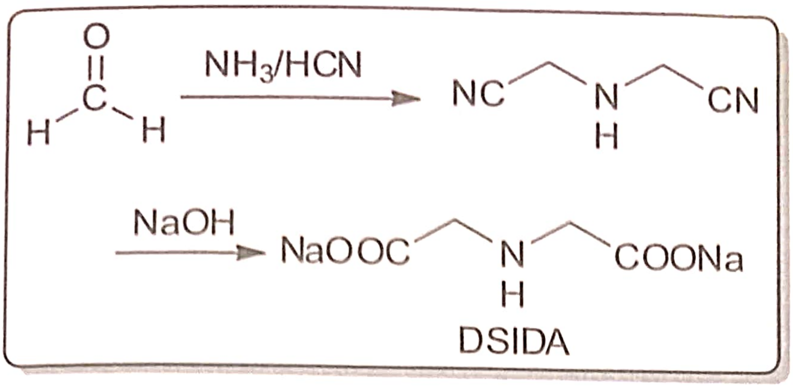
Green Synthesis of Catechol & Adipic acid

4.4.2 Synthesis of Disodium Iminodiacetate (DSIDA):

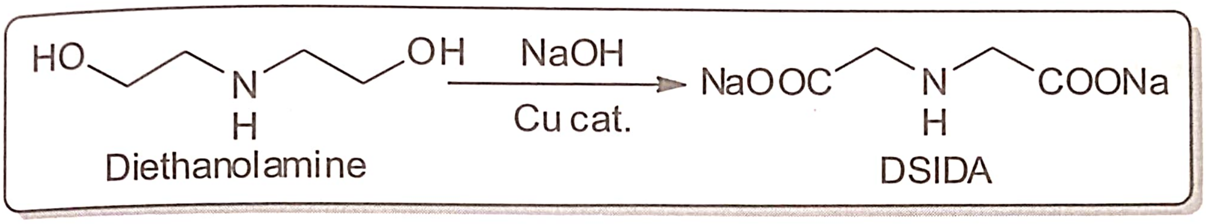
The reaction of aldehyde with ammonia in presence of cyanide followed by hydrolysis forms amino acid. It is known as Strecker synthesis.



Conventional Synthesis: Disodium iminodiacetate (DSIDA) is an intermediate in herbicide made by Monsanto. It is synthesized conventionally using formaldehyde, ammonia, hydrogen cyanide and sodium hydroxide. The **HCN is hazardous** chemical which needs special treatment to minimize the risk to workers and environment.



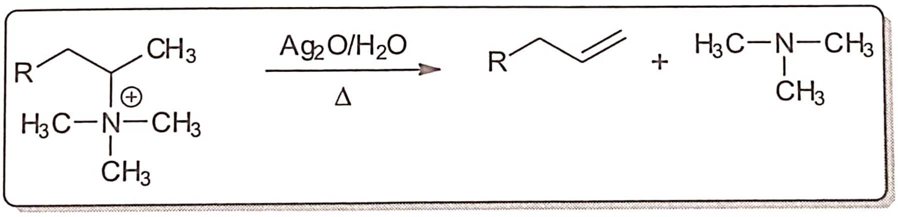
Green Synthesis: An alternative green synthesis was developed by Monsanto by avoiding HCN and formaldehyde. It is synthesized by treating diethanolamine with NaOH in presence of Cu catalyst.



4.5 MICROWAVE ASSISTED REACTIONS IN WATER

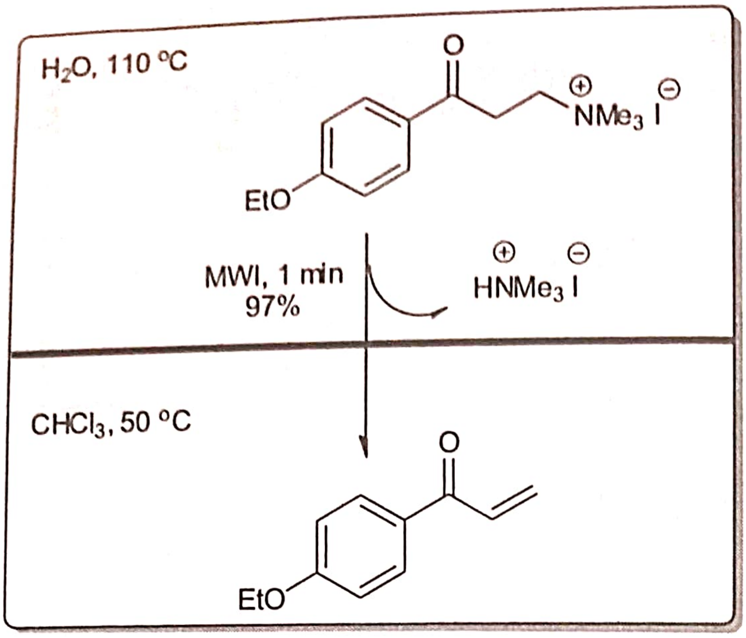
4.5.1 Hofmann Elimination

The elimination reactions of quaternary ammonium salts produce least stable alkene. It is known as Hofmann elimination.



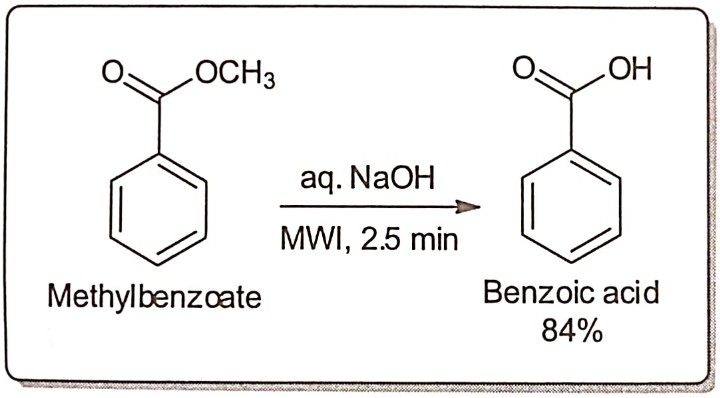
Conventional Method: In conventional method, generally quaternary ammonium salts are heated at high temperature and the yield of the product is low and are associated with long reaction period.

Green Method: The microwave assisted Hofmann elimination reaction using two-phase heterogeneous water/chloroform system has excellent **yield (97%)** of product with shorter reaction period (**1 min**). The selective heating of solvents by microwave radiation leads to higher yields and shorter reaction times. The temperatures of the aqueous and chloroform phases were 110°C and 50 °C respectively, due to differences in the dielectric properties of the solvents. This temperature difference avoids decomposition of the final product in the organic phase.



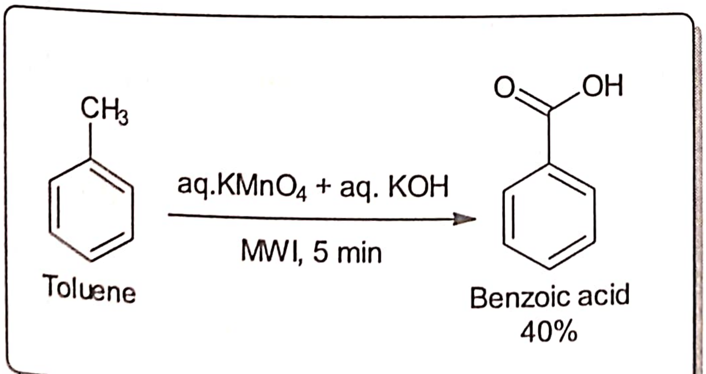
4.5.2 Methyl Benzoate to Benzoic Acid

The hydrolysis of methyl benzoate in aqueous sodium hydroxide under microwave conditions forms benzoic acid with good yield (84 %) and the reaction is completed in shorter time (2.5 min).



4.5.3 Oxidation of Toluene:

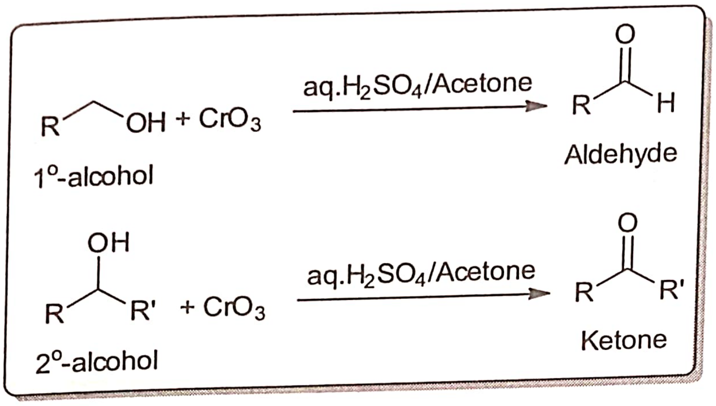
The oxidation of toluene with the solution of aqueous potassium permanganate and aqueous potassium hydroxide forms benzoic acids. In conventional method, under normal conditions, the reaction takes 10-12 h while in green synthesis, under microwave conditions it takes **5 min**, and the yield of the benzoic acid is 40%.



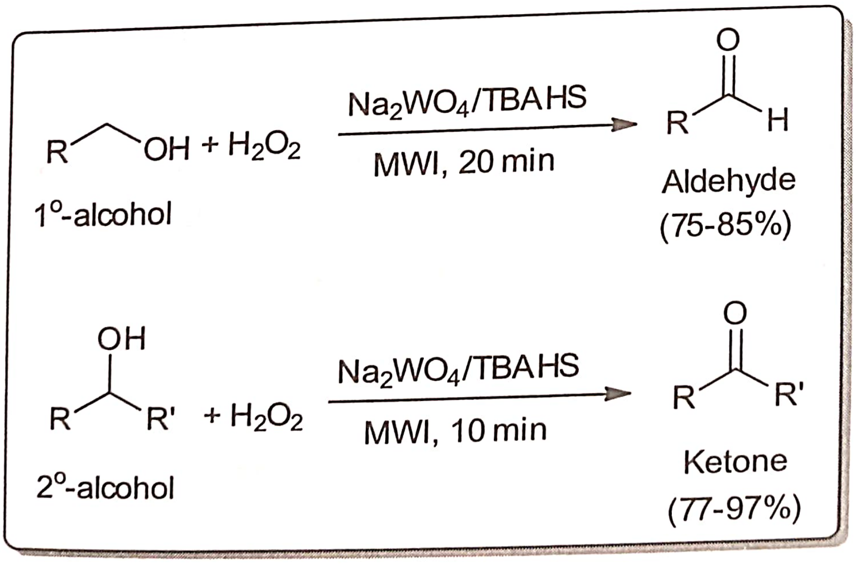
4.5.4 Oxidation of Alcohols:

The oxidation of primary and secondary alcohols forms aldehydes and ketones respectively.

Conventional Method: In conventional method, metal oxides and peracids such as CrO_3, MnO_2,etc. are used for the conversion of alcohols into carbonyl compounds. The oxides and peracids of heavy metals severely impact environmental and natural sources mainly water and soil. It can irritate nose, throat and lungs. The contact of metal oxides may cause skin ulcers.



Green Method: The replacement of oxides and peracids of metals by hydrogen peroxides is environmentally friendly since it forms water as a byproduct. The microwave irradiated oxidation of alcohols under organic/aqueous biphasic conditions using 30% hydrogen peroxide in the presence of sodium tungstate (catalyst) and tetrabutylammonium hydrogen sulfate (TBAHS) as a phase transfer catalyst forms carbonyl compounds with high yield and short reaction times.

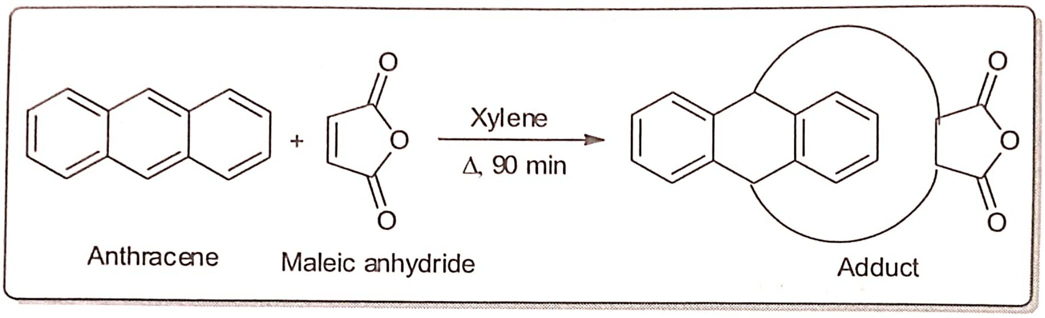


4.6 MICROWAVE ASSISTED REACTIONS IN ORGANIC SOLVENTS

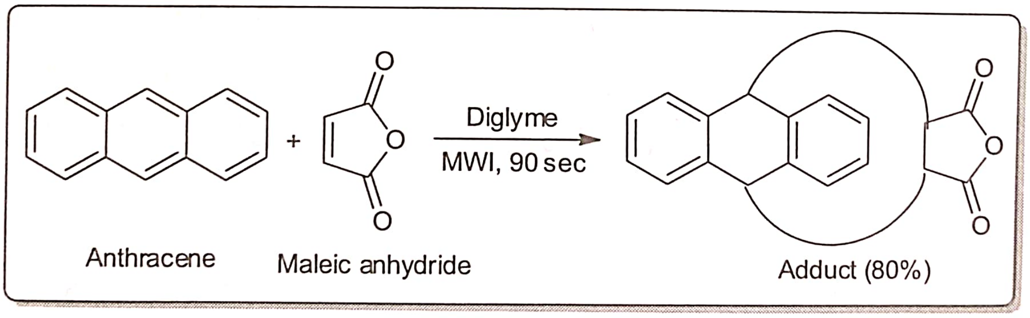
4.6.1 Diels-Alder Reactions

The Diels-Alder reaction is a thermal [4+2] π cycloaddition reaction between conjugated diene and reactive alkene or alkyne (dienophile) which forms cyclohexene derivative.

Conventional Method: The Diels-Alder reaction between anthracene (diene) and maleic anhydride (dienophile) in presence of high boiling temperature solvent xylene forms an adduct of six membered ring. Under normal conditions, the reaction requires reflux period of 90 min.

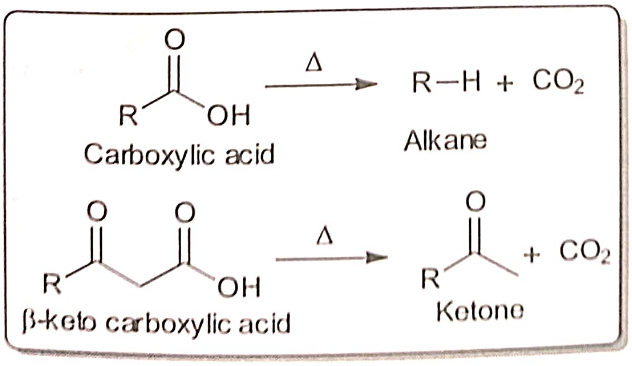


Green Method: The same reaction under microwave conditions in presence of diglyme solvent, the adduct is formed in very less tome (90 sec) with high yield (80%).

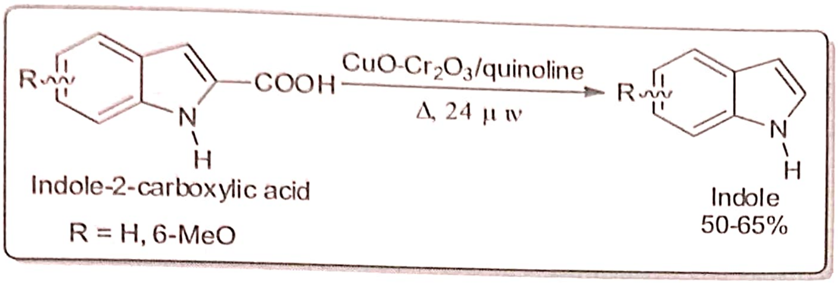


4.6.2 Decarboxylation Reactions

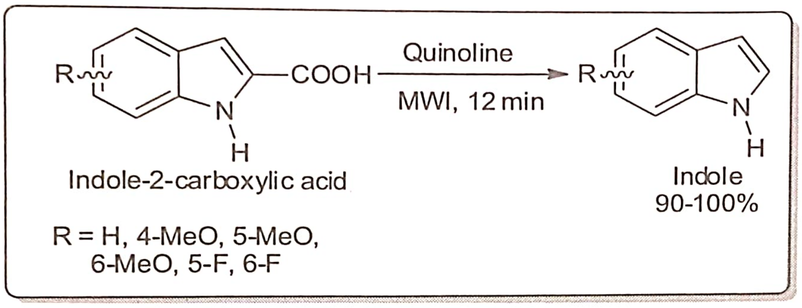
Loss of carbon dioxide (CO_2) is called as decarboxylation. Simple carboxylic acids rarely undergo decarboxylation. Carboxylic acids or esters with carbonyl group at beta position readily undergo thermal decarboxylation.



Conventional Method: The conventional decarboxylation of indole-2-carboxylic acids involves refluxing in quinoline in presence of copper chromite and the yields are low (50-65%).

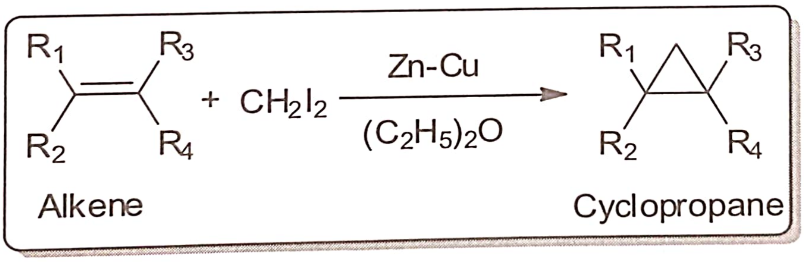


Green Method: The same decarboxylation reactions in absence of copper chromite under microwave irradiation take place in much shorter time (12 min) with high yields (90-100%).

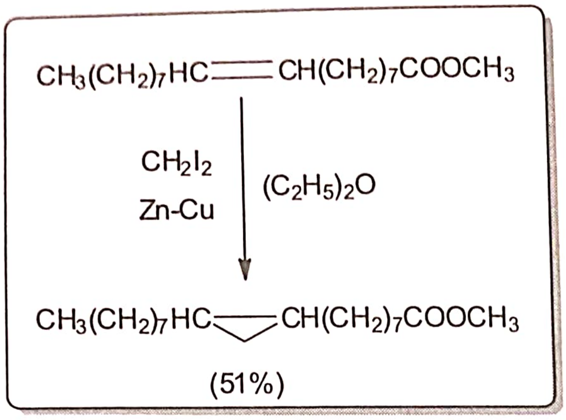


4.7. SONO CHEMICAL SIMMONS–SMITH REACTION:

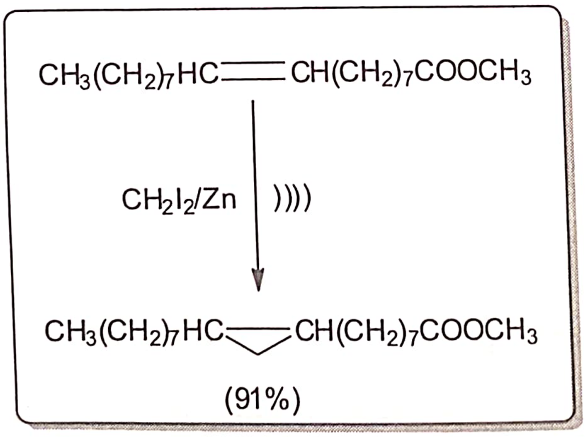
A reaction of alkene with diiodomethane and zinc-copper couple or iodomethyl zinc iodide (ICH_2ZnI) forms cyclopropane ring. It is called as Simmons-Smith reaction.



Conventional Method: The conventional method uses activated zinc and CH_2I_2 to form cyclopropane ring. It has several experimental drawbacks such as sudden release of heat after some time, formation of foam and the difficulties in removing finely divided metal from the reaction products. Generally, zinc is activated by using it in the form of a zinc–silver or zinc–copper couple or using iodine or lithium in conjunction with the metal. The yield of the reaction is low (51%).



Green Method: In this method, zinc is activated sonochemically by using ultrasound. The reaction between sonochemically activated zinc and methylene iodide forms carbene which adds on alkene and forms cyclopropane with high yield (91%). The experimental difficulties in conventional method have been eliminated using a sonochemical procedure where no special activation of the zinc is required, and good yields (91%) are obtained using zinc metal in the form of rods or foil.



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