Module 5 *Green Chemistry* *Prof Varsha Pawar*

Introduction:

Green Chemistry which is also called as Clean Chemistry, sustainable chemistry or Environmental Benign Chemistry is a highly effective approach to design harmless processes that reduce, recycle or eliminate the use and production of various hazardous substances by applying innovative scientific solutions to real world environmental situations to improve the environment and our quality of life.

Q1) Define Green Chemistry and give its significance.

Ans) **Definition**: Green Chemistry is the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical product. **OR**

Green chemistry is defined as an invention, design and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances.

Significance of Green chemistry:

1. A novel approach that blends the application of chemistry with economic growth and environmental preservation.
2. To develop strategy for sustainable chemical process industries.
3. Achieve conservation of limited resources through cost effectiveness and pollution prevention.
4. Therefore basic axiom of Green chemistry is to design product and processes that reduce or eliminate the generation of all wastes

Q2) List the Twelve principles of Green Chemistry. Explain each in detail.

Ans) 1. Prevention of waste formation

2. Atom Economy
3. Non-hazardous chemical synthesis
4. Designing safer chemical and products
5. Use of Safer solvents and auxiliaries
6. Design for Energy efficiency
7. Use of renewable feedstock's
8. Reduce chemical derivatives
9. Use catalysts, not stoichiometric reagents.
10. Design for degradation
11. Real -time analysis for pollution prevention
12. Inherently safer chemistry for accident prevention.

1.Prevention of waste:

- This principle focuses on the reduction in the amount of waste generated during any chemical process, so as to reduce environmental and health impact as well as to save the natural resources such as air, water and soil.
- The waste if discharged in air, sea or land not only causes pollution but also requires expenditure for cleaning up.
- Hence it is better to minimize the generation of waste during the synthesis stage.
- The manufacturing sectors need to take proper initiatives regarding the reduction of source, reuse of products, as well as the disposal of hazardous wastes generated.
- Thus it is better to prevent the generation of waste during synthesis rather than treating them after generation.

2. Atom Economy:

- The design of the synthesis of the product should be such that all the chemicals/materials used in the process must be converted into the products to the maximum extent.
- The byproducts/undesired products released from chemical reactions are converted as waste which causes the problem of pollution and disposal and because of this the process becomes uneconomical.
- Green Chemistry requires that new processes should be designed in such a way that most of the starting material gets converted into product.(This is called as '**Maximisation of Atom Economy**)
- It should be as high as possible ie100%
- Formula: %Atom Economy = $\frac{\text{Molecular weights of products}}{\text{Total molecular weights of reactants}} \times 100$

3. Less hazardous chemical synthesis:

- The synthetic method should be designed wherever practicable to use and generate substances having little or no toxicity to human health and the environment.
- The starting material selected should be least toxic. Thus eg, pyridine , or B-naphthyl amine being known to be carcinogenic should be avoided as starting materials.
- Instead alternative pathways should be used for synthesis.
- For example: In 1984,due to leakage of MIC (An Intermediate in manufacture of agricultural pesticides ,highly poisonous) at Bhopal there was major casualty and the after effects of the same are still suffered by many.
- Hence green chemistry recommends the design of synthesis to use and generate substances

with little or no toxicity to humans and the environment.

4. Designing safer chemical and products:

- Green chemistry emphasizes to design chemical products to be fully effective, yet have little or no toxicity.
- When any medical formulations are to be put in market, they are put first on trials to check their toxic effects on humans.
- If found to be toxic then alternatives are prepared to decrease the toxicity but maintaining the function of the medicine.
- Similarly in many insecticides like DDT, gamaxene ,aldrin etc which are found to be toxic to humans, the use of these is curtailed and alternatively biological pesticides are more in use.
- Thus green chemistry emphasizes to design chemical products to be fully effective, yet have little or no toxicity.

5. Use of Safer solvents and auxiliaries:

- The use of auxiliary substances like solvents, separating agents etc should be made unnecessary wherever possible and innocuous when used. Instead of common solvents such as acetone, chloroform, benzene, $CHCl_4$, $CHCl_3$ should be avoided.
- If a solvent is necessary, water is a good medium as well as certain eco-friendly solvents that do not contribute to smog formation or destroy the ozone.
- Eg: For dry-cleaning the fabrics, the toxic solvent like perchloroethylene was used, which is replaced during recent years by liquid CO_2.

6. **Design for Energy efficiency:**

- The aim of green chemistry is to increase energy efficiency.
- It can be achieved by use of catalysts and by stopping the use of fossil/gaseous fuels which release solid or gaseous pollutants.
- Alternative substitutes recently used are microwave radiations and ultrasound techniques which require less energy.
- Energy efficiency can be increased by:

  a) Proper heat transfer

  b) Minimum wastage of energy during the process.

- Many chemicals are produced by fermentation process where energy requirement is low and also the products are less harmful.

7) Use of renewable feedstock's:

- The raw material should be renewable (obtained from agricultural products or the wastes of other processes) and not depleting (made from fossil fuels like petroleum, natural gas or coal).Eg. Synthesis of Adipic acid.
- Adipic acid can be prepared by a new method using glucose obtained from corn-starch or cellulose .This is a green process because it replaces benzene which is a known carcinogen as starting material for production of Adipic acid.

8) Reduce chemical derivatives:

- During synthesis unnecessary derivatisation such as blocking or protecting groups or any temporary modifications should be avoided if possible.
- The use of derivatives increases the steps of the process, additional reagents are required and hence it generates more waste products.
- To avoid these effects, alternative reagents are to be used which are more selective.
- Eg. In traditional synthesis of Ibuprofen involves more number of steps and atom economy is low(40%).But in greener method, results in less number of steps with more atom economy (77%) and recoverable catalyst.

9) Use Catalysts, not stoichiometric reagents.

- Selective catalysts are preferred over stoichiometric reagents.
- By using catalysts in reactions, waste can be minimized.
- Catalysts are used in small amounts and can carry out a single reaction many times, whereas stoichiometric reagents which are used in excess work only once.
- Catalytic reactions are faster and requires less energy
- Nowadays, there are many processes which uses nontoxic recoverable catalysts and also biocatalysts.

10) Design for degradation:

- Chemical products should be designed in such a way that they break down to innocuous substances after use so that they do not accumulate in the environment.
- Eg: DDT when used as pesticide, its residues remain in soil for many years causing pollution. The alternative to this is biological insecticides.
- The packing materials like plastics or polystyrene are non-biodegradable and cause solid waste. The alternative to this is biodegradable plastics containing cellulose and packing pellets made up of starch.

11) Real -time analysis for pollution prevention:

- New analytical processes have to be developed to allow online monitoring and control prior to the formation of hazardous substances.
- Eg. Preparation of ethylene glycol in which if the reaction conditions are not monitored perfectly, toxic substances are produced at higher temperature.

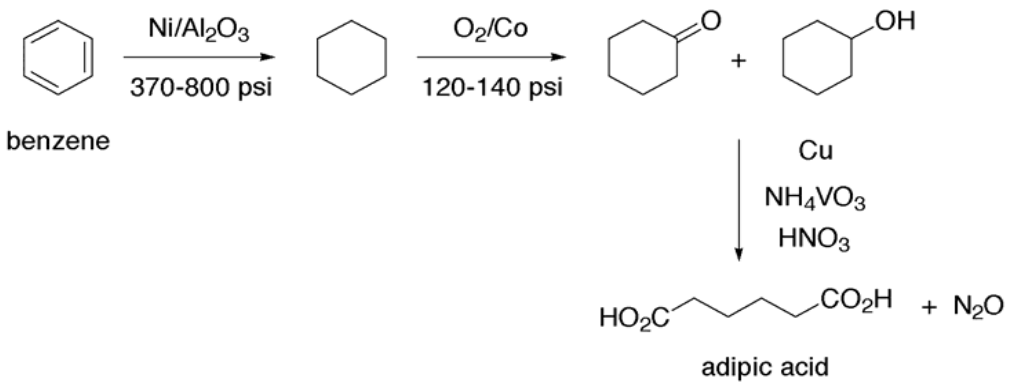
12) Inherently safer chemistry for accident prevention:

- The substances and its forms used in chemical process should be chosen to minimize the potential for the chemical releases, accidents, explosions and fire.
- The use of safer chemicals, minimizing temperature, pressure and using catalysts helps in minimizing the potential of accidents which is desirable.

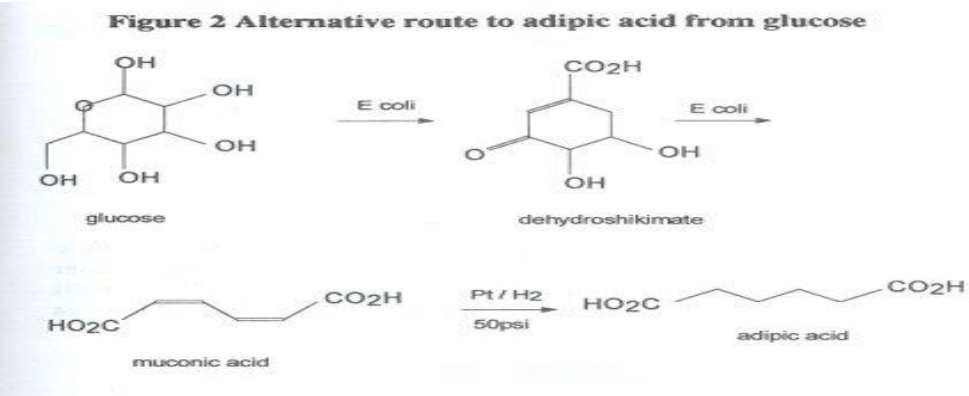
Q3) Explain conventional and greener routes of production of Adipic Acid. Highlight the green chemistry principle involved in the process.

Ans) In the conventional/ traditional pathway, adipic acid is synthesized from benzene, whereas in the greener pathway it is synthesized from D-glucose. Benzene is a highly carcinogenic compound; hence adipic acid synthesized from benzene would also be carcinogenic or toxic in other ways. Hence replacing benzene by D-glucose is safer for health and environment.

A) Traditional Pathway: Using Benzene (Carcinoginic solvent)



B) Greener Pathway :Using glucose (absolutely safe)

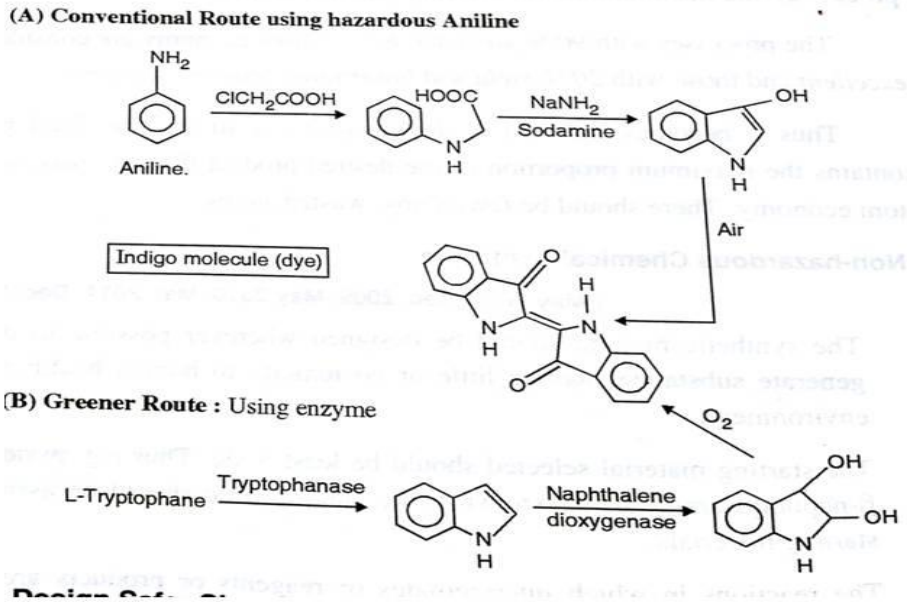


Thus the principle highlighted in this synthesis is the use of renewable feedstock which uses glucose which is absolutely safe instead of benzene which is a fossil fuel based and carcinogenic feedstock.

Q4) Explain conventional and greener routes of production of Indigo. Highlight the green chemistry principle involved in the process.

Ans) Indigo, the dye used to colour blue jeans is synthesized by using Aniline as the starting material which is highly toxic. Moreover, it produces considerable amount of waste salts, thereby causing disposal problems.

A greener way to produce indigo is by raising a crop called **Tryptophan** by enzymatic dehydroxylation, which on successful oxidation imparts indigo colour. It is one of the innovative routes and can lead to five times more yield of indigo than the conventional pathway.



The principle highlighted in the synthesis is Non-hazardous chemical synthesis by using the greener synthesis replacing toxic reagents like Aniline.

Q5) Explain conventional and greener routes of production of Ibuprofen. Highlight the green chemistry principle involved in the process.

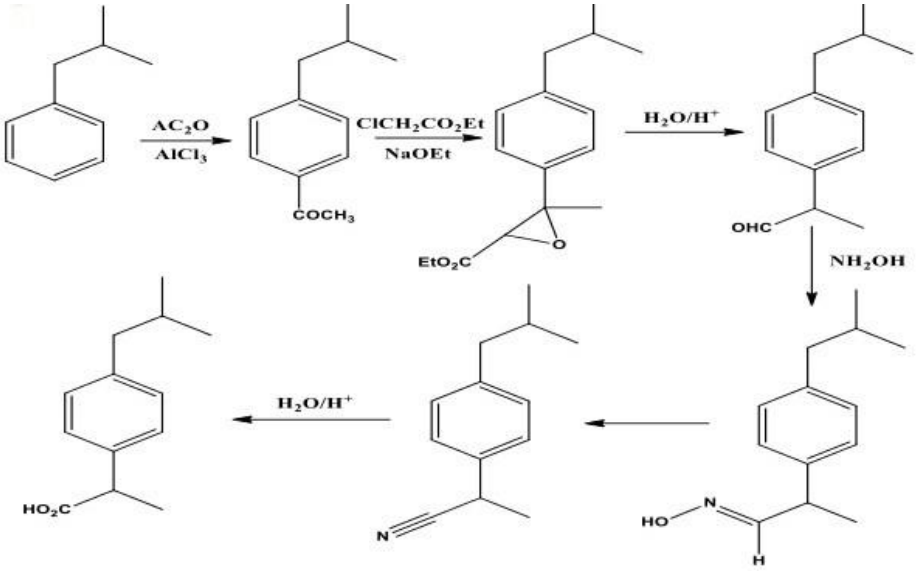
Ans) Ibuprofen is one of the drug used in large quantities for making pharmaceuticals drugs, in particular various types of analgesics (pain killers)

- In the conventional pathway, ibuprofen was originally made in a six step synthesis from the starting material iso-butyl benzene using stoichiometric reagents.
- The greener synthesis is more efficient as it uses only three steps.

- The first step involves the use of anhydrous HF both as catalyst and solvent in Friedal-Craft acylation. The HF is recyclable and the waste is essentially eliminated.
- This is followed by two catalytic processes like hydrogenation and carboxylation both of which are 100% atom efficient.

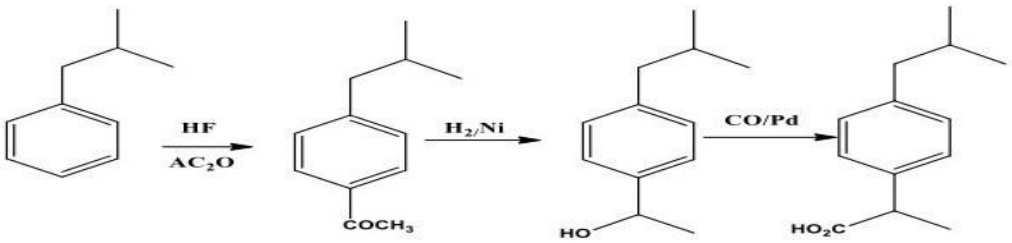
Conventional/Traditional pathway:

Synthesis by the traditional pathway not only involves more number of steps, but also poor atom economy at 40%.



Greener pathway:

The alternative greener method involves lesser number of steps and also employs recovery of strong acid as the catalyst along with a good atom economy at 77%.



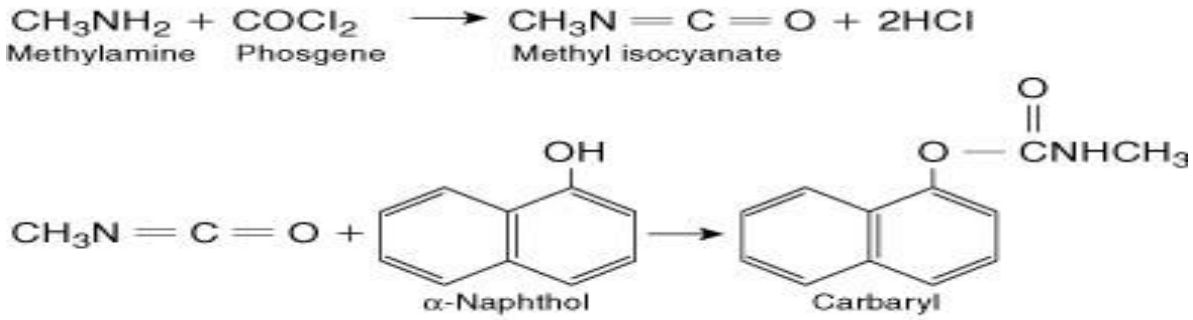
The principle highlighted in this synthesis is Atom Economy and Reduce derivatives as due to greener synthesis the Atom Economy increases from 40% to 70% and also employs lesser number of steps .

Q6) Explain conventional and greener routes of production of Carbaryl. Highlight the green chemistry principle involved in the process.

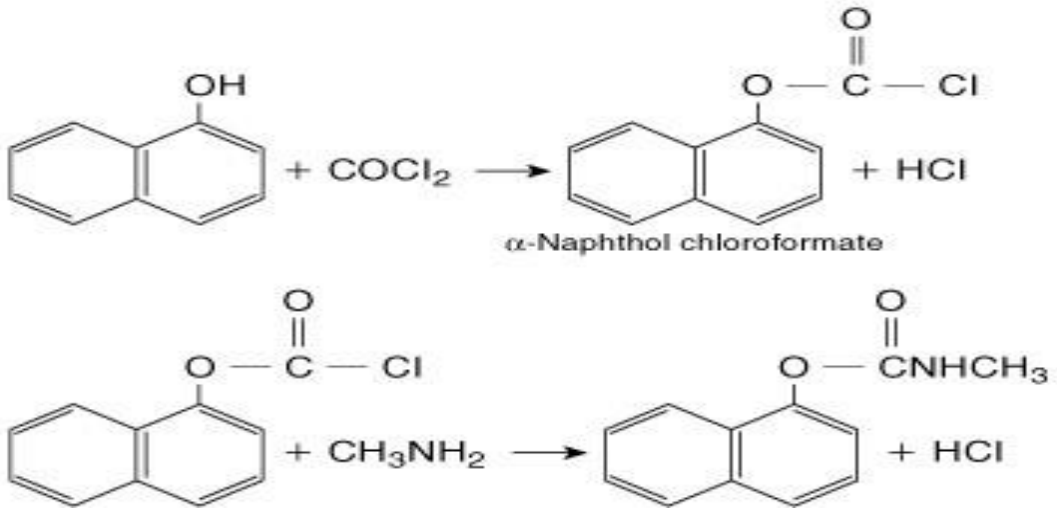
Ans) Carbaryl is chiefly used as an insecticide .This was prepared by traditional method using 1-napthol and methyl isocyanate as reactants. The Bhopal gas tragedy which took place in 1984 due to the release of methyl isocyanate at Union Carbide Subsidiary pesticide plant which released approximately 40 tonnes of toxic Methyl Isocyanate (MIC) gas, exposing more than 5,00,000people.

An alternative reaction pathway is suggested to minimize the use of hazardous materials. In this method 1-naphthol and phosgene are used as reactants to produce 1-naphtholenyl chloroformate. It is then treated with methyl amine to give carbaryl. This alternative process eliminates the formation of methylisocyanate which is highly hazardous.

A) Traditional Pathway



B) Greener Pathway

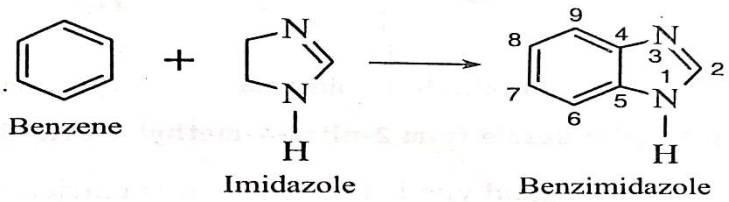


The principle highlighted in this synthesis is ‘Designing safer chemical and products’ as the formation of 1-naphtholenyl chloroformate by greener way eliminates the formation of methylisocyanate which is highly hazardous.

Q7) Explain conventional and greener routes of production of Benzimidazole. Highlight the green chemistry principle involved in the process.

Ans) <u>Synthesis of Benzimidazole.</u>

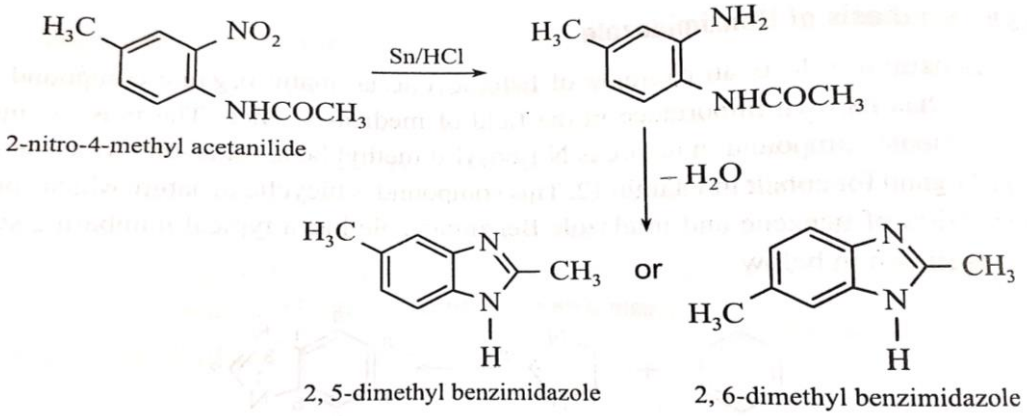
- Benzimidazole is a heterocyclic aromatic compound.
- It is having a variety of therapeutic uses including antitumor, antifungal, antiparasitic, analgesics, antiviral, antihistamine, as well as use in cardiovascular disease, neurology, endocrinology, and ophthalmology.
- The most important compound in nature is N-ribosyl-dimethyl benzimidazole which is highly useful as a ligand for cobalt in vitamin 12.
- Benzimidazole is a bicyclic molecule formed by Benzene and Imidazole which has a typical numbering system as shown below:



Structure of Benzimidazole

a) Conventional (Traditional Pathway)

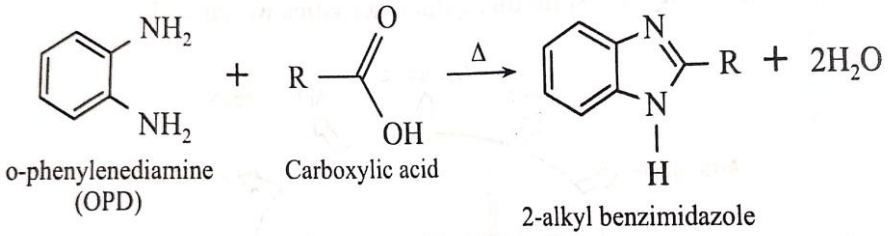
i) The first benzimidazole was prepared by Hoebrecker in 1872, who obtained 2,5-dimethylbenzimidazole or 2,6-dimethyl benzimidazole by the reduction and dehydration of 2-nitro-4-methylacetanilide.



Synthesis of Benzimidazole from 2-nitro-4-methyl acetanilide by Hoebrecker

ii) Benzimidazole is prepared practically by using benzene derivatives possessing nitrogen-containing functions ortho to each other.ie. the starting material o-Phenylenediamines (OPD) reacts readily with the most carboxylic acids to give 2-substituted benzimidazoles usually with a good yield.

The reaction is carried out usually by heating together on a steam bath under reflux or at an elevated temperature in a sealed tube.



General Laboratory method of synthesis of benzimidazole

Disadvantages:

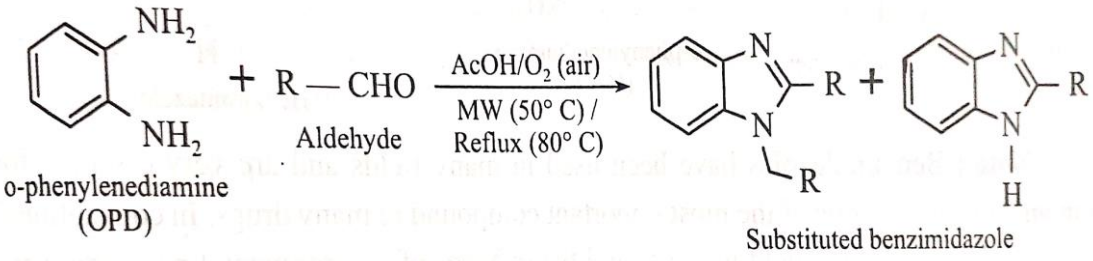
It causes severe environmental problems like waste generation and its disposal. Hence it leads to the significant increase in the E(environmental)factor (kilograms of waste per kilogram of product) which represents the actual amount of waste produced in the process.

b) Alternative Greener Pathway:

In order to overcome the problem associated with the conventional route, scientist tried to synthesize Benzimidazole with the help of green chemistry route by following green chemistry principles. Some examples of Green synthesis are explained below:

i) By condensation of o-phenylene diamine (OPD) under microwave assistance:

Benzimidazole is synthesised by condensation of o-Phenylenediamines (OPD) promoted by acetic acid under microwave. It was observed that a mild, manipulatable procedure, Eco-friendly and green aspects avoiding hazardous solvents, shorter reaction times and high yields of the products are the advantages of this method.

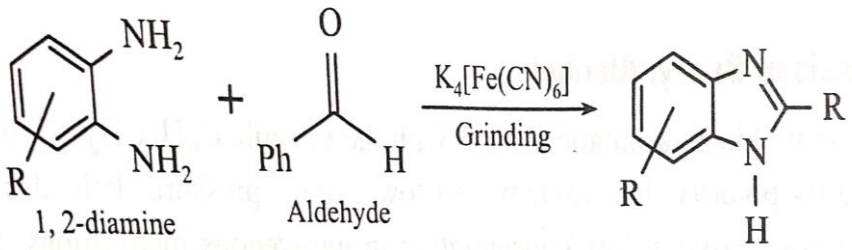


Microwave assisted benzimidazole synthesis from o-phenylene diamine (OPD)

ii) By treatment of 1,2diamine with aldehydes using K4[Fe(CN)6]:

Solvent free synthesis of 1,2diamine with aromatic aldehydes using metal coordinate complex like potassium ferrocyanide $K_4[Fe(CN)_6]$ has been synthesized with high yields.

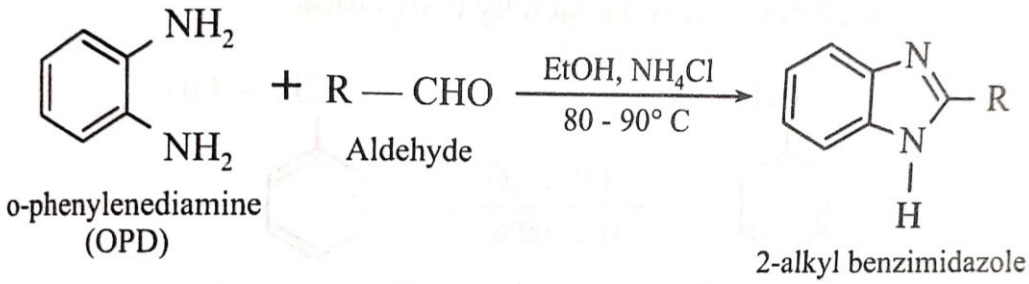
It is inexpensive as it is carried out in solvent free conditions via oxidation of C-N bond. Thus, it provides green route synthesis under milder conditions.



Solvent free synthesis of benzimidazole from 1, 2-diamine with aldehydes

iii) By using o-phenylene diamine (OPD) with green catalyst.

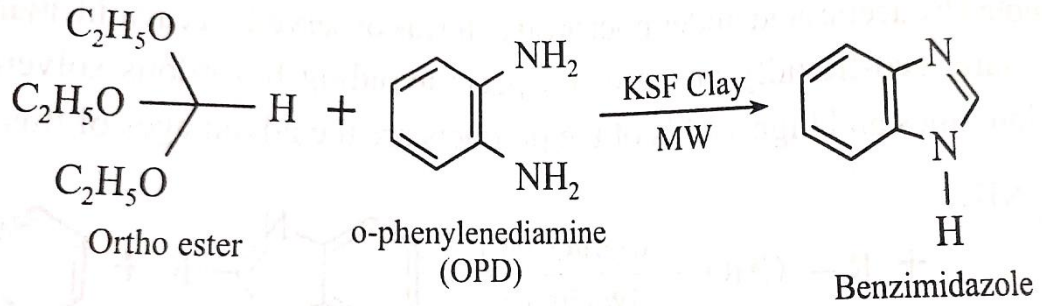
Further, various 2-substituted benzimidazole in moderate to good yields in a one pot reaction by condensation of o-phenylene diamine (OPD) and an aldehyde in the presence of ammonium chloride as a catalyst at 80 to 90^0c were synthesised and it was concluded that this method was green and economical.



Synthesis of benzimidazole from o-phenylene diamine by using green catalyst

iv) By condensation of ortho esters with o-phenylene diamine (OPD):

Benzimidazole can be prepared by condensation reaction of ortho esters with o-phenylene diamine (OPD) in the presence of KSF clay under reflux toluene or solventless condition using focused microwave in few minutes.



The principle highlighted in this synthesis is 'Prevention of waste', Less Hazardous chemical synthesis and Use of Safer solvents and auxiliaries by using microwave assistance, solvent free synthesis and minimization of waste products.

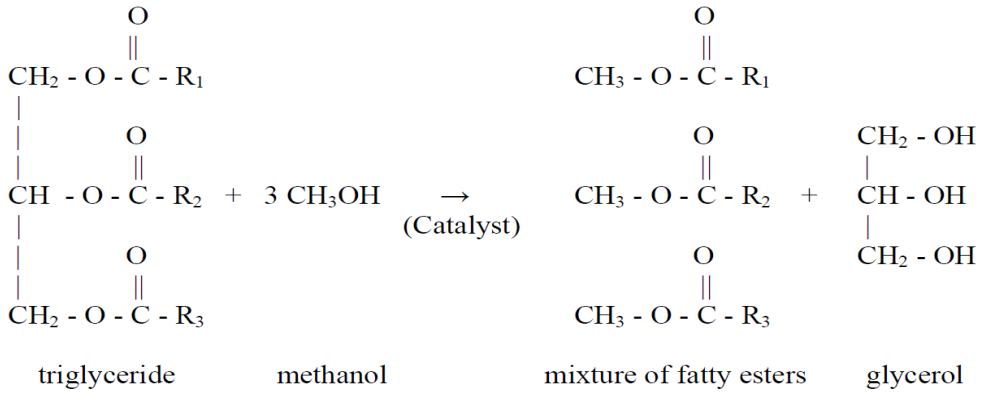
Q8) Write a short note on Green Fuel-Biodiesel.

Ans) Green fuel, also known as biofuel, is a type of fuel distilled from plants and animal materials, believed to be more environmentally friendly than the widely-used fossil fuels which are fast depleting .Thus there is a need for an alternative diesel fuel which is easily available and eco-friendly. On this basis, biodiesel derived from vegetable oils, Petro crops, agriculture wastes are considered as alternative diesel fuels.

Biodiesel synthesis:

- Biodiesel is defined as the mono-alkyl esters of fatty acids derived from vegetable oil or animal fats.
- This reaction requires a catalyst such as sodium or potassium hydroxide and is called as **'Trans esterification'**
- This is nothing but displacement of alcohol from an ester by another alcohol. The trans-esterification reaction of triglycerides present in vegetable oils using methanol may be represented as follows,

Reaction:



- Triglycerides can readily be trans esterified batch wise at atmospheric pressure and at temperature of about 60 to 70^{o}c with an excess of methanol in presence of alkaline catalyst.
- After the reaction is complete, the mixture is allowed to settle down and the lower glycerine layer is drawn off.
- The upper layer of the methyl esters is washed and purified further. The unreacted methanol is recovered in a condenser, purified in a rectifying column and recycled.

Advantages:

1) It can be prepared from renewable resources.

2) Biodiesel is biodegradable and non-toxic.

3) The exhaust gas emissions are lesser as compared to the conventional diesel fuels.

4) It is free from sulphur and aromatics.

5) It is safer to handle and easy to manufacture.

Since the organic compound present in biodiesel is photosynthetic in origin, it does not contribute to raise the level of environmental CO_2 and the subsequent greenhouse effect.
