GREEN CHEMISTRY

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Introduction

Definition:

'Green chemistry is the designing of chemical products and processes that reduce or eliminate the use or generation of hazardous substances.'

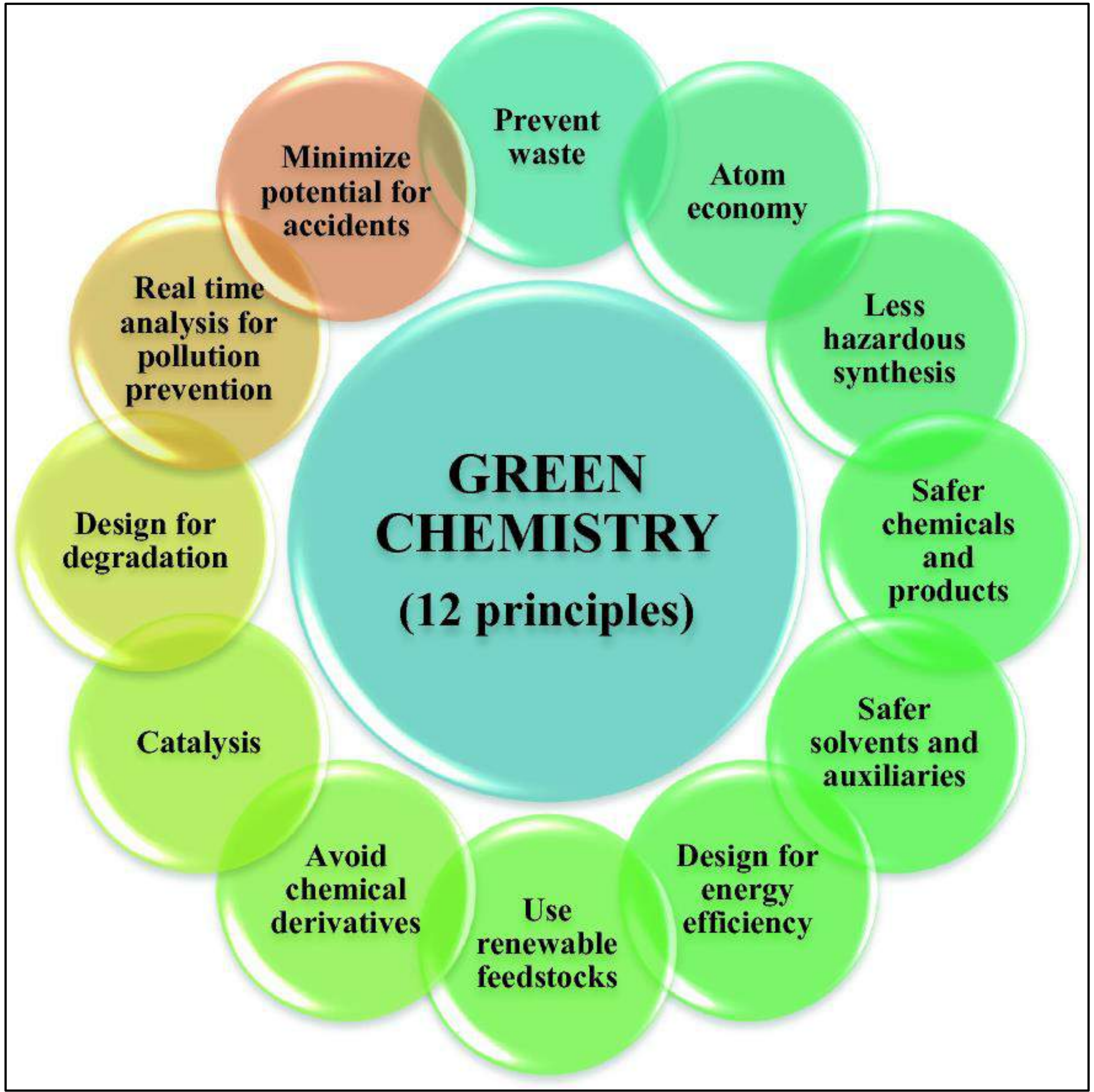
Green chemistry applies across the life cycle of a chemical product, including its design, manufacture, use and ultimate disposal. Green chemistry is also known as sustainable chemistry.

Importance and significance of Green chemistry:

- **Prevents pollution at the molecular level**
- **Is a philosophy that applies to all areas of chemistry, not a single discipline of chemistry**
- **Applies innovative scientific solutions to real-world environmental problems**
- **Reduces pollution at its source by minimizing or eliminating the hazards of chemical feed stocks, reagents, solvents, and products.**
- **Reduces the negative impacts of chemical products and processes on human health and the environment**
- **Lessens and sometimes eliminates hazard from existing products and processes**
- **Designs chemical products and processes to reduce their intrinsic hazards**

12 Principles of Green Chemistry

The "Twelve Principles of Green Chemistry" were initially established by Paul Anastas and John Warner, who are world-renowned founding fathers of Green Chemistry.



1. Prevent waste: Design chemical syntheses to prevent waste. Leave no waste to treat or clean up.

2. Maximize atom economy: Design syntheses so that the final product contains the maximum proportion of the starting materials. Waste few or no atoms.

3. Design less hazardous chemical syntheses: Design syntheses to use and generate substances with little or no toxicity to either humans or the environment.

4. Design safer chemicals and products: Design chemical products that are fully effective yet have little or no toxicity.

5. Use safer solvents and reaction conditions: Avoid using solvents, separation agents, or other auxiliary chemicals. If you must use these chemicals, use safer ones.

6. Increase energy efficiency: Run chemical reactions at room temperature and pressure whenever possible.

7. Use renewable feedstock: Use starting materials (also known as feedstock) that are renewable rather than depletable. The source of renewable feedstock is often agricultural products or the wastes of other processes; the source of depletable feedstock is often fossil fuels (petroleum, natural gas, or coal) or mining operations.

8. Avoid chemical derivatives: Avoid using blocking or protecting groups or any temporary modifications if possible. Derivatives use additional reagents and generate waste.

9. Use catalysts, not stoichiometric reagents: Minimize waste by using catalytic reactions. Catalysts are effective in small amounts and can carry out a single reaction many times. They are preferable to stoichiometric reagents, which are used in excess and carry out a reaction only once.

10. Design chemicals and products to degrade after use: Design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.

11. Analyze in real time to prevent pollution: Include in-process, real-time monitoring and control during syntheses to minimize or eliminate the formation of byproducts.

12. Minimize the potential for accidents: Design chemicals and their physical forms (solid, liquid, or gas) to minimize the potential for chemical accidents including explosions, fires, and releases to the environment.

1. Prevent Waste

The proper definition says that it is better to prevent waste than to treat or clean up waste after it has been generated. Generally, it describes the ability to update chemical transformations in order to limit the generation of hazardous waste as a significant advancement towards contamination or pollution avoidance.

By preventing waste generation, the risks associated with waste storage, transportation, and treatment could be limited.

A solid example can be the pulp and paper industry, usage of chlorine compounds in processes produce toxic chlorinated organic waste. Green chemistry developed a method to convert wood pulp into paper using oxygen, water, and polyoxometalate (early transition metals w salts while producing only water and carbon dioxide as by-products.

"Less Waste is directly proportional to Less Pollution"

2. Maximise Atom Economy

- **The Atom economy is a primary criterion for green chemistry.**
- **The idea of the atom economy is to improve chemical processes, by avoiding the waste of atoms from reactants to products.**
- **The atom economy of a reaction is a measure of the amount of starting materials that end up as useful products. It is important for sustainable development and for economic reasons to use reactions with high atom economy.**
- **Atom economy can be assessed easily by calculating the number of atoms in the Chemical Reaction. Atom Economy is the ratio of "the mass of the desired product" to "the total mass of the reactants", and can be expressed in percentage as illustrated in the formula below.**

Assume for a reaction:

$$A + B \rightarrow C + D,$$ **where 'C' is the desired product**

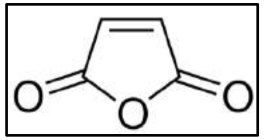
The % Atom Economy can be calculated as,

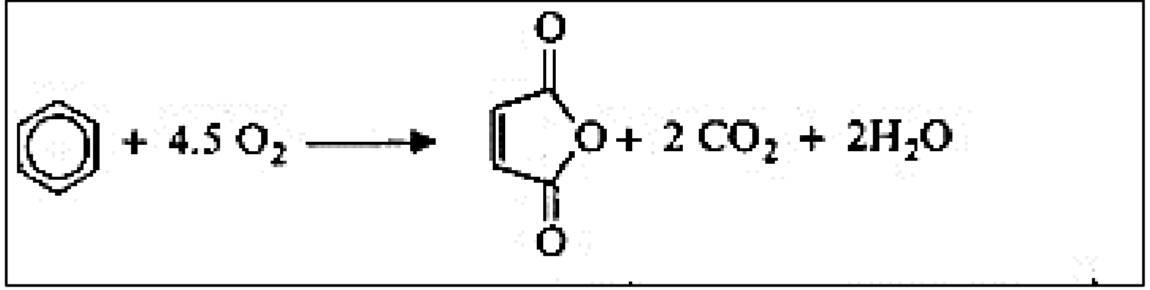
$$\%\ \text{Atom economy} = \frac{(\text{Molecular weight of Desired product})}{(\text{Molecular weight of all reactants})} \text{X100}$$

$$= [(\text{Molecular weight of C})/(\text{Molecular weight of A+B})]\text{X100}$$

For an optimal process, the atom economy should be near or equal to 100%

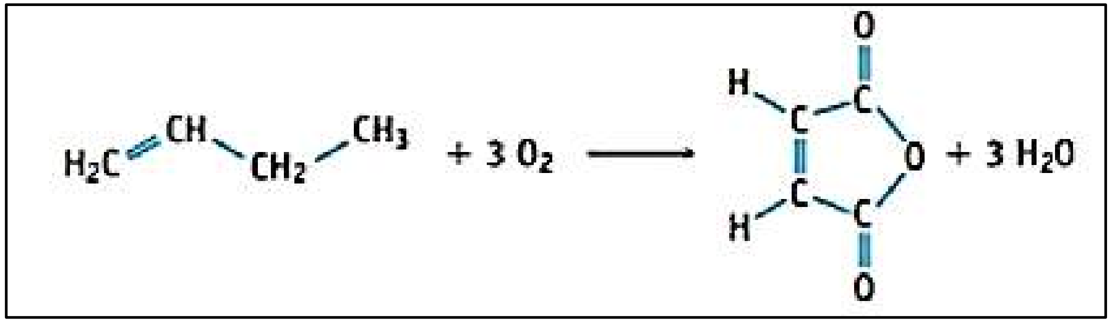
Atom economy (Example) – Synthesis of Maleic anhydride ($C_4H_2O_3$) =





% Atom economy = 44.14

% Atom Economy = 57. 65



% Atom Economy = 67.47

Greener Route

Numerical 1

Hydrogen can be manufactured by reacting methane with steam:

$$CH_4(g) + H_2O(g) \dashrightarrow 3H_2(g) + CO(g)$$

Calculate the atom economy for the reaction.

Solution:

Desired product is Hydrogen

$$\%\ \text{Atom economy} = \frac{(\text{Molecular weight of Desired product})}{(\text{Molecular weight of all reactants})} \times 100$$

$$= \frac{(\text{Molecular weight of Hydrogen})}{(\text{Mol. wt methane} + \text{Mol. Wt of Water})} \times 100$$

$$= \frac{3 \times 2}{16 + 18} \times 100$$

$$= 17.65$$

Numerical 2

Ethanol, CH_3CH_2OH, can be produced by the fermentation of glucose, $C_6H_{12}O_6$.Calculate the atom economy for the reaction.

$$C_6H_{12}O_6(aq) \longrightarrow 2CH_3CH_2OH(aq) + 2CO_2(g)$$

Solution:

Desired product is Ethanol

$$\text{\% Atom economy} = \frac{\text{(Molecular weight of Desired product)}}{\text{(Molecular weight of all reactants)}} \times 100$$

$$= \frac{\text{(Molecular weight of ethanol)}}{\text{(Mol. wt glucose)}} \times 100$$

$$= \frac{2 \times 46}{180} \times 100$$

$$= 51.11$$

Numerical 3

Calculate % Atom Economy for the following reaction with respect to cinnamaldehyde.

$$C_6H_5CHO + CH_3CHO \xrightarrow{NaOH} C_6H_5CH=CHCHO + H_2O$$

Cinnamaldehyde

Solution:

Desired product is Cinnamaldehyde

$$\%\ \text{Atom economy} = \frac{(\text{Molecular weight of Desired product})}{(\text{Molecular weight of all reactants})} \times 100$$

$$= \frac{(\text{Molecular weight of Cinnamaldehyde})}{(\text{Mol. wt of benzaldehyde} + \text{MW of Acetaldehyde})} \times 100$$

$$= \frac{132}{106 + 44} \times 100$$

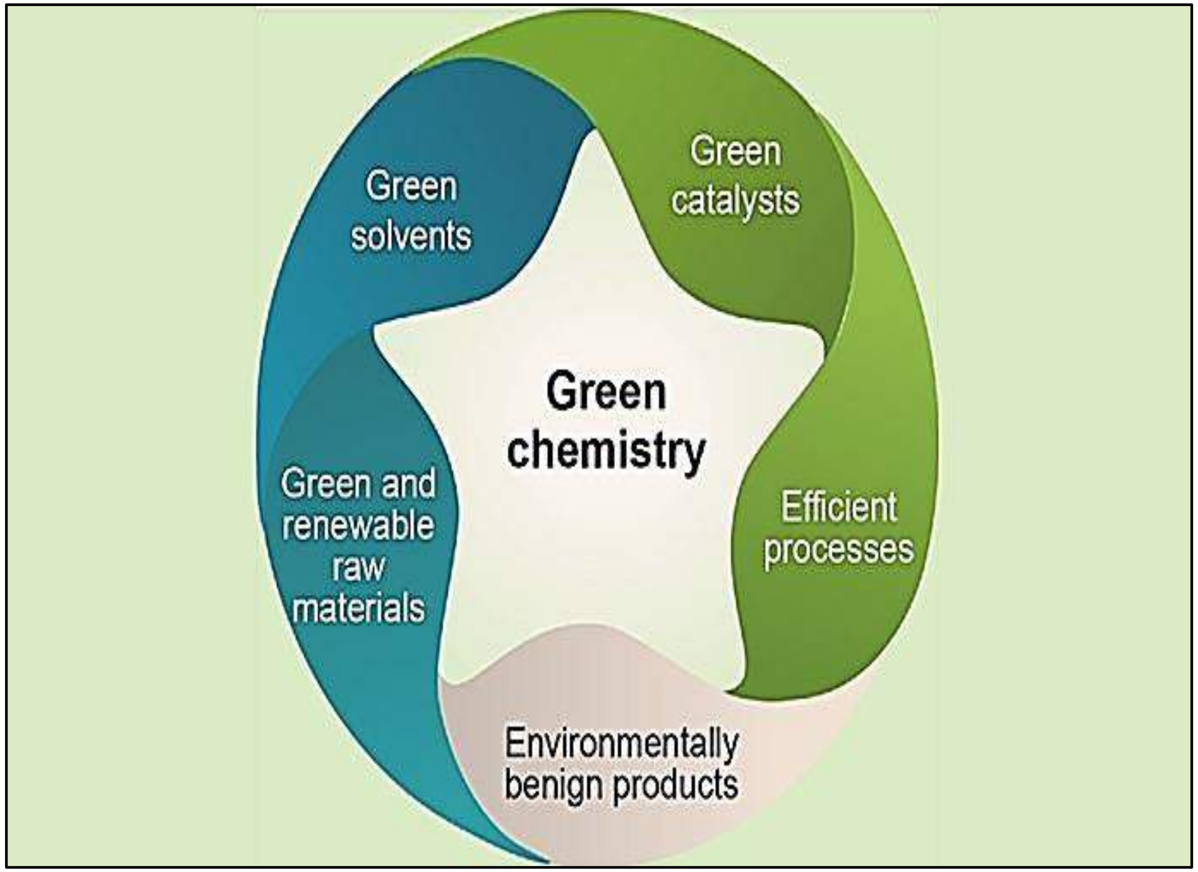
$$= 88.00$$

3. Design less hazardous chemical syntheses

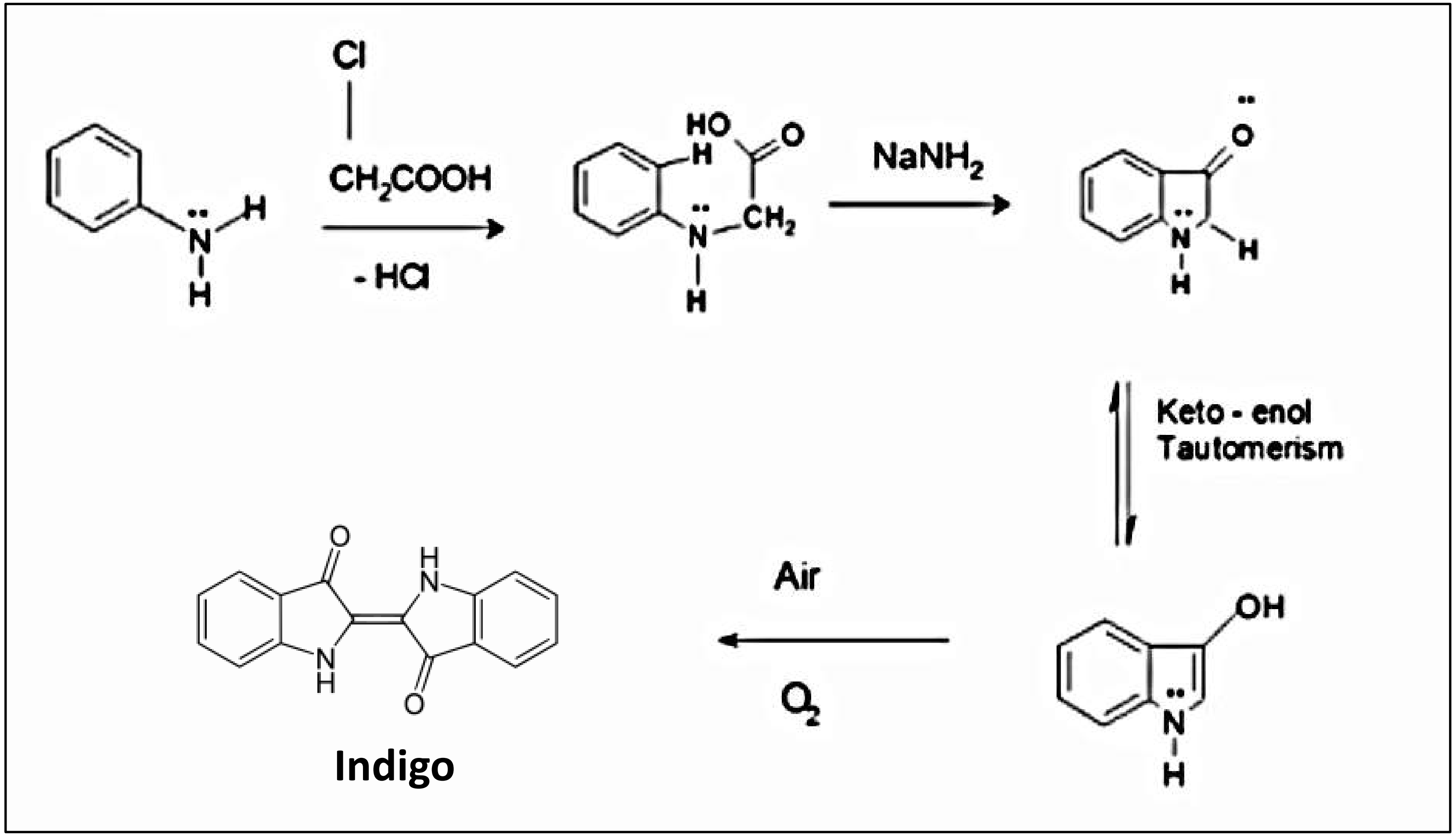
Wherever practicable, synthetic methods should be designed to use or generate chemicals that pose little or no toxicity to the environment and human health.

'The goal should be to avoid reactions that give hazardous by-products'.

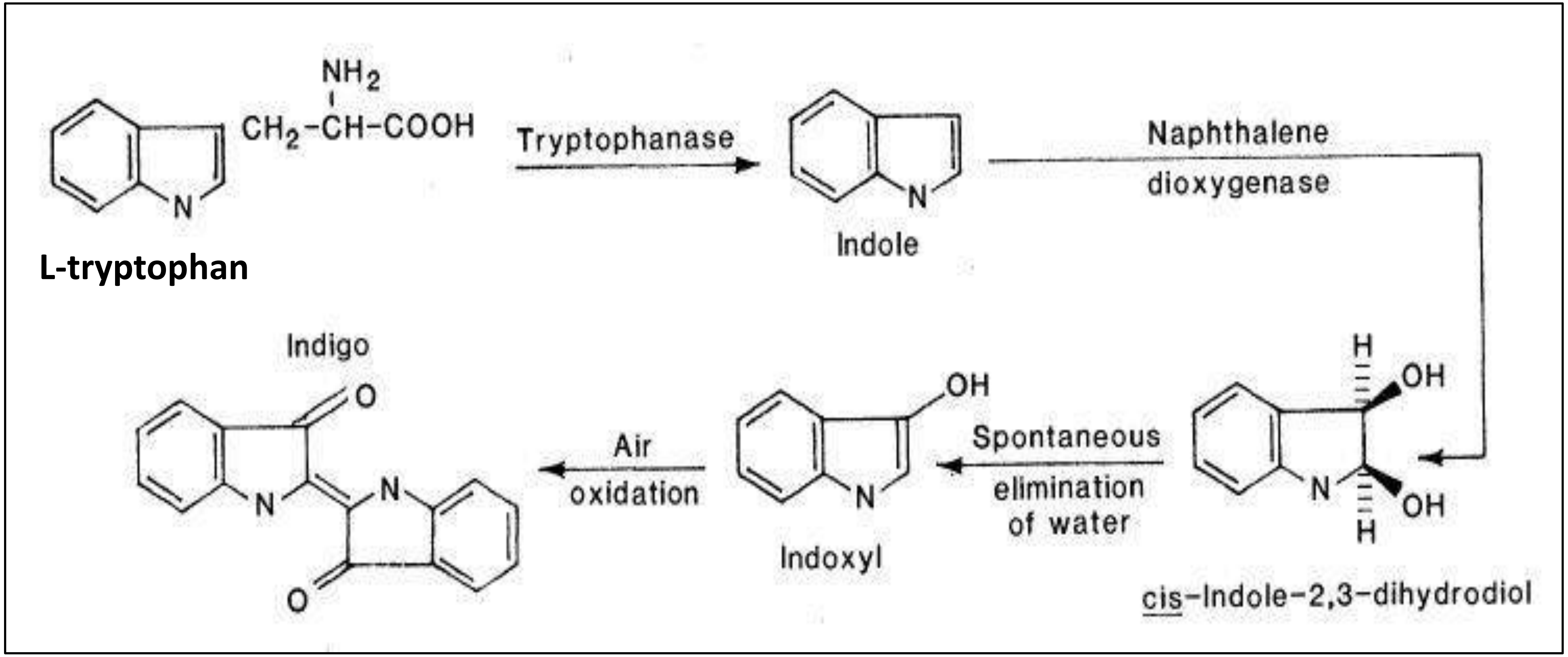
The Retrosynthesis principle can be applied in synthesis so that less toxic starting material can be used in synthesis and a safer route can be designed so that toxic by-products are not produced. Reducing the number of steps in synthesis will also ensure less by-product formation.



Synthesis of Indigo (Conventional Route – From hazardous Aniline)



Synthesis of Indigo (Greener Route – From enzyme Tryptophan)



4. Design safer chemicals and products

- The design of safer chemicals deals with the rendering of chemicals which fulfill their intended purpose and yet are benign and harmless to the ecosystems.
- This modification should be reflected up to the molecular level of the chemical's design.
- This principle will be beneficiary as it eliminates the necessity of chemicals which are carcinogenic, neurotoxins, asthmagens or hormone, etc. such disruptors and is essentially safe to the Earth.

e.g. 1) DDT – This pesticide has several long term bad effects on soil as well as on life therefore it is replaced by biological pesticides.

2) Thalidomide – A drug used in late 50's and early 60's for nausea during pregnancy but in 1960 it was found that the defects (limb deformation, defective organs) produced in babies were due to consumption of this drug

5. Use safer solvents and auxiliaries (separating agents, etc.)

- **Most of the industries from polymer to pharmaceutical industries and other chemical allied industries use solvents (such as acetone, Chloroform, carbon tetrachloride, Benzene) at some point in their manufacturing.**
- **CFCs used as refrigerants, cleaning agents cause depletion of Ozone layer resulting bad effects on human health**
- **In general, the use of solvents should be avoided, but that is not possible in all cases. So we can possibly replace toxic, non-recyclable solvents with safer and innocuous solvents like water or carry out reactions with non aqueous solvents.**

e.g. As a case study, a good success story in such a replacement is Bayer in 2000, effectively replacing Volatile Organic Compounds (VOCs) in their polyurethane coatings with water.

6. Increase energy efficiency

Recognition of the energy requirements, their impact on the environment and economy, and its minimization to the extent possible will pave way for a greener process. Processes should be carried out at ambient conditions of temperature and pressure.

Some ways in which this can be achieved are –

1) Well-maintained equipment in plants,
2) Recovery of waste heat,
3) Removal of solvents,
4) Proper utilization of catalysts, and
5) Combined heat and power (CHP) also known as cogeneration. This means allowing the heat that would normally be lost in the power generation process to be recovered to provide useful thermal energy - such as steam, hot water – that can be used for space heating, cooling, industrial processes

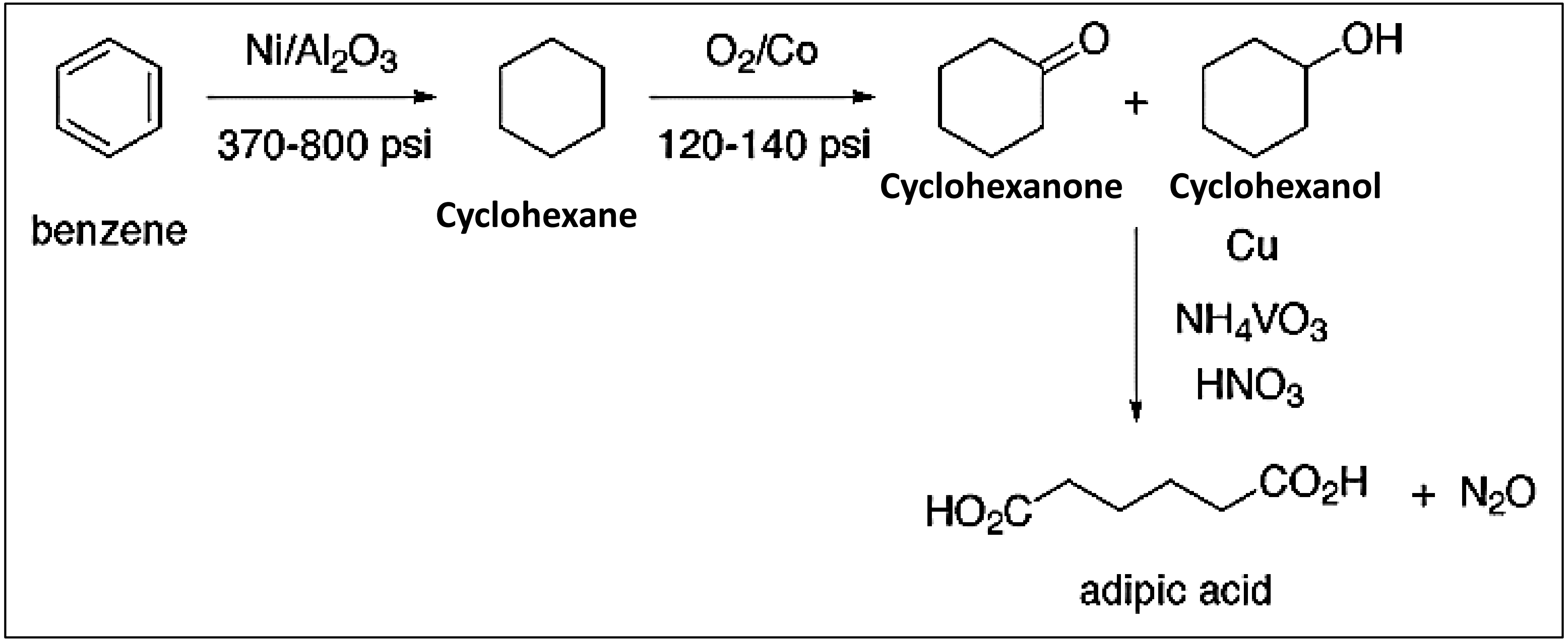
7. Use renewable feedstock

- The increasing awareness of sustainability in our modern society has led to switch to the use of biomass as a feedstock and an energy source. Biomass – plants and plant-based materials not used for food or feed, is abundant in nature, renewable, and sustainable resource for producing biofuels, bio products, and bio power.

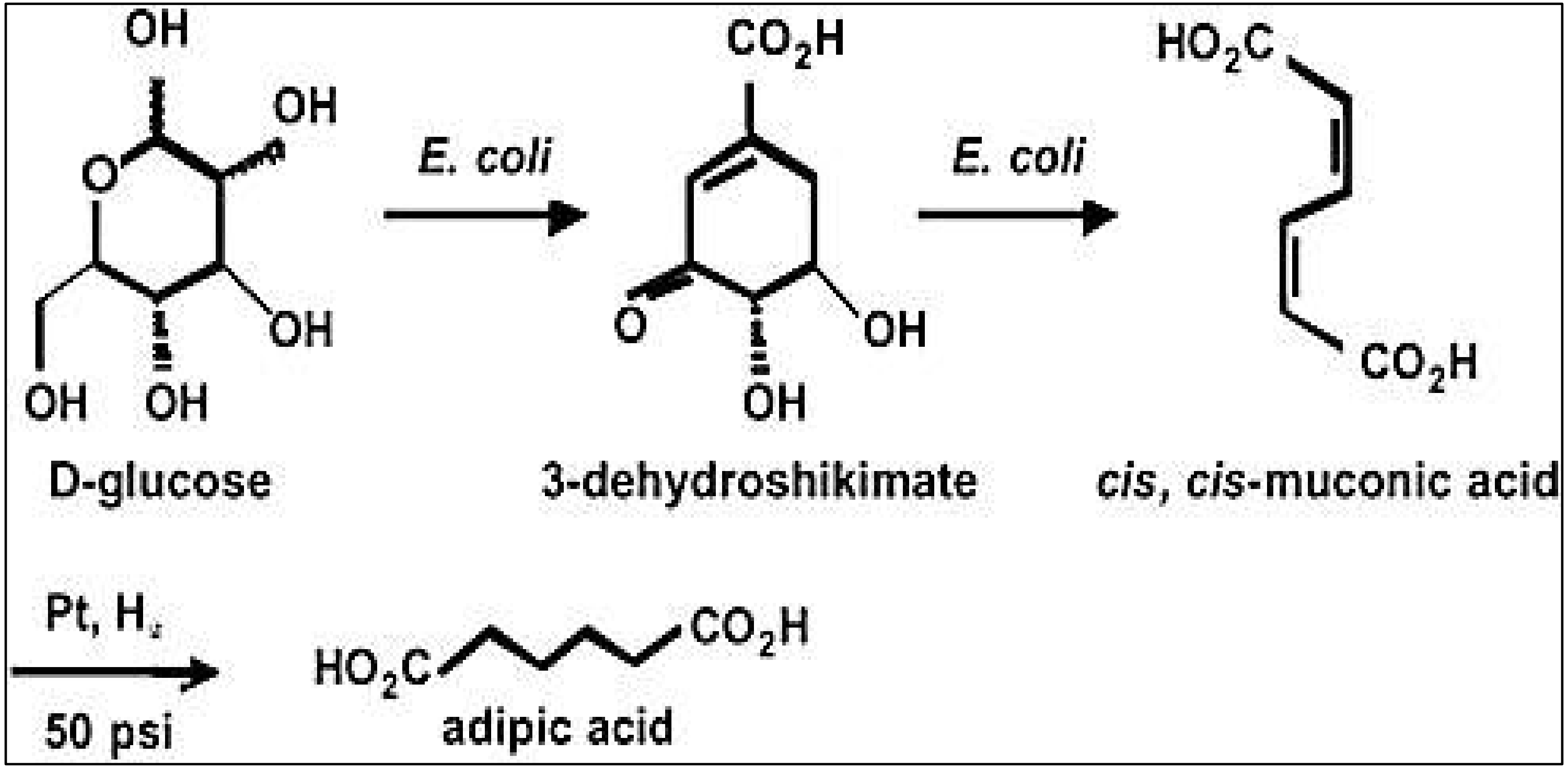
e.g. 1. Synthesis of Adipic acid

2. Synthesis of Biodiesel

Synthesis of Adipic Acid (Conventional Route – from Benzene)



Synthesis of Adipic Acid (Greener Route – From Glucose)

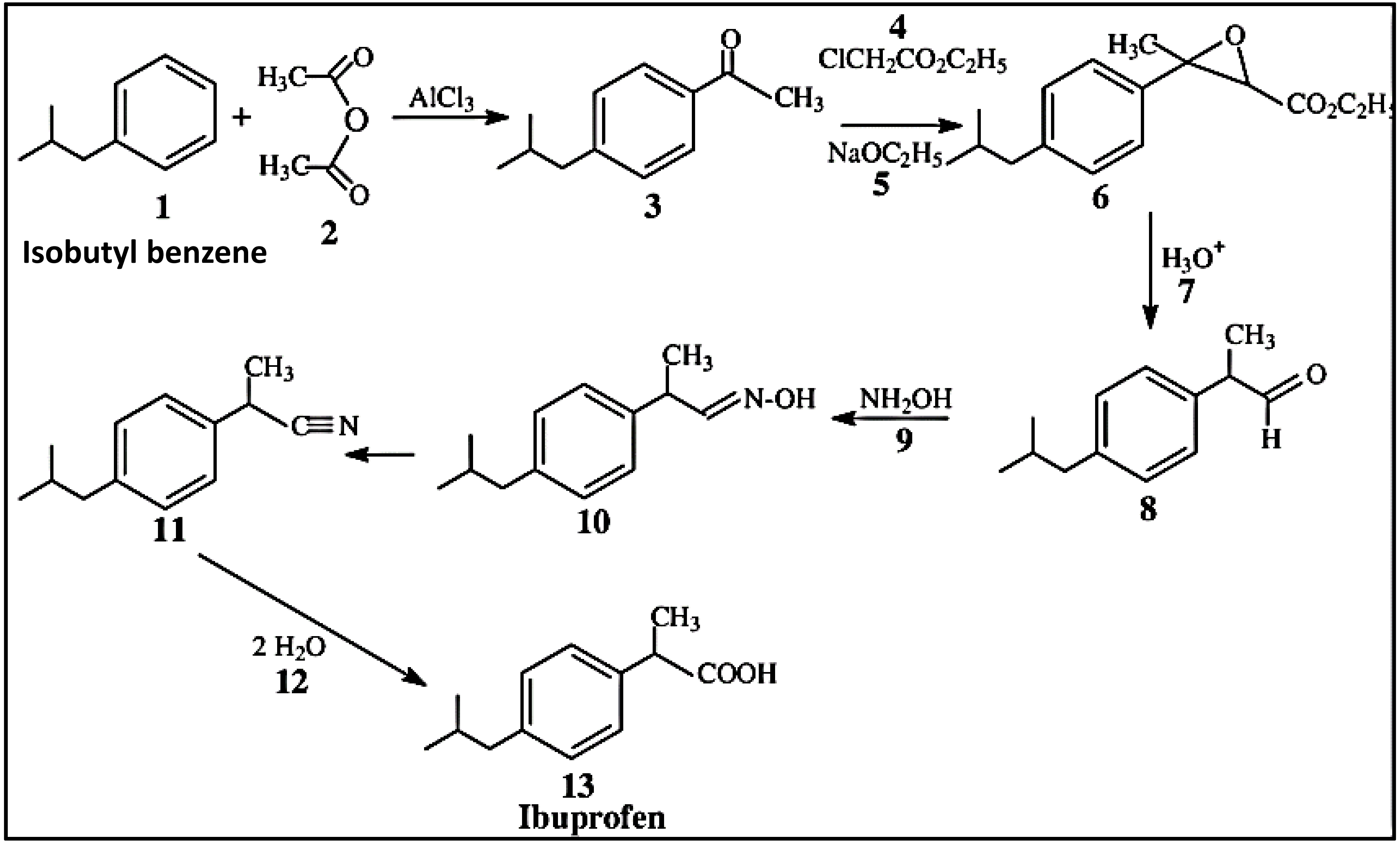


8. Avoid chemical derivatives

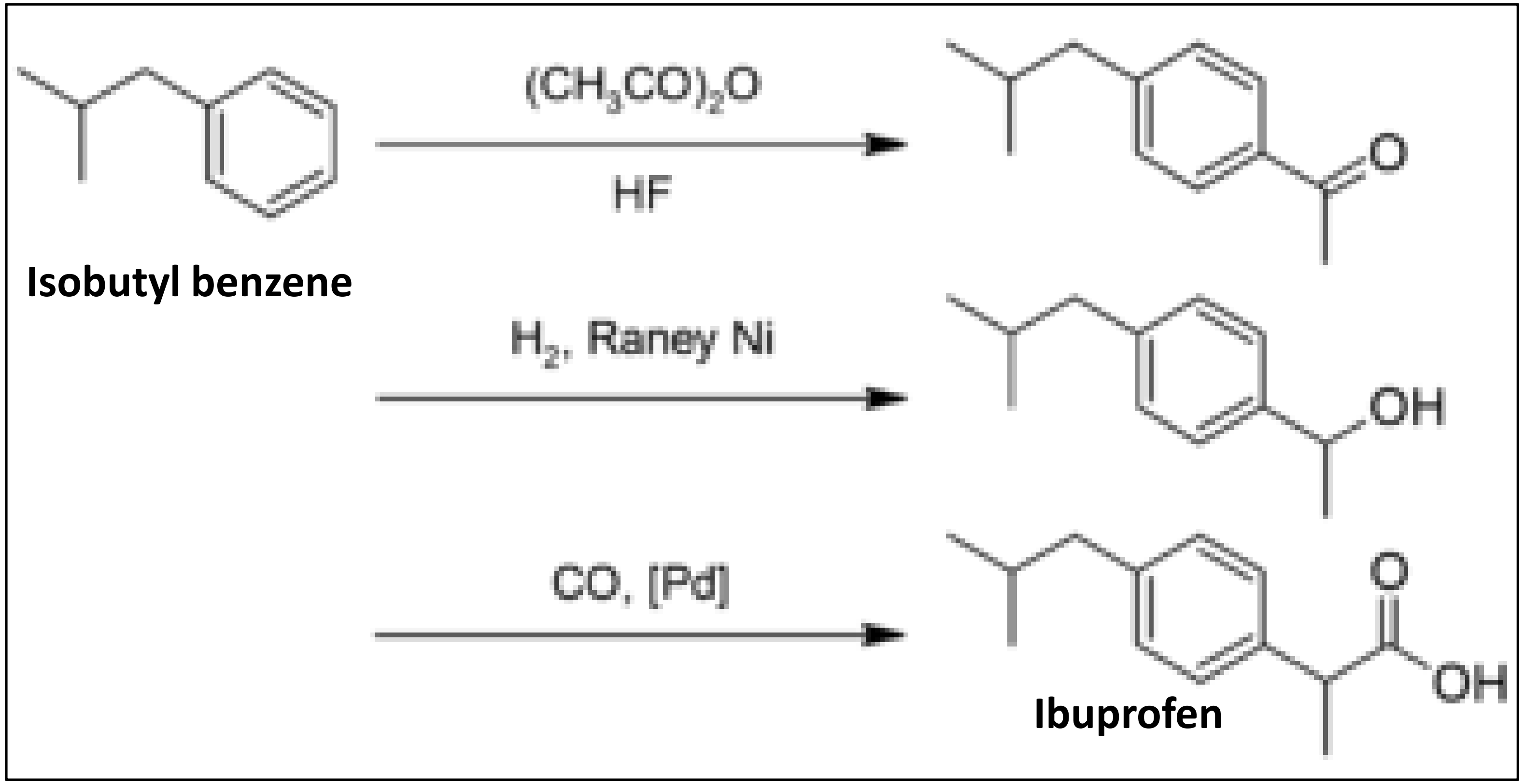
- **In this principle, the reaction takes place at a particular functional group blocking unnecessary waste generation by reducing the process steps with the use of enzymes, catalysts, or solvents therefore, reducing demand for feedstock and utilities required for down-streaming hence increasing overall economy and efficiency of the process.**

For example, the manufacturing of Ibuprofen (a painkiller) is a 6 step process by the conventional methods. By using anhydrous HF the process minimizes to 3 steps which are recyclable. BASF Pvt. Ltd. has come up with the innovative method of manufacture of Ibuprofen.

Synthesis of Ibuprofen (Conventional Route – 6 steps – Atom economy 40%)



Synthesis of Ibuprofen (Greener Route – 3 steps – Atom economy 77%)



Green Chemistry - 2

DR. ANUPAMA SAWANT

9.Use catalysts, not stoichiometric reagents

- Catalysis is one of the most important pillars of Green Chemistry. "Stoichiometric" technologies are the primary source of waste; on the other hand, "Catalytic Processes" are achieving the goals of Environmental protection and economic benefit.
- Catalysts provide many benefits from lower energy consumption to increased selectivity of the reaction and allow a decreased use of harmful and toxic reagents.
- Catalyst is required in small amount and can carry out single reaction many times.
- Catalysis can help us build a more sustainable world and can play a major role to decrease the global environmental impacts of unsustainable chemical processes.

e.g. 1. Zeolites, Clays are promising and benign catalysts used in Heterogeneous Catalysis, which can replace the use of harmful catalysts.

2. Enzymes are Biocatalysts which are natural substances derived from Biological sources, are renewable and Biodegradable.

10. Design chemicals and products to degrade after use

- Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment ie the usage of chemicals it should be stable and do not persist the environment but after usage, it should be degraded into small molecules that are not harmful to the environment and humans.

e.g. 1. branched and linear sodium dodecylbenzene sulfonate (SDBS) which is used as a detergent.

The branched SDBS is less toxic but it will not readily break down into small molecules and harmful to the environment on the other side the liner SDBS is degraded and friendly to the environment.

2. Pesticides – DDT

3. Plastics

The care has to be taken to design the chemicals which are susceptible to hydrolysis, photolysis, oxidation so that the product will undergo biodegradation and products of biodegradation are also not harmful

11. Analyze in real time to prevent pollution

- Real-time analysis in Chemical and allied industries are essential for production, transportation, and especially in the case of pollution prevention.
- Pollution in the industrial premises could become a potential threat to various probable hazards. Therefore real-time analysis makes it better to understand and act best according to the situation.
- Using various analytical techniques, a chemical process can be monitored for generation of hazardous intermediates, by-products and side reactions.
- The real-time analysis opens the scope of online process control and prevents any possible threats hence increasing overall profit to the industry as well as ensure safety to the environment.

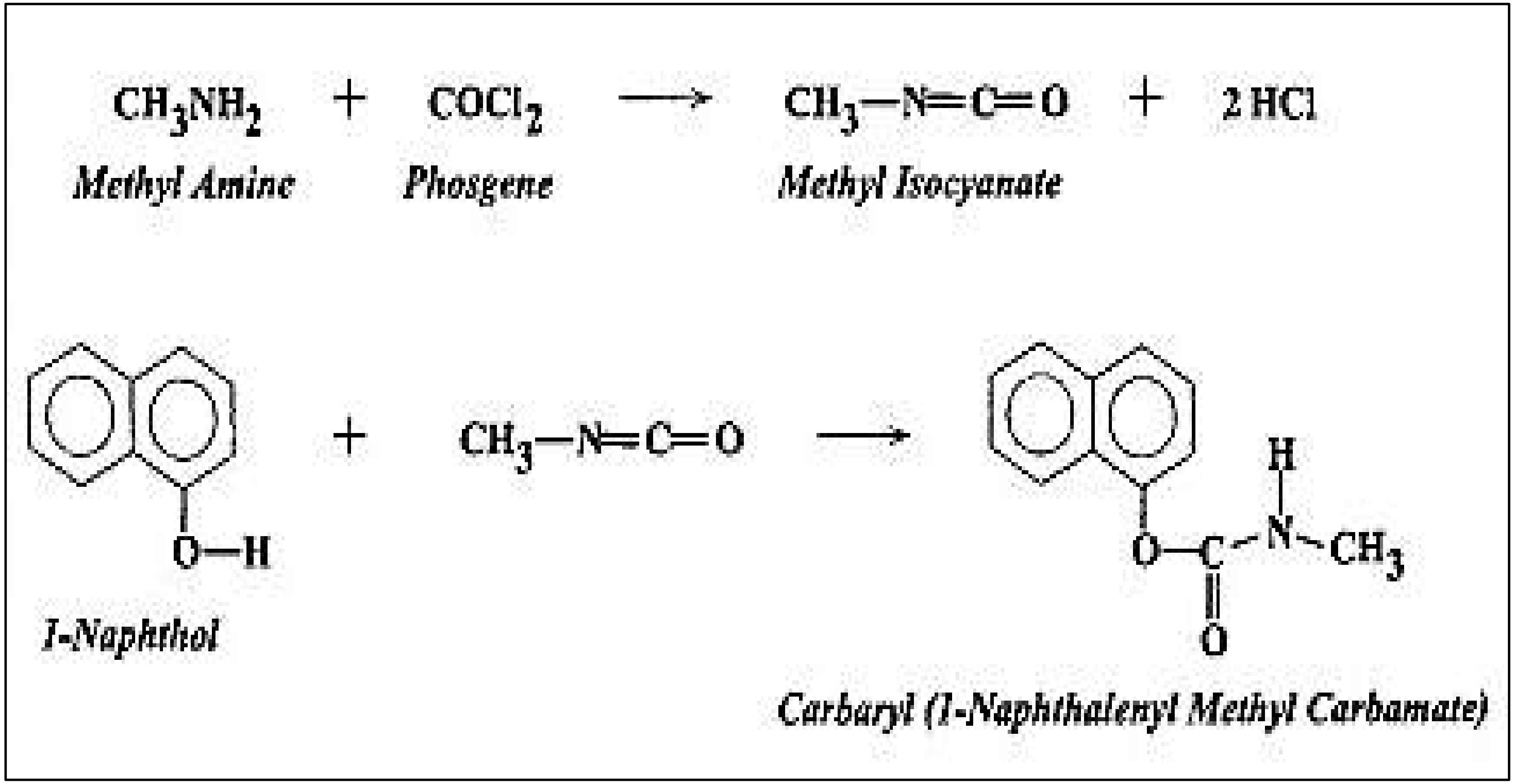
12. Minimize the potential for accidents

- It involves choosing a safe or safer chemical to mitigate the chances of occurrence of an accident.
- It benefits the industry as well as the environment as it acts as a safeguard against calamitous industrial or laboratory accidents.
- Avoidance of hazard is the key.

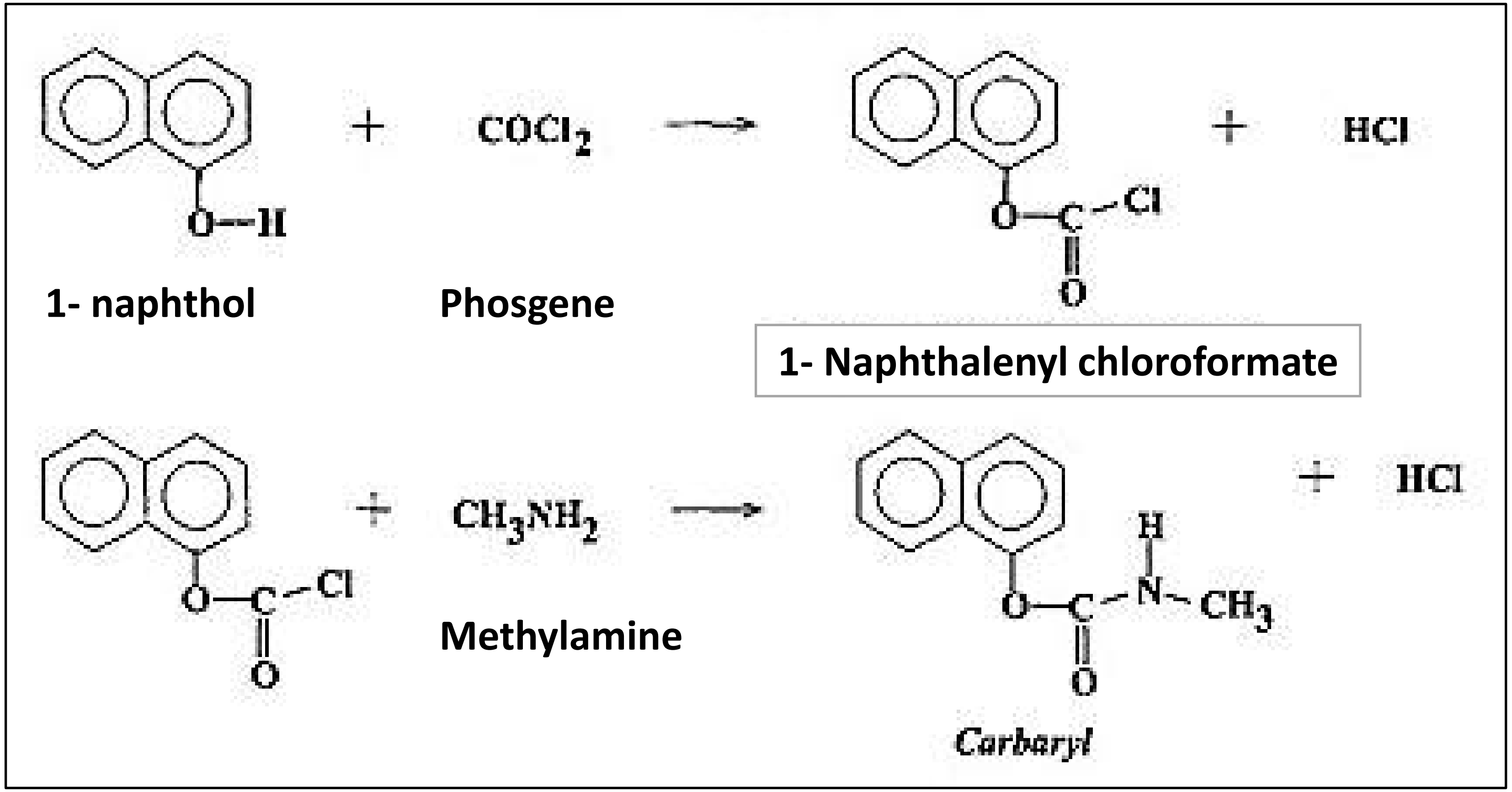
e.g. The infamous Bhopal Gas Tragedy could have been avoided by the usage of methylamine in lieu of methyl isocyanate (MIC).

1-naphthol reacts with phosgene to give 1-napthylcholoroformate which can react with methylamine to produce carbaryl(the target product of the Union Carbide plant in Bhopal).

Synthesis of Carbaryl (Conventional Route)



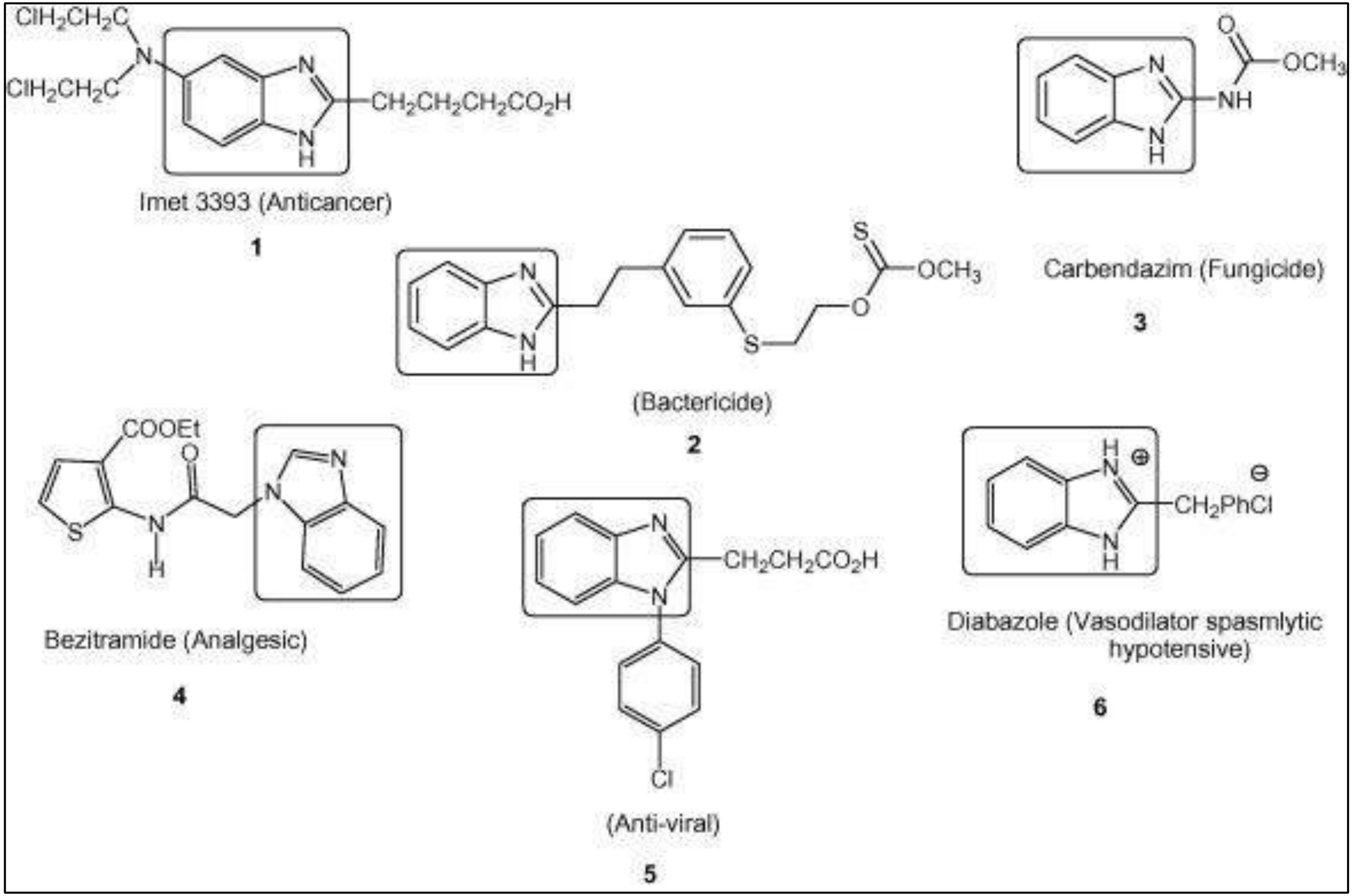
Synthesis of Carbaryl (Green Route)



Benzimidazole (Introduction)

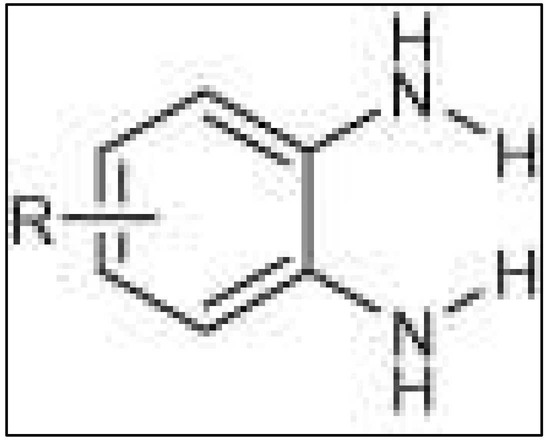
- **Benzimidazole is considered as potential bioactive heterocyclic aromatic compound exhibiting remarkable pharmacological activities.**
- **It is an important pharmacophore and a privileged structure in medicinal chemistry.**
- **This compound is bicyclic in nature which consists of the fusion of benzene and imidazole.**
- **The methods for the synthesis of benzimidazoles have become a focus of synthetic organic chemists, as they are useful building blocks for the development of important therapeutic compounds in medicine. Benzimidazole nucleus plays a very important role as a therapeutic agent e.g. antiulcer and anthelmintic drugs. Other benzimidazole derivatives exhibit pharmacological activities such as antimicrobial, antiviral, anticancer, anti-inflammatory and analgesic.**

Important drugs from Benzimidazole



Synthesis of Benzimidazole (Introduction)

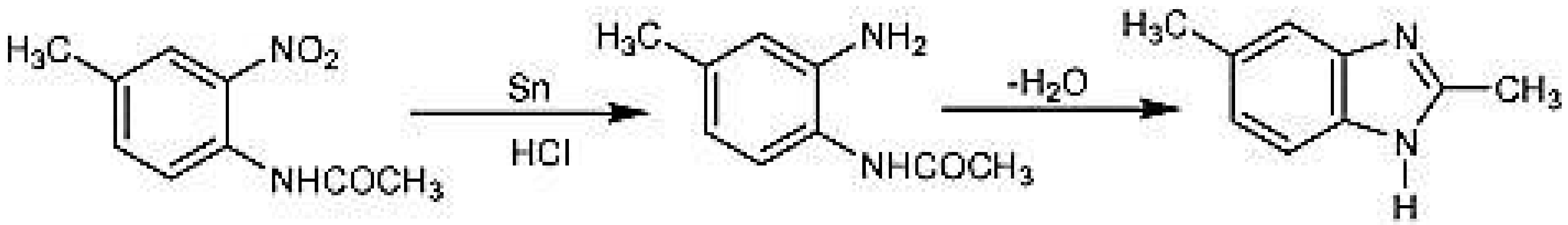
Almost all syntheses of benzimidazoles start with benzene derivatives possessing nitrogen-containing functions ortho to each other. Many methods have been reported for the synthesis of benzimidazoles. Most of these methods involve the condensation of ortho-phenylenediamine, and its derivatives with carboxylic acids, or aldehydes.



o- phenylene diamine (OPD)

Synthesis of Benzimidazole (Conventional Route-1)

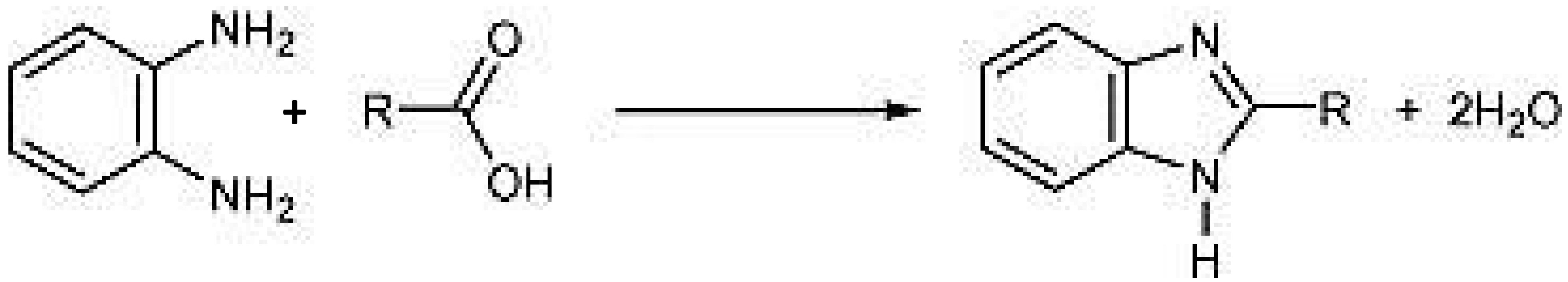
The first benzimidazole was prepared by Hoebrecker, who obtained 2,5-dimethylbenzimidazole by the reduction and dehydration of 2-nitro-4-methylacetanilide



2-nitro-4-methyl acetanilide **2,5- dimethyl benzimidazole**

Synthesis of Benzimidazole (Conventional Route-2)

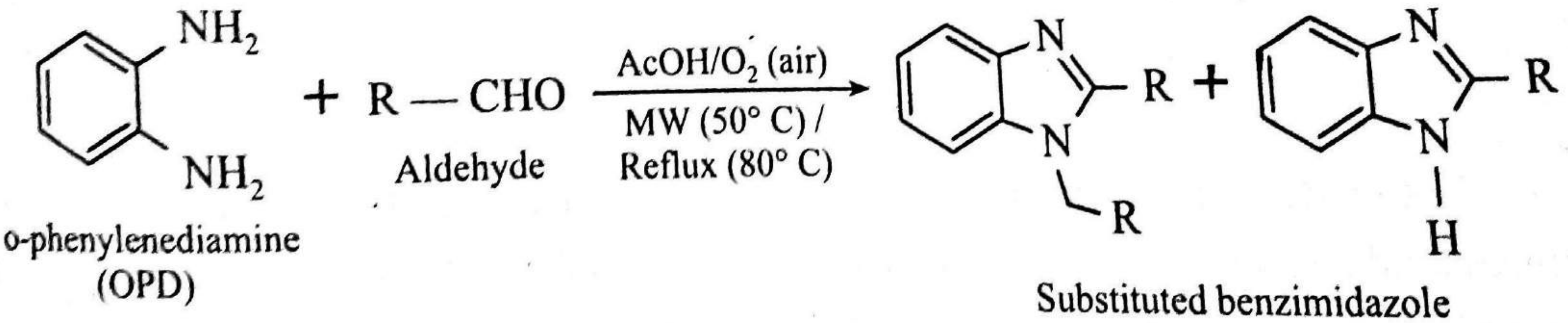
Literature survey has revealed that *o*-phenylenediamines react readily with most carboxylic acids to give 2-substituted benzimidazoles, usually in very good yields. The reaction is carried out usually by heating the reactants together on a steam bath, by heating together under reflux or at an elevated temperature, or by heating in a sealed tube



OPD **Carboxylic acid** **2-alkyl benzimidazole**

Synthesis of Benzimidazole (Green Route)

i) Benzimidazole is synthesised by condensation of o-phenylene diamine (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)

Biodiesel (Green Fuel)

- **Biodiesel is a renewable, biodegradable fuel manufactured domestically from vegetable oils, animal fats, or recycled restaurant grease.**
- **Biodiesel meets both the biomass-based diesel and overall advanced biofuel requirement of the Renewable Fuel Standard.**
- **Biodiesel is a liquid fuel often referred to as B100 or neat biodiesel in its pure, unblended form. Like petroleum diesel, biodiesel is used to fuel compression-ignition engines.**
- **Made from an increasingly diverse mix of resources such as recycled cooking oil, soybean oil and animal fats, biodiesel is a renewable, clean-burning diesel replacement that can be used in existing diesel engines without modification. It is the nation's first domestically produced, commercially available advanced biofuel.**
- **Biodiesel is made through a chemical process called transesterification whereby the glycerin is separated from the fat or vegetable oil. The process leaves behind two products – methyl esters and glycerin.**
- **Methyl esters is the chemical name for biodiesel and glycerin is used in a variety of products, including soap.**

Synthesis of Biodiesel

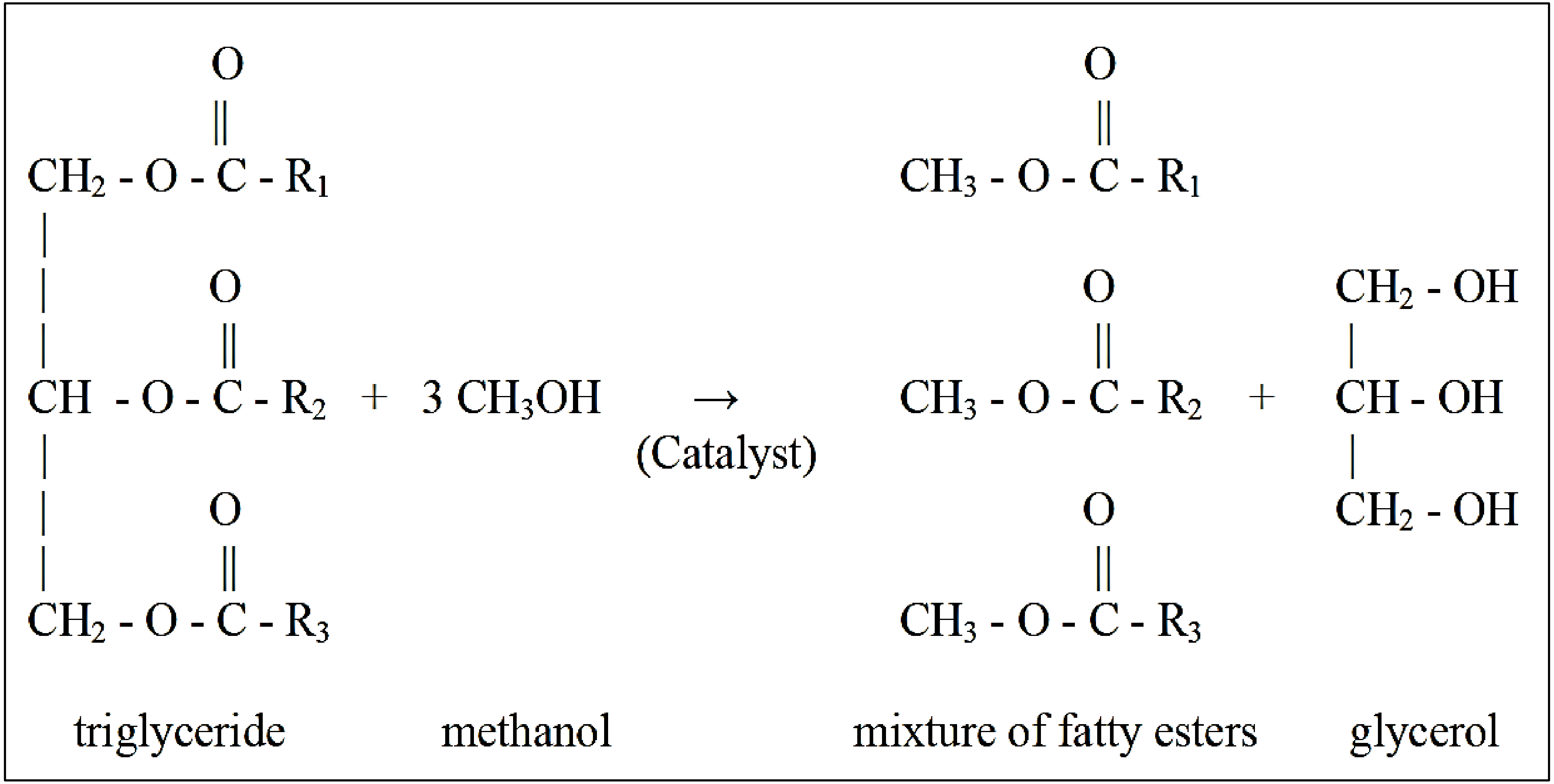
- The transesterification of vegetable oils, animal fats or waste cooking oils is the process behind conventional biodiesel. In the transesterification process a glyceride reacts with an alcohol (typically methanol or ethanol) in the presence of a catalyst forming fatty acid alkyl esters and an alcohol.
- The feedstock for transesterification can be any fatty acids from vegetable or animal origin, or used cooking oils (UCO). Typically used vegetable oils originate from rapeseed, sunflower, soy and oil palms.
- Depending on the origin of the oils and fats some pretreatment is necessary before processing -

1. In any case water is removed as it causes the triglycerides to hydrolyze during base-catalyzed transesterification, producing soap stock instead of biodiesel
2. Virgin oils are refined, but not to food grade level
3. In some cases the removal of phospholipids and other plant matter is done by degumming
4. Recycled oils as UCO are purged from impurities such as dirt or charred Food

Synthesis of Biodiesel (Procedure)

- The transesterification process is a reversible reaction and carried out by mixing the reactants – fatty acids, alcohol and catalyst.
- A strong base or a strong acid can be used as a catalyst.
- At the industrial scale, mostly sodium or potassium methanolate is used.
- The end products of the transesterification process are raw biodiesel and raw glycerol.
- In a further process these raw products undergo a cleaning step.
- In case of using methanol as alcohol FAME (fatty acid methyl ester) biodiesel is produced.
- The purified glycerol can be used in the food and cosmetic industries. The glycerol can also be used as a substrate for anaerobic digestion.

Synthesis of Biodiesel (Reaction)



(Vegetable oil) **(Biodiesel)**

Advantages of Biodiesel

1. Produced From Renewable Resources
2. Can be Used in Existing Diesel Engines
3. Less Greenhouse Gas Emissions (e.g., B20 reduces CO_2 by 15%)
4. Grown, Produced and Distributed Locally
5. Cleaner Biofuel Refineries
6. Biodegradable and Non-Toxic
7. Better Fuel Economy
8. Positive Economic Impact
9. Reduced Foreign Oil Dependence
10. More Health Benefits
11. Improved Air Quality
12. Biodiesel Improves the Engine Operation of a Vehicle
13. Biodiesel is Undoubtedly a Safer Alternative to Fossil Fuels

Biodiesel (Environmental Impact)

Biodiesel has several environmental benefits when compared to petroleum-based diesel fuel:

- Biodiesel is non-toxic and biodegradable.
- Reduces lifecycle greenhouse gases by 86 percent
- Lowers particulate matter by 47 percent, reduces smog and makes our air healthier to breathe
- Reduces hydrocarbon emissions by 67 percent
- For every unit of fossil energy it takes to produce biodiesel, 3.5 units of renewable energy are returned

Biodiesel (Disadvantages)

1. Variation in Quality of Biodiesel
2. Not Suitable for Use in Low Temperatures
3. Biodiesel Could Harm the Rubber Hoses of Some Engines
4. Biodiesel is Way More Expensive than Petroleum
5. Food Shortage
6. Increased use of Fertilizers
7. Clogging in Engine
8. Slight Increase in Nitrogen Oxide Emissions

Numericals on Atom Economy (Assignment 2)

Calculate % atom economy of following reactions w.r.t. Product A:

1. $CH_3 - CH = CH_2 + Cl_2 \text{ ----> } \underset{A}{Cl - CH_2 - CH = CH_2} + HCl$

2. $C_6H_6 + CH_3Cl \xrightarrow{AlCl3} \underset{A}{C_6H_5CH_3} + HCl$

3. $C_6H_5NH_2 + (CH_3CO)_2O \text{ ----> } \underset{A}{C_6H_5NHCOCH_3} + CH_3COOH$

4. $CH_3NH_2 + COCl_2 \text{ ----> } \underset{A}{CH_3 - N = C = O} + 2HCl$

5. $C_6H_5NH_2 + C_6H_5COCl \text{ ----> } \underset{A}{C_6H_5NHCOC_6H_5} + HCl$