Unit I

Introduction to green Chemistry

Section A

1 Give any two differences between green chemistry and environmental chemistry
2 Write the name of any two green catalyst?
3 Define green chemistry?
4 What is the need of green chemistry?
5 What are the use of renewable feedstocks?

Section B

6 What are roles of green chemistry?
7 List out the tools of green chemistry
8 What is the need of green chemistry?
9 Explain alternative catalysts and solvents used in green chemistry.
10 What are the uses of green solvent?

Section C

11 Describe anastas twelve principle of green chemistry.
12 Explain about uses of greener solvents
13 Write a breif note on green solvents?

Introduction to green Chemistry

Green Chemistry is defined as: it designs the chemical processes and products that reduce or eliminate the use and formation of hazardous substances. The main purpose of green chemistry are mentioned.

- **Ecofriendly chemical technology:**
  Green Chemistry aims to protect the environment and also described as environmentally benign chemistry.
- **Replacement of organic solvent and to minimize the waste product:**
  Green chemistry aims to devise greener reaction condition for the synthesis of chemicals so that waste product formation can be minimized. It needs the replacement of organic solvent by water or complete elimination of the use of solvent. It also needs to minimize the formation of by products.

- **Use of renewable feedstock's:**

  Green chemistry aims to develop the greener synthesis of the required chemical products by using the renewable resources(e.g. biomass rather than petrochemical feedstock's).It reduces the consumption of nonrenewable resources(e.g. Crude oil).

- **To minimize the energy consumption:**

  Green chemistry aims to develop the greener conditions for the synthesis of chemical products so that energy consumption can be minimized. For many existing chemical technologies, drastic reaction conditions(e.g. high temperature, high pressure,etc.).Which are energy requiring are applied. Greener synthesis aims to develop the mild or modest conditions.

- **Use of more ecofriendly chemical products:**

  Green chemistry aims to design new chemical products to replace the existing hazardous chemical products provided the new chemicals are having the same desirable propertied of the existing onces(e.g development of new pesticide which is only toxic to the target species and at the same time it biodegrades easily to harmless products).

- **Four R's(4R's)and integrated waste management:**

  These four R's are :reduction, recycling, reuse and recovery.

The Twelve principle of Green chemistry:

1. **Heart of Green chemistry-to minimize the waste product formation:**

   It is better to prevent the formation of waste than to treat or clean up the waste after the formation.

   Illustration of the Ist principle: The first principle aims to develop the zero waste technology. In terms of ZWT,in the chemical synthesis, waste product should be zero or minimum. It also to use waste product of one system as the raw material for other systems. As one example, bottom ash of thermal power station can be used as a raw material for cement and brick industry; effluent coming out from cleaning of machinery parts may be used as coolant water in thermal power station; municipal waste as a source of energy etc.

2. **Atom economy:**

   During the synthesis of a chemical product, the methodology should be designed in the way to maximize the incorporation of starting materials into the desired final product. Thus it demands to minimize the formation of by-product.

3. **To avoid the use and formation to toxic materials**:

If possible and the synthetic methodologies should avoid the use and generation of toxic and environmentally hazardous substances.

Illustration of the 3rd principle: This principle aims to develop the methodologies that will minimize the use and formation of toxic and hazardous substances .In other words, the synthetic methodologies should use and generate the ecofriendly substances that no toxicity to human health and environment.

4. **Use of nontoxic chemical products:**

Chemical products aims to be used in different activities should have the efficacy to function but with reduced environment.

Illustration of the 4th principle: In many chemical industries, not only the waste product but the starting materials are also quite hazardous to the workers and environment. For example, adipic acid is widely used in polymer industries. Benzene is the starting materials for the synthesis of adipic acid but benzene is carcinogenic and benzene being a VOC pollutes air.

5. **Minimum use of auxiliary substance:**

In a chemical synthesis ,the use of auxiliary substance like solvents, separating agents,etc,should be avoided. If, these are to be used, they should be eco-friendly.

Illustration of the 5th principle: This principle aims to use of green solvents(e.g, water, supercritical CO_2)in the place of volatile halogenated organic solvents eg. CH_3Cl_3,$CHCl_3$,C_2Cl_4,CCl_4 for chemical synthesis and other purposes. For example Clsisen rearrangement

6. **Minimum energy consumption:**

In the synthesis of a chemical product, the energy, the energy consumption should be minimized to make the process more and more economic, Ideally, the synthetic methods be carried out at ambient temperature and pressure.

Illustration of the 6th principle: To save energy, synthetic methodologies should needs more and more moderate conditions and the ambient temperature and pressure are the best choices. It needs suitable catalysts that will accelerate the reaction rate even at lower temperature. The biocatalysts can work at the ambient conditions.

7. **Use of renewable sources:**

If it is technically and economically possible, then the renewable resources(e.g. biomass) rather than the non renewable recourses (e.g. crude oil)should be used as the raw material or feed stock.

Illustration of the 7th principle: If encourages the use of starting material(i.e. raw material or feedstock)which should be renewable, if technically and economically practicable. In fact,continous use of the nonrenewable feedstock (e.g. petroleum product, fossil fuel) will deplete the resource and future generation will be deprived. Moreover, use of the these nonrenewable resources puts a burden on the environment.

On the other hand, use of sustainable or renewable resources e.g agricultural or biological product ensures the sharing of resources by future generation. Moreover, this practice generally does not put much burden on the environment. The products and wastes are generally biodegradable. The practice of this principle has been illustrated in many cases like bio plastic and biopolymer,biodisel,CO2 feedstock in the manufacture of polycarbonate, greener synthesis of furfural from biomass, greener synthesis of adipic acid and catechol from biomass.

8. **Minimization of steps:**

The steps blocking groups, production/reproduction of the group , temporary modification of physical and chemical processes etc., should be avoided as for as possible during the synthesis of a chemical product. Thus there should be a minimum of steps to synthesize a target product.

Illustration of the 8th principle: Specially in organic synthesis need very often protection of some functional groups. Finally need their reproduction. It is illustrated in the example of synthesis of m-hydroxybenzoic acid from m-hydroxybenzaldehyde.

9. **Use of catalytic reagents:**

Selective catalytic reagents are superior to stoichiometeric reagents in a chemical synthesis, This will save the energy and reduce the burden of by-product.

Illustration of the 9th principle: This principle of green chemistry states that catalytic of the following advantages.(i) 100% atom economy because the true catalysts are fully recovered without any change in their chemical and physical properties.(ii) the catalyzed reactions are faster i.e energy save possible.(iii) reaction yields are better. (iv) Selective reaction products.(v) maximum utilization of the starting material and minimum production of the waste material.

10. **Life time of a chemical product**:

At the end of function, the chemical products(e.g pesticides) should degrade easily to harmless products,i.e after their function, they should not persist in the environment. DDT is the best example. It is an effective pesticide but its stability in the natural environment causes several environment hazards.

Illustration of the 10th principle: It states that the waste product should degrade automatically to clean the environment. Thus the biodegradable polymer and pesticides are always preferred. Sometimes, the polymers are to be made degradable photochemically.It should be mentioned that the degraded products should not be toxic.

11. **Monitoring the generation of hazardous substance:**

    Analytical methodologies should be further developed to allow for real time in process monitoring and control prior to the generation of hazardous substance in the synthesis of chemical products.

    Illustration of the 11th principle: analytical methodologies should be developed or modified, so that continuous monitoring of the manufacturing and processing units is possible. This is very much important for the chemical industries and nuclear reactors. This efficient monitoring is quite essential to avoid the accident.

12. **Use of chemical safer substances:**

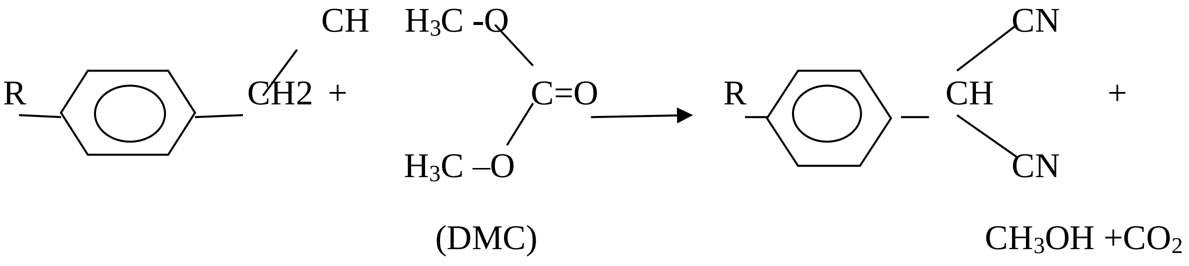
    The substances to be used in a chemical reaction should be selected in a way that they can minimize the occurrence of chemical accidents,explosions,fires and emissions. In other words, the substance to be used should not be hazardous.

    Illustration of the 12th principle : The substance used in chemical industries should be in such forms so that the possibility of accidents can be minimized. For example ,if the chemical process works with the gaseous substances, then the possibility of accidents including explosion is relatively higher compared to the systems working with the nonvolatile liquid and solid substances. In the risk is minimum if the process works with solid substance at every step.

Use of safer reagents:

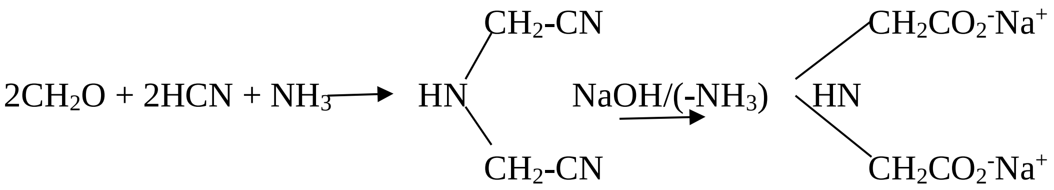
Green chemistry aims to replace the hazardous reagents. It is illustrated for the methylation reaction which conventionally uses the hazardous reagents like CH3-X(methyl halide),DMS(dimethylsulfate), etc. The green alternative is DMC (dimethylcarbonate).

Methylation of an active methylene group can be done by using the green reagents

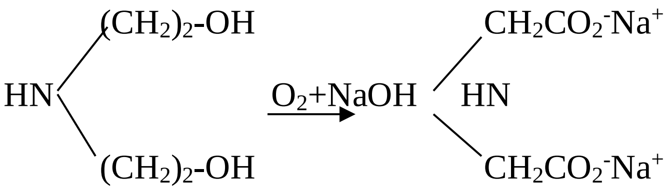


The Conventional methylation process produces the hazardous toxic by product while in the above methylation reaction, the reagents are green and the by products are also green.

Disodium iminodiacetate is an essential reagentin manufacturing a herbicide. Conventional route uses the hazardous chemicals like formaldehyde and HCN while the green synthesis does not use any such hazardous substance.



(Strecker Process) **(Na_2ida)**



(Na2ida)

(Diethanol amine) (Green Synthesis)

K2CO3 is also a green reagent that finds uses in the synthesis of different heterocyclic compounds. It acts as a base and provides a solvent free condition in many cases.

Conventional synthesis of polyurethanes needs the use of the toxic chemical like phosgen gas. The green technique avoids the use of phosgen gas.

$RNH_2 \; + \; \xrightarrow{CO_2/-H_2O} \; RNCO \longrightarrow RNHCOOR'$

Use of Green Solvent:

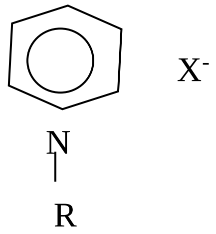
The hazardous organic solvents need replacements. The ecofriendly reaction media are water,polyethylene glycol,room temperature ionic liquids, supercritical water, super critical carbondioxide etc. microwave assisted organic reactions in such green solvents are playing important roles in green chemistry. Organic synthesis in aqueous media is becoming inceasingly popular. Different organic reactions in aqueous media coupled with microwave/ultersonic irradiation have now been established. Supercritical water in which organic compounds are more soluble compound to water at ordinary condition is also a potential alternative.

Use of room temperature ionic liquids as green solvents:

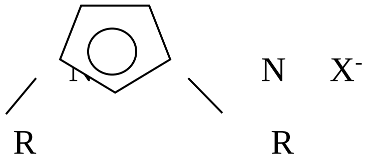
Commonly used organic solvents are generally volatile organic compounds(VOCs) that cause several environmental hazards including smog production in air, ozone depletion, health hazards etc. The ionic liquids are the green alternatives. These ionic liquids are generally organic salts like alkylammonium salts, N-alkylpyridinium salts, and N,N'-dialkylimidazolium salts.

$[R_xNH_{4-x}]^+$

Alkylammonium Salt



N-alkylpyridinium salt



N,N'-dialkylimdazolium salt

These nonvolatile ionic liquids can be easily recovered after use. They can be recovered and purified. The product can be isolated from the ionic liquid by using some common solvent like either in a separating funnel.

Supercritical fluids as green solvents:

Use of supercritical CO_2 fluids as green solvents: Use of supercritical CO_2 emerging with a great substitute the VOC's. The important uses of SO-CO_2 are: dry cleaning of clothes, polymerisatio reaction etc.

Supercritical CO_2 may be used to extract the organic pollutants like MTBE,PCBs,DDT etc.present in water,soils and sediments.

Supercritical water(T_c=374^{o}C) is too hot for many organic compounds.But near critical water appears as a benign solvent for many organic reactions.

Use of greener catalyst:

Some times the used catalysis are toxic and these are accumulated in the industrial waste product.For example HF is the catalyst used in the production of linear alkylbenzenes and it has been replaced by the greener catalyst i.e., fluorided silica alumina catalyst. Other example of greener catalyst are zeolites acting as acid catalysts in Friedle crafts reaction,synthesis of oxime by titanium(IV) –silicate (TS-1) catalyst, dehydration of organic molecules etc by ZSN-5 (used in the manufcture of synthetic gasoline, TiO_2 (used as a photocatalyst in removing water pollutants.

Biocatalysts are the most ideal,green catalysts and these are finding applications in many biocatalytic transformations. These biocatalysts may be developed in the genetically engineered bacteria.

UNIT – II – Green Chemistry

Microwave Mediated Organic Synthesis (MAOS)

Green chemistry :

Green chemistry also called Sustainable chemistry is an area of chemistry and chemical engineering focused on the design of products and processes that minimise or eliminate the use and generation of hazardous substances.

Father of Green chemistry – Paul. T. Anastas.

Green chemistry 12 Principles developed by – John. C. Warner

Microwave activation :

Microwave chemistry is the Science of applying Microwave radiation to chemical reactions. Microwave acts as high frequency electric fields and will generally heat any material containing Mobile electric charges such as polar molecules in a Solvent or conducting ions in solid.

Mechanism of Microwave :

- Di-electric heating.
- Generation of thermal energy in non conducting material by the application of a electromagnetic force.
- Wasted energy appears as heat called dielectric – loss.

* The non metallic material with poor thermal conductivity can be very effectively heated by dielectric heating.

* Dielectric losses proportional to frequency and square of the supply voltage.

* Microwave dielectric heating Mechanism are of two types.

  (i) Dipolar Polarization Mechanism.
  (ii) Conduction Mechanism.

Microwave assisted synthesis in green technologies:

The term green chemistry is defined as the invention design and the application of chemical products and processes to reduce the use and generation of hazardous substances. Green Chemistry can diminish the need for other approaches to the environmental pollution. The application of green chemistry principles and practice renders regulation, control clean-up and remediation unnecessary and the resultant environmental benefit can be expressed in terms of economic impact.

Advantages of Microwave radiation.

Uniform heating occurs throughout the material.

* Process speed is increased.
* High efficiency of heating.
* Reduction in unwanted side reaction.
* Purity in the final product.
* Reproducibility
* Environmental heat loss can be avoided
* Reducing wastage of heating reaction vessel.
* Low operating cost.
* Chemically homogeneous compositions and by product efficiency.

Specific effects of Microwave :-

Microwave Irradiation has been successfully applied in Organic Chemistry. The effect of microwave irradiation in organic synthesis is a combination of thermal effects, arising from the heating rate. Superheating or "hot spots" and the selective absorption of radiation by polar substances. Such phenomena are not usually accessible by classical heating and the existence of non-thermal effects of highly polarizing radiation.

The specific microwave effect is still Controversial topic. An overview of the

Thermal effects and the currents state of non-thermal microwave effects is presented in their critical review along with a view on how these phenonmena can be effectively used in organic synthesis.

Neat Reaction

'Neat' Means you run your reaction without a solvent. For example, a reaction where benzaldehyde was one of the reactants. Benzaldehyde is a liquid at room temperature and it also was able to solvate others. reactants / catalyst. For this reason the reaction was just run in stoichiometric benzaldehyde as opposed to in a solvent. It provides better atom efficiency.

Neat reaction technology is a step forward in the direction of solvent free reactions and an alternative approach that eliminates the use of a solid support as well as solvent from the reaction.

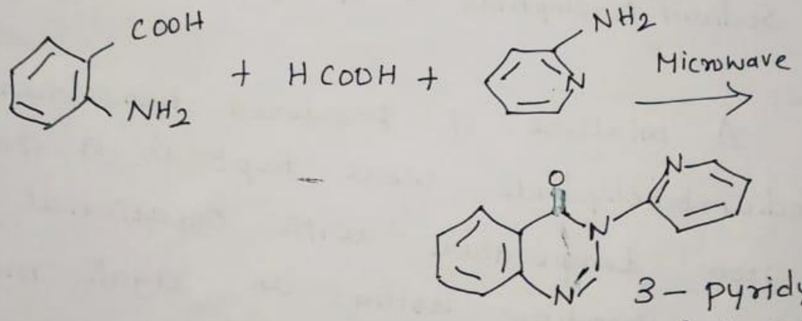
Solid state (Solvent less) Reactions:

3-Pyridyl-4(3H) quinazolone

It is obtained by the reaction of anthranilic acid with formic acid and 2-aminopyridine under Microwave irradiation.

Materials:-

Anthranilic acid	1.26g
Formic acid	5g
2-Aminopyridine	0.92g



3-pyridyl-4(3H) quinazolone.

Procedure:-

A mixture of anthranilic acid, formic acid and 2-amino pyridine was heated in a Microwave oven for 4 mins. The product obtained Melted at 156-157°C and gets 92% yield.

The Methodology is enviromentally benign and completely eliminates the need of Solvent from the reaction.

Dr. E. Hema

Diphenyl Carbinol :-

It is obtained by the reduction of benzophenone with Sodium borohydride in Solid State.

$$Ph_2CO + NaBH_4 \longrightarrow Ph_2CHOH$$

Benzophenone Sodium borohydride diphenyl carbinol.

Materials:

Benzophenone – 1.8 gm
Sodium borohydride – 4.8 gm

Procedure:

A mixture of Powdered benzophenone and Sodium borohydride were kept in a dry box at room temperature with occasional mixing and grinding using an agate morter and pestle for 5 days. Diphenyl Carbinol was Obtained in 100% yield.

Solvent free Synthesis using Focussed Microwave

The Combination of Solvent-free Procedures and Microwave irradiation Can be used to carry out a wide range of reactions within Short time and with high Conversions and Selectivity. This approach is efficient easy to perform economic and less polluting. Some major advantages of the organic synthesis under microwaves are,

* Very rapid reactions, requiring few miniutes brought about by high and homogeneous temperature and combined with pressure effects (if conducted in closed vessels)

* Higher degree of purity achieved due to short residence time at high temperature, no local overheating, minor decomposition and minor occurence of secondary reactions.

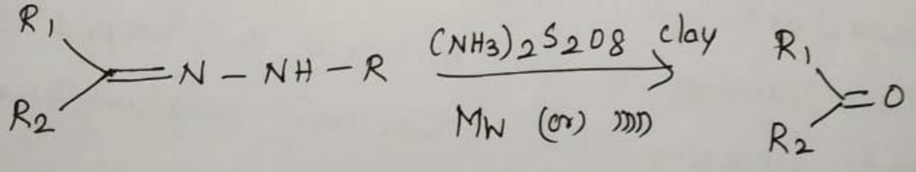
* Yields are often better obtained within shorter times to give purer products. These reactions can be performed in open glass containers simply by mixing of neat reactants with the catalyst / promoter or their absorption on mineral or "doped" supports and exposing the reaction mixture briefly to microwave

" Solid state reaction or solvent free reaction follows the fifth principle of Green chemistry which avoid using toxic solvents in the chemical reaction".

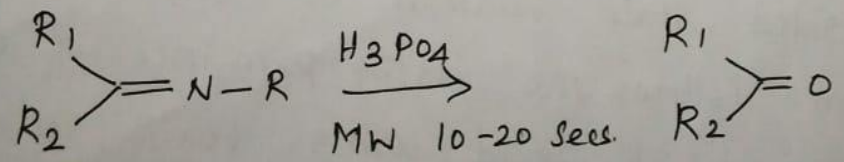
A) Functional Group Tranformations :-

Clevage reactions are expedited by microwave exposure of protected molecules on mineral oxides or benign "doped" reagents. For, examples, - a Solvent-free deprotection procedure uses relatively benign reagent, ammonium Persulfate on clay for regeneration of Carbonyl Compounds from the Corresponding Semicarbazone and phenylhydrazone derivative by microwave or ultrasound irradiation. Microwave irradiation of phenyl hydrazones and tosylhydrazones with Phosphoric acid also regenerate the Carbonyl Compound in excellent yield.

Reaction 1.



Reaction 2.

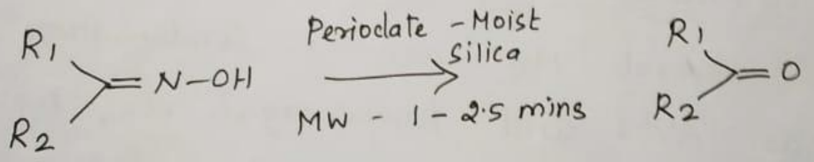


$R = -NHPh, -NHTs$

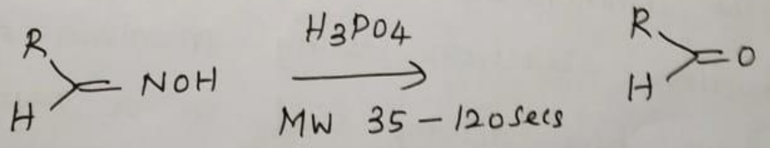
Similarly ketones can be regenerated in a MW oven by simply admixing neat Ketozimes with Periodate on wet silica and then exposing them to MW irradiation. The role of the surface is very critical as the deoximation reaction that occurs on silica surface predominant delivers the Beckmann rearranged products on clay.

Another facile method of Microwave assisted regeneration of aldoxime using phosphoric acid in Solvent-free condition at ambident pressure has been reported recently.

Reaction 1

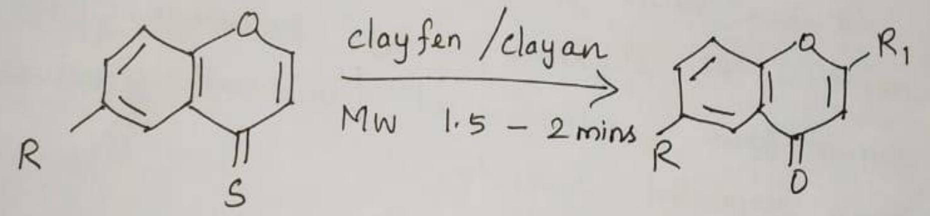


Reaction 2



Another important conversion is the Thiocarbonyls to Carbonyls unfortunately, This transformations by Conventional method have certain limitations such as the use of stoichiometric amounts of the oxidants that are often inherently

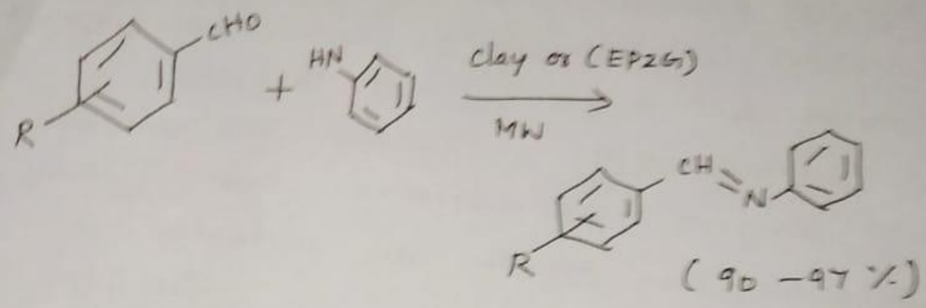
toxic or require longer reaction time or involve tedious process. These difficulties have been overcomed by developing on efficient Solvent-free dethiocarbonylation process using clayfen [Iron (III) nitrate on clay] or clayan [Ammonium nitrate on clay] that is accelerated by MW irradiation.



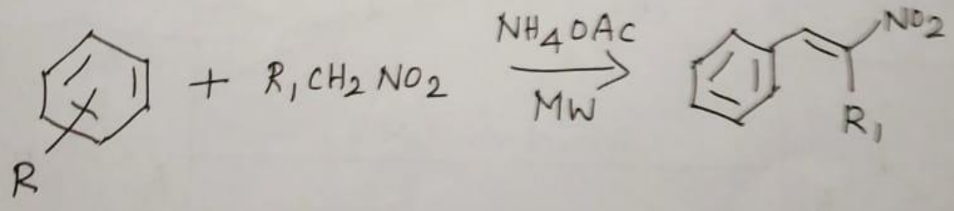
B. Condensation Reaction :

Several MW - assisted Condensation reaction Such as Aldol and Knoevenagal etc., have been accompanied using relatively benign reagents Such as ammonium acetate. MW - expedited dehydration reaction using montmorillonite K10 clay have been accomplished in a rapid Synthesis of imines and enamines Via the reactions of primary and Secondary amines with aldehydes and ketones respectively.

Reaction 1



Similarly Herry reaction the Condensation reaction of nitroalkanes with carbonyl Compounds to generate nitroalkanes also proceeds rapidly via this MW approach in the presence of only Catalytic amounts of ammonium acetate Thus avoiding the use of large excess of polluting nitrohydrocarbons usually employed in These reactions



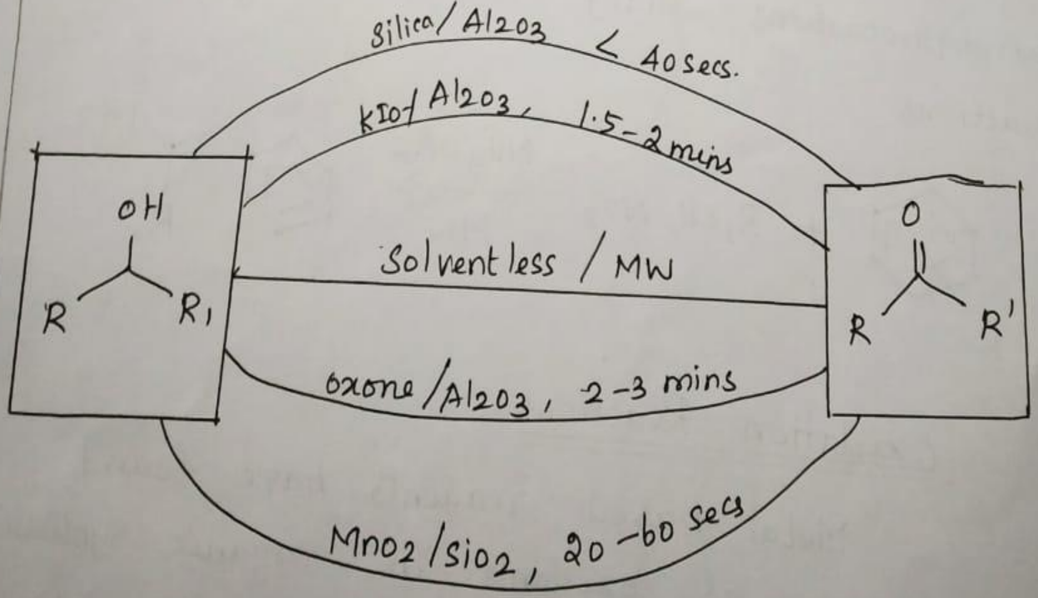
C. Oxidation Reactions.

Metal based reagents have found extensive use as oxidants in organic synthesis. The utility of such reagents in the oxidation

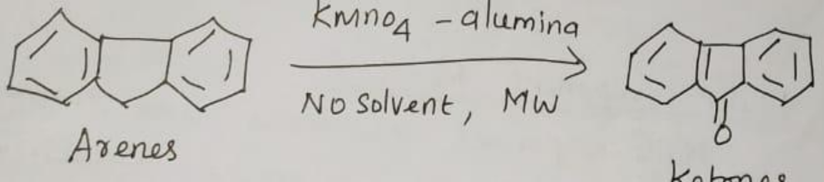
Process is compromised due to several reasons such as potential danger in handling of metal complexes, inherent toxicity, cumbersome product isolation and waste disposal problems.

Immobilization of metallic reagents on solid supports has addressed some of these limitations and provided an alternative in organic synthesis because of the selectively and prevention of leaching of the metals into environment

Recently several MW - assisted oxidative protocols have been introduced which are applicable to both alcohols and sulfides using a wide variety of supported oxidants.



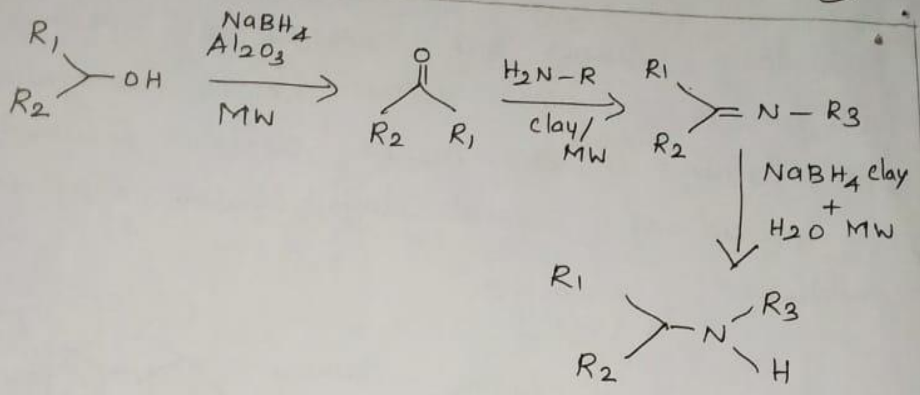
Similarly, Arienes are oxidized into ketones with in 10 – 80 mins using $KMnO_4$ impregnated onto alumina in dry media under focussed MW instead of several days under classical conditions.



Ketones.

D. Reduction Reactions.

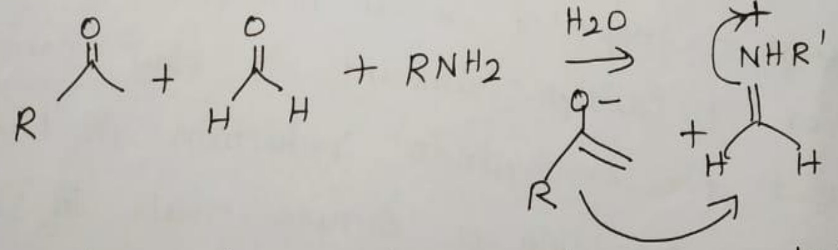
The solid state selective reduction of carbonyl compounds occurs readily with alumina – supported sodium borohydride ($NaBH_4$), However, a catalytic amount of clay can also be used for borohydride reduction in the same pot, thus providing a simple route to secondary and tertiary amines. Clay serves the dual purpose of a Lewis acid and also provides water from its interlayers that enhance the reducing ability of $NaBH_4$



E. Multi Component Reaction:-

Multi component reactions are Convergent reagent in Which Three or more Starting materials react to form a product, Where basically all (or) most of The atoms Contribute to The newly formed by product

Mannich Reaction :-



obviously this reaction only proceeds if one Carbonyl Compound react faster with reaction. Carbonyl Compound act as a nucleophile in This reaction.

Question Bank

I 2 Mark Questions.

1. What is Microwave activation ?
2. Define Microwave chemistry ?
3. Define Neat reaction ?
4. What is solid state reactions in green Chemistry . ?
5. What is the fifth principle of Green Chemistry ?

II 5 Mark Questions.

1. Explain the Mechanism of Microwave irradiation ?
2. List out the advantages of Microwave radiation?
3. Illustrate about neat reaction with example?
4. Explain the Functional group transformation using Solvent free Synthesis ?
5. Explain Solvent free Condensation reaction?
6. Explain Solvent free oxidation reaction?
7. Explain Solvent free Reduction reaction?
8. Explain Solvent free multicomponent reaction

III 10 Mark Questions.

1. What is microwave activation ? Briefly explain

The Mechanism and advantages of MW radiation ?

2. Illustrate about solvent free Synthesis using focussed microwave ?

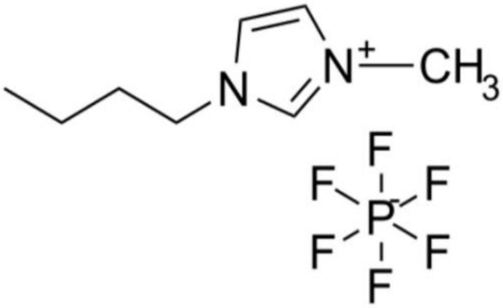
— x —

Unit - 3

1. What are ionic liquids?
2. Write the properties of ionic liquids
3. What are the advantages of ionic liquids?
4. Why ionic liquids are green?
5. What is PTC? Give an example
6. How do you synthesis of ionic liquids?
7. How is ionic liquids applied in alkylation?
8. How will you explain epoxidation using ionic liquids?
9. Explain witting reaction using ionic liquids
10. Discuss the Diels Alder reaction in using ionic liquids
11. Give a brief account of FriedelCrafts reaction in ionic liquids
12. Write a note on application of ionic liquids in alkylation reaction
13. Write a short note on application of ionic liquids in hydroformylations
14. What are phase transfer catalyst? Their general properties and synthesis

ionic liquid:

An ionic liquid is a salt in the liquid state. In some contexts, the term has been restricted to salts whose melting point is below some arbitrary temperature, such as 100 °C . While ordinary liquids such as water and gasoline are predominantly made of electrically neutral molecules, ionic liquids are largely made of ions and short-lived ion pair. These substances are variously called liquid electrolytes, ionic melts, ionic fluids, fused salts, liquid salts, or ionic glasses.



Properties of ionic liquid:

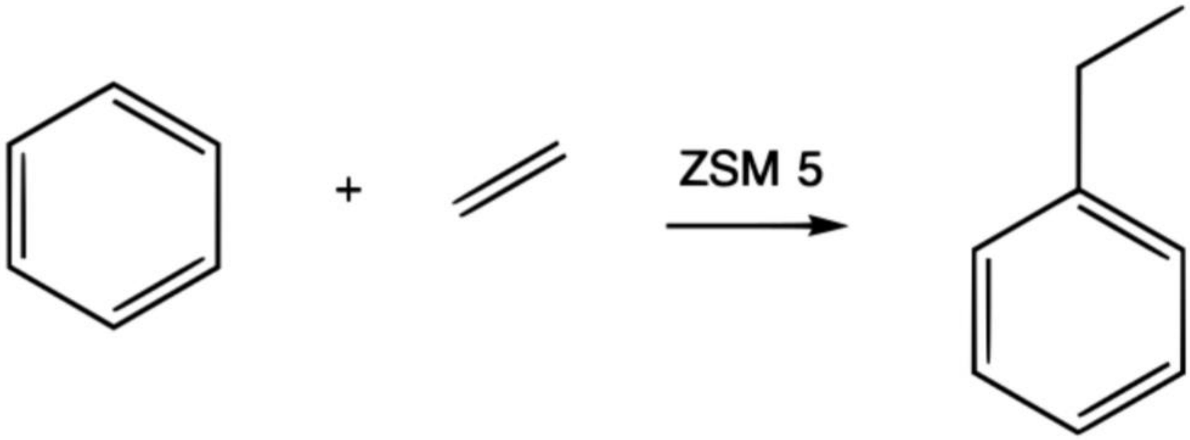
Ionic liquids also have a high thermal stability, which means they are more resistant to changes in their chemical or physical structure. They also tend to have high electrical conductivity, allowing electricity to flow through them well, and have no vapor pressure which means they are not very reactive. They also have a low viscosity, which means they flow easily.

Applications of ionic liquid:

Ionic liquids have many potential applications. Because of these unique properties, ionic liquids have a number of useful applications. For example, because they have a low volatility (that low vapor pressure mentioned before) and because they can dissolve many different things, they have been used as 'green' solvents in different industrial practices.Their properties also make ionic liquids useful for gas transport and storage. Instead of using pressurized containers, gases can be dissolved into ionic liquids and easily removed when needed. Ionic liquids can also be useful in recycling, aiding in the separation of similar but different materials from one another. For example, separating polymers from plastics.

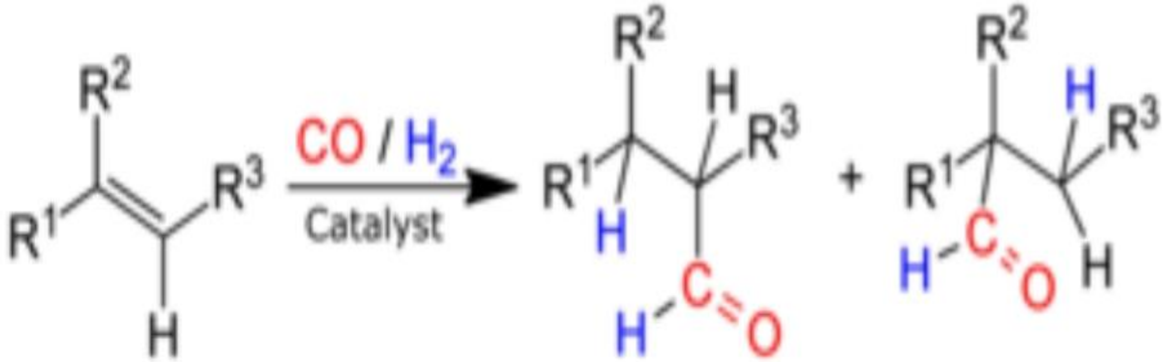
Application in alkylation:

Aldoximes react with α,β-unsaturated carbonyl and sulfonyl compounds in organized aqueous media using dodecylbenzenesulfonic acid (DBSA) as surfactant to generate *N*-alkylated nitrones, which undergo intermolecular cycloaddition in the same pot with maleimides to give the desired cycloadduct in absence of any organic solvent and catalyst. Divinyl sulfone was successfully used for both *N*-alkylation and intramolecular cycloaddition, affording only one cycloadduct. This is a new example of green chemistry and provides a new aspect of reactions in water.



Application in Hydroformylation:

Hydroformylationalso known as oxo synthesis or oxo process, is an industrial process for the production of aldehyde from alkene. This chemical reaction entails the net addition of a formyl group (CHO) and a hydrogen atom to a carbon-carbon double bond. This process has undergone continuous growth since its invention: Production capacity reached 6.6×10^{6} tons in 1995. It is important because aldehydes are easily converted into many secondary products. For example, the resulting aldehydes are hydrogenated to alcohol that are converted to detergents. Hydroformylation is also used in chemical, relevant to the organic synthesis of fragrance and drugs.

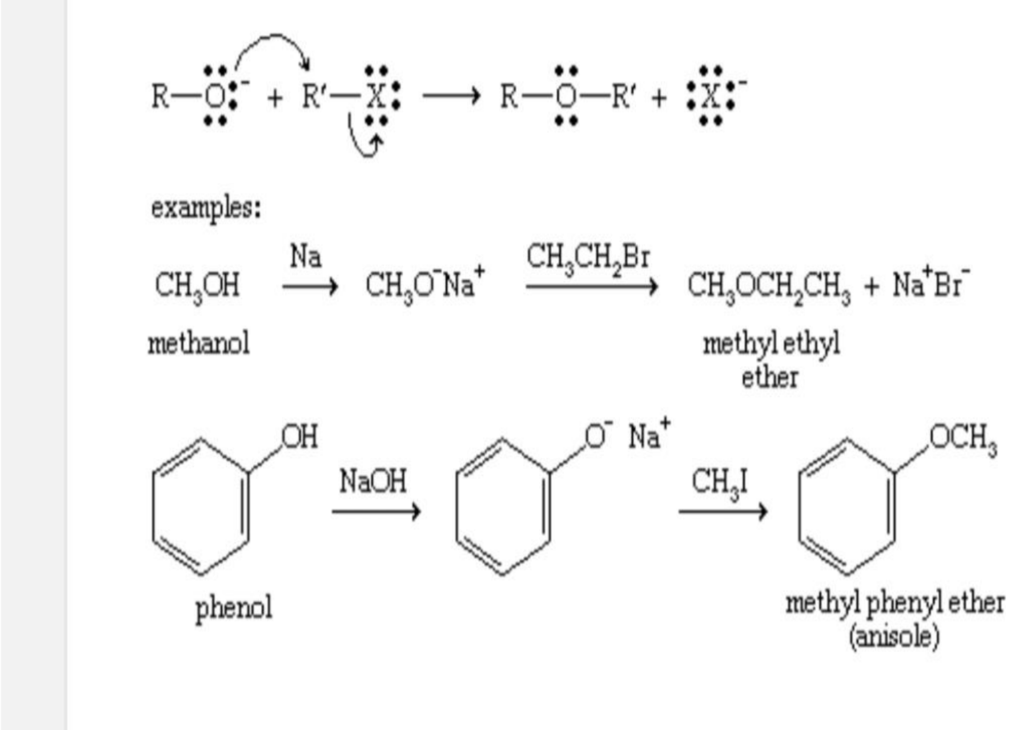


Application in epoxiedation:

Ethylene epoxide has many uses including generation of surfactants and detergents.Epoxy glues and structural materials are a result of epoxides reaction with amines.It is used as a stabilizer in materials like PVC. They are also used in manufacture of Epoxy resists that have low viscosity and without compromising strength and physical properties.Epoxides are also used in things like insecticides, aerosols, resins and chemical intermediates.

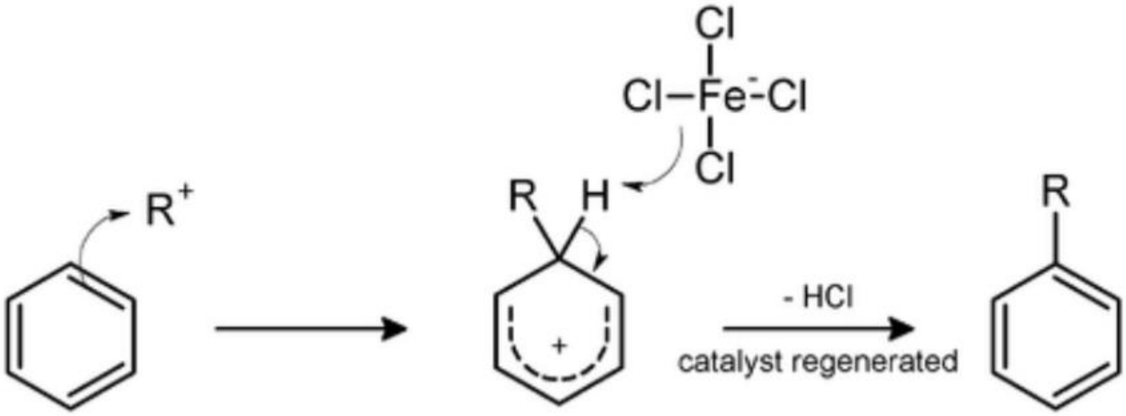
Synthesis of ether:

The most versatile method for making ethers is the Williamson ether synthesis, named for English chemist AlexanderWilliamson, who devised the method in the 19th century. It uses an alkoxide ion to attack an alkyl halide, substituting the alkoxy (—O—R) group for the halide. The alkyl halide must be unhindered or elimination will compete with the desired substitution.



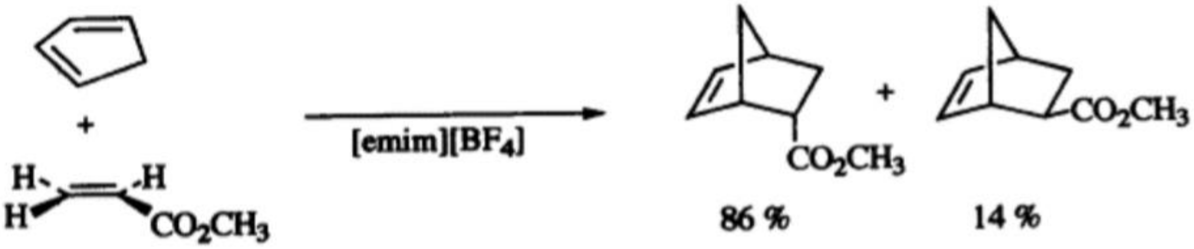
Friedelcraft reaction:

The Friedel–Crafts reactions are a set of reactions to attach substituents to an aromatic ring. Friedel–Crafts reactions are of two main types: alkylation reactions and acylation reactions. Both proceed by electrophilic aromatic substitution. Friedel–Crafts alkylation involves the alkylation of an aromatic ring with an alkyl halide using a strong lewis acid, such as aluminium chloride, ferric chloride, or other MX_n reagent, as catalyst. The general mechanism for tertiary alkyl halides is shown below.



Diels-Alder reaction:

The Diels-Alder cycloaddition reaction between methyl acrylate and cyclopentadiene has been investigated in a number of air and moisture stable ionic liquids. The endo/exo ratio of the reaction has been used as an initial probe of the nature of the solvents.Room-temperature ionic liquids are used as solvents for regioselective Diels-Alder reactions.

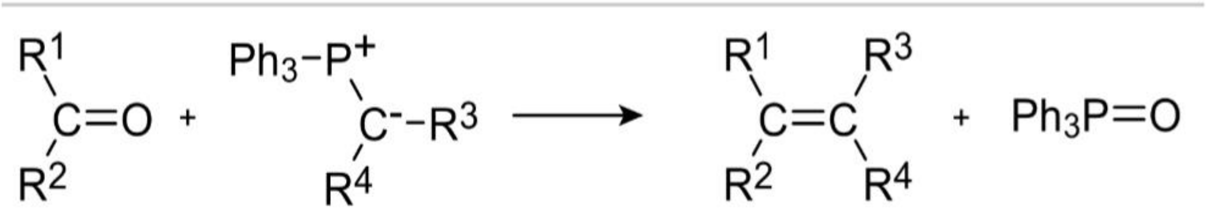


Knoevenagel condensation:

AKnoevenagel condensation is a nucleophilic additionof an active hydrogen toa carbonyl group followed by a dehydration in which a molecule of water is eliminated. The product is often an α,β-unsaturated ketone

Wittig reaction:

The ionic salt [bmim][BF_4] is an attractive solvent for Wittig reactions, allowing both easier separation of alkenes from Ph_3PO together with efficient reuse of the solvent.



phase-transfer catalyst:
PTC is a catalyst that facilitates the migration of a reactant from one phase into another phase where reaction occurs. Phase-transfer catalysis is a special form of heterogeneous catalysis.. Ionic reactants are often soluble in an aqueous phase but insoluble in an organic phase in the absence of the phase-transfer catalyst. The catalyst functions like a detergent for solubilizing the salts into the organic phase. Phase-transfer catalysis refers to the acceleration of the reaction upon the addition of the phase-transfer catalyst.
By using a PTC process, one can achieve faster reactions, obtain higher conversions or yields, make fewer by-products, eliminate the need for expensive or dangerous solvents that will dissolve all the reactants in one phase, eliminate the need for expensive raw materials and/or minimize waste problems. Phase-transfer catalysts are especially useful

in green chemistry—by allowing the use of water, the need for organic solvent is reduced.Contrary to common perception, PTC is not limited to systemswith hydrophile and hydrobolic reactants. PTC issometimes employed in liquid/solid and liquid/gas reactions. As the name implies, one or more of the reactants are transported into a second phase which contains both reactants.

Synthesis of Phase transfer catalyst:

Most of the pharmaceuticals or agricultural chemicals are the result of organic synthesis. Most of the syntheses require a number of steps in which additional reagents, solvents and catalysts are used. In addition to the syntheses of the desired products, some waste material is generated, the disposal of which causes problems and also environmental pollution. In view of this, attempts have been made to use procedures that minimise these problems. One of the most general and efficient methodologies that takes care of the above problems is to use a phase-transfer catalyst (PTC).

Application of Phase transfer catalyst:

Phase-transfer catalysis (PTC) has been widely used for the synthesis of organic compounds for more than three decades. The scope and mechanistic features of PTC have been the aim of numerous studies. This review is approaching the subject by focusing on the extraction-preconcentration-derivatization prior to analysis, reporting recent progress made. Moreover an attempt is made to approach the salient aspects of PTC modes including a brief review of mechanistic pathways and kinetics pointing out the potency of PTC in analytical chemistry. Optimization guidelines for PTC-based analysis are given with respect to all parameters influencing the analytical method under development, highlighting the capabilities and limitations of PTC reactions.

UNIT-IV

SUPPORTED CATALYSTS AND BIO-CATALYSTS FOR GREEN CHEMISTRY

TWO MARKS

1.What is atom economy in green chemistry?

2.How can you improve atom economy?

3.What is the formula for atom economy?

4.What type of reaction have the highest atom economy?

5.Which of the following is a reason atom economy is important?

6.What is the difference between percentage yield and atom economy?

7.What is meant by supported matal catalysts?

8.Define fermentation.

9.What do you mean by biotransformation?

10.Give the expansion of NAD and MCPBA

FIVE MARKS

1.Write any five atom economy based green reactions.

2.Write short notes on supported metal catalysts.

3.Explain the uses of mesoporous silicas.

4.Write a note on microbial fermentation.

5.Briefly explain microbial polyster synthesis.

TEN MARKS

1.Atom Economy –Explain in detail.

2.Briefly explain Bakers yeast mediated biotransformations.

3.Describe: Baeyer-villiger reactions mediated by bio-catalyst.

ATOM ECONOMY

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.

The maximum atom economy possible for a reaction is 100%. This will be the case if there is only one product (the desired product) and no by-products. The atom economy of a particular reaction can only be improved by finding a use for the other product, which makes it another desired product.

Atom economy and percentage yield

Atom economy is the percentage of the total mass of reactants that successfully converted to the desired product. Percentage yield is calculated from the mass of reactants and the mass of products.

The reactions that only give one product, have the maximum atom economy of 100% and these are the most economic reactions e.g. synthesis of ammonia and reacting ethene with water to make ethanol.

E-Factor = Total waste (kg) / Total product (kg)

If you're generating 1 kilogram of waste for every 5 kilograms of final product, your E-Factor is 1/5 or 0.2. The lower your E-Factor, the better performing your product is.
The atom economy of a chemical reaction is a measure of the percentage of reactants that become useful products. Efficient processes have high atom economies, and are important for sustainable development, as they use fewer natural resources and create less waste.

$$\text{\% Atom Economy} = \frac{\text{Molar Mass of Product}}{\text{Molar Mass of All Reactants}} \times 100\%$$

$$= \frac{206.29 \text{ g/mol}}{(134.22 + 102.09 + 122.55 + 68.05 + 19.02 + 33.03 + 36.04) \text{ g/mol}} \times 100\%$$

$$= \frac{206.29 \text{ g/mol}}{515.00 \text{ g/mol}} \times 100\%$$

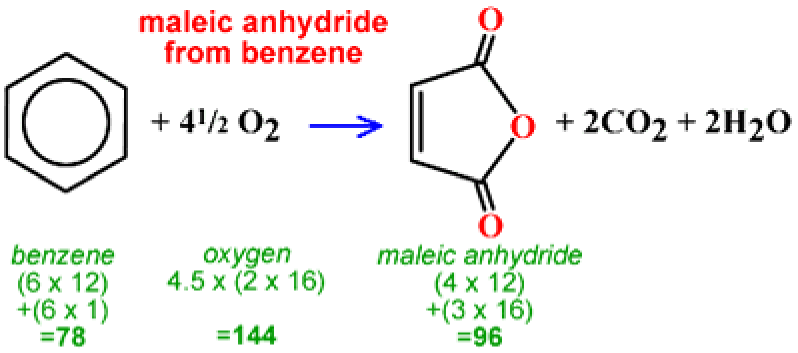
% Atom Economy = 40%

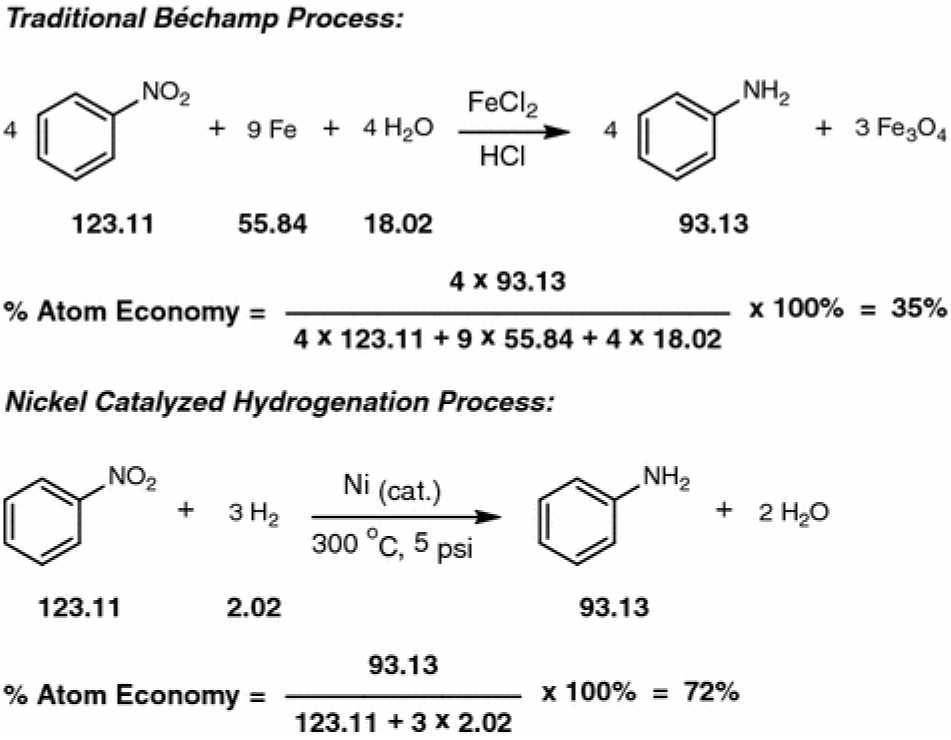
$$\text{atom economy} = \frac{\text{mass of atoms in desired product}}{\text{mass of atoms in reactants}} \times 100\%$$

$$= \frac{96}{(78 + 144)} \times 100\%$$

$$= 43\%$$

EXAMPLES FOR ATOM ECONOMY BASED REACTION





$$\% \text{ Atom Economy} = \frac{4 \times 93.13}{4 \times 123.11 + 9 \times 55.84 + 4 \times 18.02} \times 100\% = 35\%$$

$$\% \text{ Atom Economy} = \frac{93.13}{123.11 + 3 \times 2.02} \times 100\% = 72\%$$

SUPPORTED METAL CATALYSTS

Supported metal catalysts are used for hydrogenation in organic solvent; however, several **metal** species do not work for hydrogenation in supercritical carbon dioxide solvent. Reverse water-gas shift reaction ($CO_2 + H_2 \rightarrow CO + H_2O$) proceeds over some **metal catalysts** and Carbon monoxide molecules deactivate **metal** sites.

Catalyst support

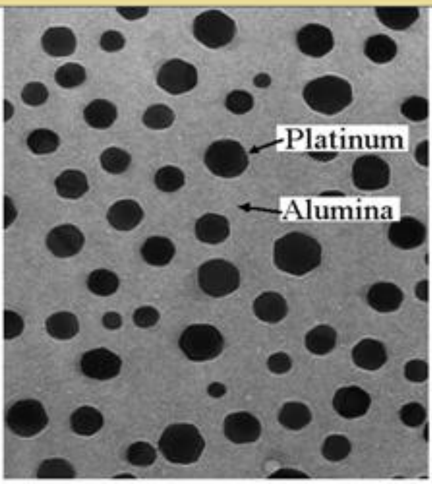
In chemistry, a catalyst support is the material, usually a solid with a high surface area, to which a catalyst is affixed. The activity of heterogeneous catalysts occurs at the surface atoms. Consequently, great effort is made to maximize the surface area of a catalyst.

Supported Metal Catalysts

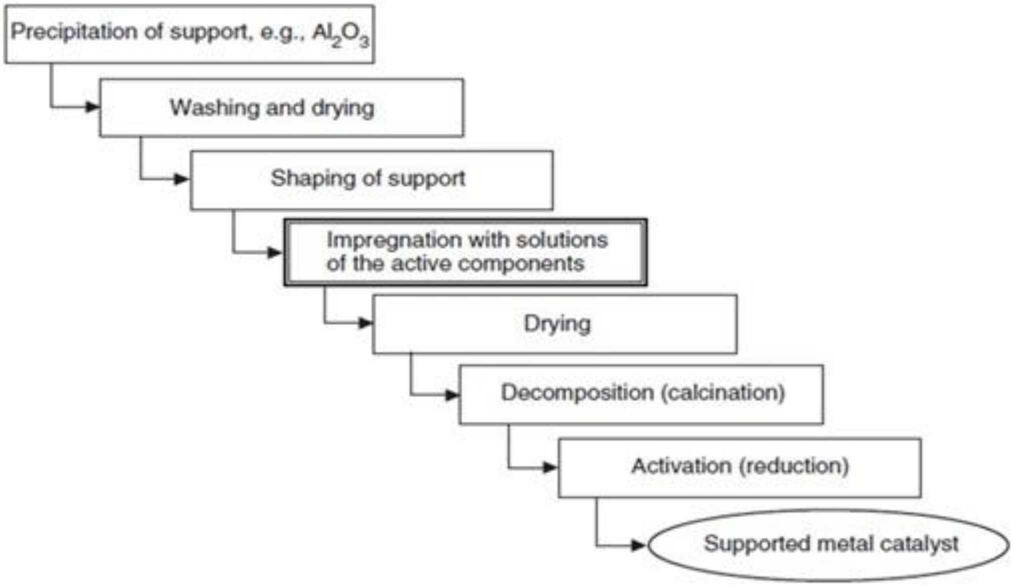
Use support because platinum very expensive and only the surface is active.

Spread platinum out on cheap support.

Support also provides strength



Supported metal catalyst



Precipitation of support, e.g., Al_2O_3

Washing and drying

Shaping of support

Impregnation with solutions of the active components

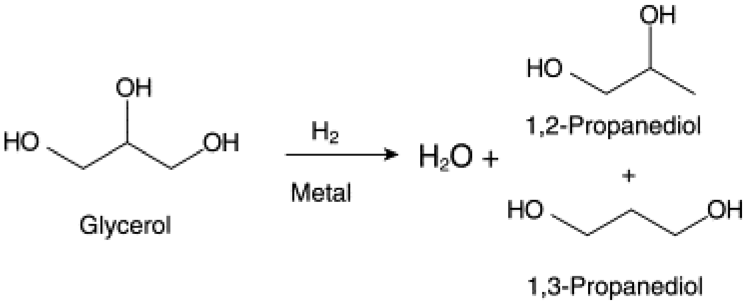
Drying

Decomposition (calcination)

Activation (reduction)

Supported metal catalyst

EXAMPLE

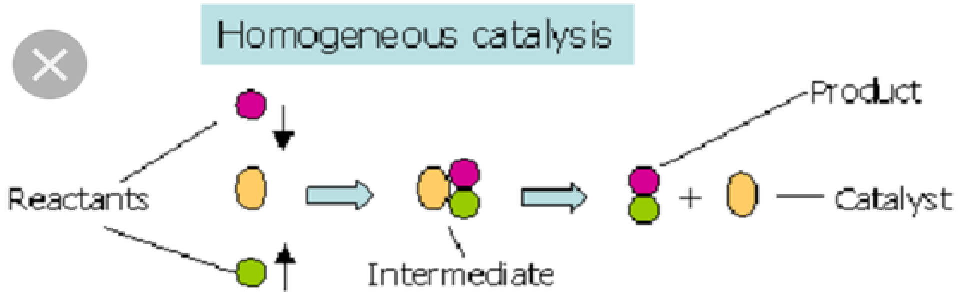


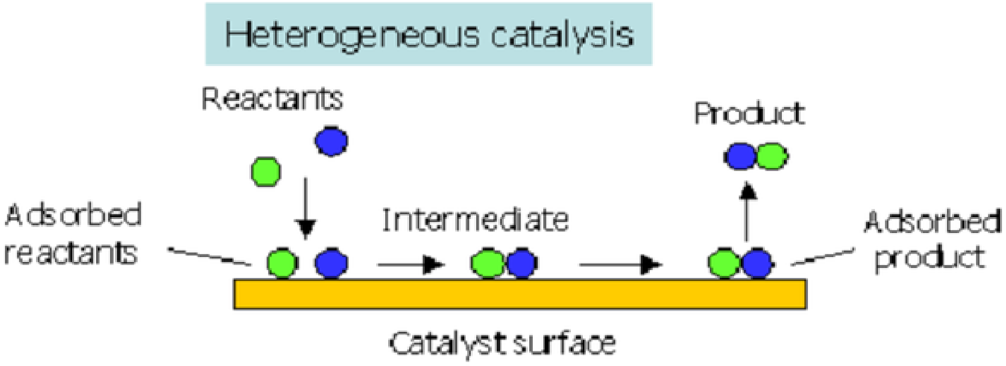
TYPES OF CATALYSIS

BIOCATALYST

Biocatalysis is defined as the use of natural substances, like enzymes or cells, to catalyze chemical reactions . An enzyme is simply a protein **catalyst** that helps the digestion, produces vital nutrients, or moves muscles. biocatalyst are substances (enzyme or hormone) that activates or speeds up biochemical **reactions**. e.g.digestive enzymes like pepsin ,trypsin etc.

HOMOGENEOUS AND HETEROGENOUS CATALYSIS

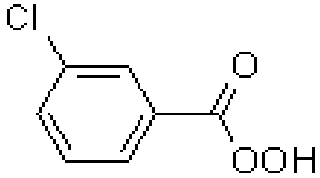




Type of catalyst	Homogeneous catalysts	Heterogeneous catalysts	Heterogenized homogeneous catalysts	Biocatalysts
Examples	Acid- base catalysis and transition metal complexes	Metals, metal oxides and supported metal oxides	Immobilization of Homogeneous catalyst on solid support	Enzymes from animal tissues, microbes and plants
Phase	Liquid / Gas	Solid	Solid	Liquid
Active sites	Well-defined	Poorly defined	Well defined	Well defined
Concentration	Low	High	Low	Low
Activity	High	Low	High	High
Selectivity	High	Low	High	High
Temperature	Low	High	Low, High	Low
Thermal stability	Low	High	High	Low
Product separations	Difficult	Easy	Easy	Easy
Catalyst regeneration	Generally problematic	Facile	Facile	Optional
Catalyst modification	Easy	Difficult	Easy	Difficult
Catalyst cost	Low	High	High	Intact cell are economical, isolated enzymes are expensive
Reaction rate	Slow	Fast	Fast	Fast
Reaction mechanism	Reasonably well understood	Poorly understood	Same as Homogeneous catalysis	Well understood
Life time of catalyst	Variable	Long	Long	Short

MCPBA, *meta*-Chloroperbenzoic acid

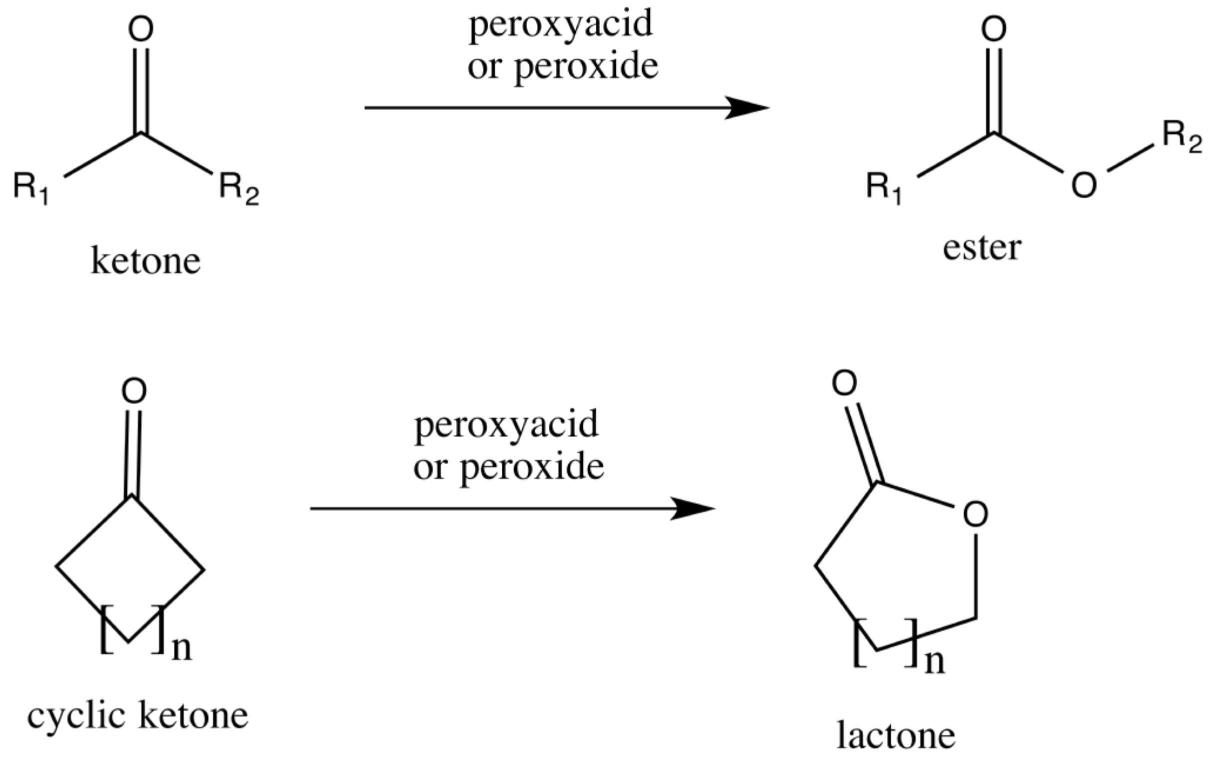
MCPBA is a strong oxidizing agent, which is comparable with other peracids. Advantages of 3-chloroperbenzoic acid is its handling, because it is present as powder, which can be kept in the refrigerator. Nevertheless, material of purity >75% is rarely available commercially, since the pure compound is not particularly stable. Therefore the transport in airplanes with a content of > 72% is forbidden. Main pollution is 3-chlorobenzoic acid (10%) as well as for safety reasons water.



MCPBA is versatile applicable as peracid for use in laboratories.

BAYEARS VILLIGER OXIDATION

The **Baeyer–Villiger oxidation** is an organic **reaction** that forms an ester from a ketone or a lactone from a cyclic ketone, using peroxyacids or peroxides as the oxidant. The **reaction** is named after Adolf von **Baeyer** and Victor **Villiger** who first reported the **reaction** in 1899.



USES OF MESOPOROUS SILICA

Zeolites and mesoporous silica nanoparticles are silicate or aluminosilicate nanomaterials with well-defined pore networks. Zeolites are widely used in industry for applications such as catalysis, separations and gas adsorption. Mesoporous silica nanomaterials have not been as extensively applied relative to zeolites due to the cost and reduced thermal stability, but are being intensively investigated for potential environmental and biomedical applications. In this article, zeolite and mesoporous silica nanomaterials are reviewed with emphasis on connections to the environment. Specifically, the topics of greener syntheses, environmental applications and biological toxicity will be addressed. Both of these materials are typically synthesized with a template, which is then removed to produce the pore volume. Synthetic strategies for the “greening” of the syntheses of zeolites and mesoporous silica will be discussed. Environmental applications including the adsorption of environmental contaminants and environmental catalysis will also be presented. Finally, the toxicity of zeolite and mesoporous silica nanomaterials will be considered.

FERMENTATION

Fermentation is the enzymatic decomposition and utililization of foodstuffs, particularly carbohydrates, by microbes**.** Fermentation takes place throughout the gastrointestinal tract of all animals, but the intensity of fermentation depends on microbe numbers, which are generally highest in the large bowel.

Fermentation is a metabolic process that produces chemical changes in organic substrates through the action of enzymes. In biochemistry, it is narrowly defined as the extraction of energy from carbohydrates in the absence of oxygen. In the context of food production, it may more broadly refer to any process in which the activity of microorganisms brings about a desirable change to a foodstuff or beverage. The science of fermentation is known as zymology.

In microorganisms, fermentation is the primary means of producing adenosine triphosphate (ATP) by the degradation of organic nutrients anaerobically. Humans have used fermentation to produce foodstuffs and beverages since the Neolithic age. For example, fermentation is used for preservation in a process that produces lactic acid found in such sour foods as pickled cucumbers, kombucha, kimchi, and yogurt, as well as for producing alcoholic beverages such as wine and beer. Fermentation also occurs within the gastrointestinal tracts of all animals, including humans.

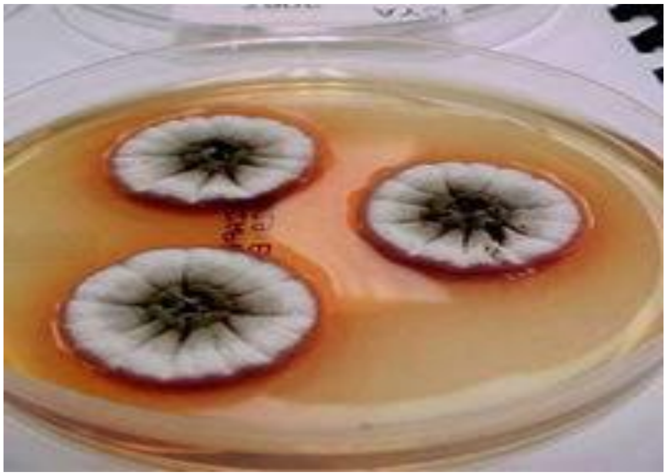
For many years, man has worked to improve agricultural productivity by taking advantage of the work of millions of soil microbes. These microbes can be cultivated on a large scale and made to produce important biofertilizers, to assist plant growth; and biopesticides, to control weeds, pests, and diseases. This process is known as **microbial fermentation**.

Microbes function as both providers and defenders. They can contribute to plant nutrition by converting important macromolecules into forms usable by plants, as biofertilizers; or they can defend plants from other invasive, parasitic plants and pests, as bioherbicides and bioinsecticides.

Biofertilizers

Phosphate and nitrogen are important for plant growth. However, plants have a limited ability to extract them from the environment, and thus need microbes to help them absorb these nutrients at optimal concentration.

Colonies of Penicillium bilaii growing on a culture plate



These same microbes are also involved in “nutrient recycling,” i.e. they help a plant take up energy sources, while plants donate waste byproducts to microbes for food. With this symbiotic relationship, plants develop stronger and bigger root systems. The larger the plants’ roots, the more living space and food there is for the microbes to use. In a way, microorganisms serve as biofertilizers.

An example is the fungus *Penicillium bilaii*, which allows plants to absorb phosphates from the soil. It does this by producing an organic acid which dissolves soil phosphates into a form which plants may use. A biofertilizer made from this organism is applied either by coating seeds with the fungus (called inoculation), or applying the fertilizer directly into the ground.

Another example is the bacterium *Rhizobium*. This bacterium lives on the plant’s roots in cell collections called nodules. The nodules are biological factories that can take nitrogen out of the air and convert it into an organic form that the plant can use. Because the bacteria live within the roots, they transfer the nutrient directly into the plant. *Rhizobium* works with legumes, such as beans, groundnut, and soybean.

Biofertilizers have been found to:

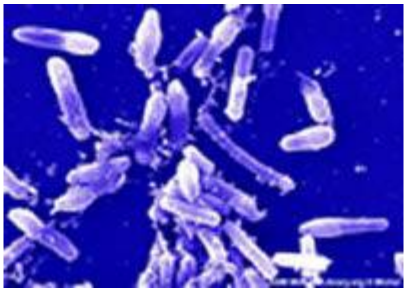
- Increase crop yield by 20-30%.
- Replace chemical nitrogen and phosphorus by 25%.

- Stimulate plant growth.
- Activate the soil biologically.
- Restore natural soil fertility.
- Provide protection against drought and some soil borne diseases.

Bioinsecticides

Insect pests of important crops can be difficult to control. Thanks to fermentation methods, however, bioinsecticides have been developed, based on the insecticidal proteins of bacteria, fungi, and viruses.

Bacteria-based bioinsecticides



One of the most widely used bioinsecticides is a naturally occurring soil bacterium called *Bacillus thuringiensis* or Bt. Bt produces a protein which is poisonous to insects. Within 15 minutes of being eaten, the Bt toxin begins to create ulcers in the insect's stomach lining. The insect stops eating and eventually dies. Researchers have identified between 500 and 600 strains, or types of *Bacillus thuringiensis*. Bt is very selective — it affects only a specific species of insect pest and does not harm humans, birds, fish, or beneficial insects.

Fungi-based bioinsecticides

Some fungi can cause disease in insects, and as many as 200 different insects are known to be susceptible to such diseases. These fungi are thus used in fungi-based bioinsecticides.

Culture of *Beauveria bassiana* fungus

Inexpensive fermentation technology is used to mass produce fungi. Spores are harvested and packaged so they can be applied to insect-ridden fields. When the spores are applied, they use enzymes to break through the outer surface of the insects' bodies. Once inside, they begin to grow and eventually cause death.

One bioinsecticide, Bb, is based on the action of *Beauveria bassiana*, a fungus which is found worldwide in soils and plants. In China, over two million hectares are sprayed with Bb annually to control forestry pests.

Bioinsecticides based on Bb have many advantages. The fungus does not grow in warm-blooded organisms (such as humans), nor does it survive long in water reservoirs or rivers. However, its spores can withstand long periods of dryness and other harsh environmental conditions. Studies to date have shown that the fungus also does not harm plants and becomes inactivated by the sun's ultraviolet rays in one to eight weeks.

Virus-Based Bioinsecticides

Insect pests are also susceptible to viral diseases, and virus-based insecticides exploit this property in order to control the spread of pests.

An example currently being tested is the Baculovirus group. Baculoviruses affect insect pests like corn borers, potato beetles, flea beetles, and aphids. One particular strain is being used as a control agent for Bertha army worms. These worms attack canola, flax, and vegetable crops, and have been known to clean out as many as one million hectares of prairie crops at high infestation levels. Farmers used chemical insecticides to control the worms in the past. Bioinsecticides do not persist long in the environment, unlike synthetic pesticides. They also have shorter shelf lives and are effective in small quantities, safer to humans and animals compared to synthetic insecticides, and very specific, often affecting only a single species of insect. However, bioinsecticides also have some disadvantages. They work slowly and the timing of their application is relatively critical. Moreover, because most of these bioinsecticide agents are living organisms, their success is affected by several factors like temperature, pH, moisture, UV, soil conditions, and other microbial competitors present in the environment.

Bioherbicides

Weeds are a constant problem for farmers. They compete with crops for water, nutrients, sunlight, and space; harbor insect and disease pests; clog irrigation and drainage systems; undermine crop quality; and deposit weed seeds into crop harvests. If left uncontrolled, weeds can reduce crop yields significantly.

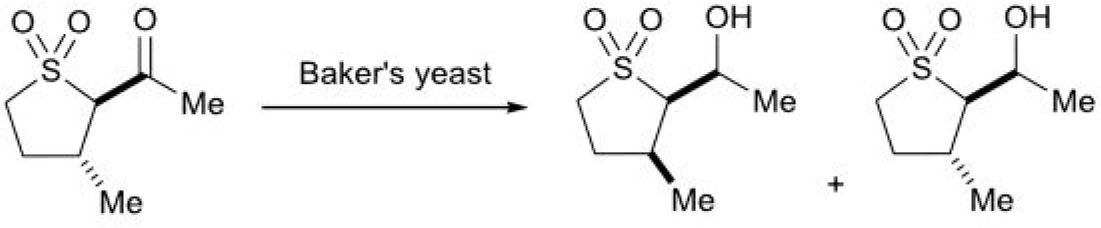
Farmers fight weeds with tillage, hand weeding, synthetic herbicides, or a combination of all techniques. Unfortunately, tillage leaves valuable topsoil exposed to wind and water erosion, a serious long-term consequence for the environment. For this reason, more and more farmers prefer reduced or no-till methods of farming.

The use of bioherbicides is another way of controlling weeds without the environmental hazards posed by synthetic herbicides. Bioherbicides are made up of microorganisms and certain insects (e.g. parasitic wasps, painted lady butterfly) that can target very specific weeds. The microbes possess invasive genes that can attack the defense genes of the weed, thereby killing it.
Due to better understanding of the genetics of both microorganisms and plants, scientists have been able to isolate pathogens whose genes match particular weeds, and which can cause fatal diseases in those weeds, and in those weeds alone. Some bioherbicides contain such microorganisms, and they are sent out into the field when weeds are most susceptible to illness. The specificity of the microbes for a specific weed makes such bioherbicides very useful, since they can kill only certain weeds without damaging important crops.

Bioherbicides can also survive in the environment long enough for the next growing season, when there will be more weeds to infect. They are cheaper compared to synthetic pesticides, and could essentially reduce farming expenses if managed properly.

BAKER’S YEAST MEDIATED REDUCTION OF 2-ACETYL-3-METHYL SULFOLANE

The baker’s yeast mediated reduction of 2-acetyl-3-methyl sulfolane **1** to provide the corresponding alcohol **2** is described. Excellent efficiency and enantioselectivity (>98% *ee*) has been achieved under these mild environmentally benign reaction conditions. In direct contrast, the chemical reduction of **1** proceeds with poor yield (≤25%) and diastereocontrol.



1

2a (>98% ee) **2b** (>98% ee)

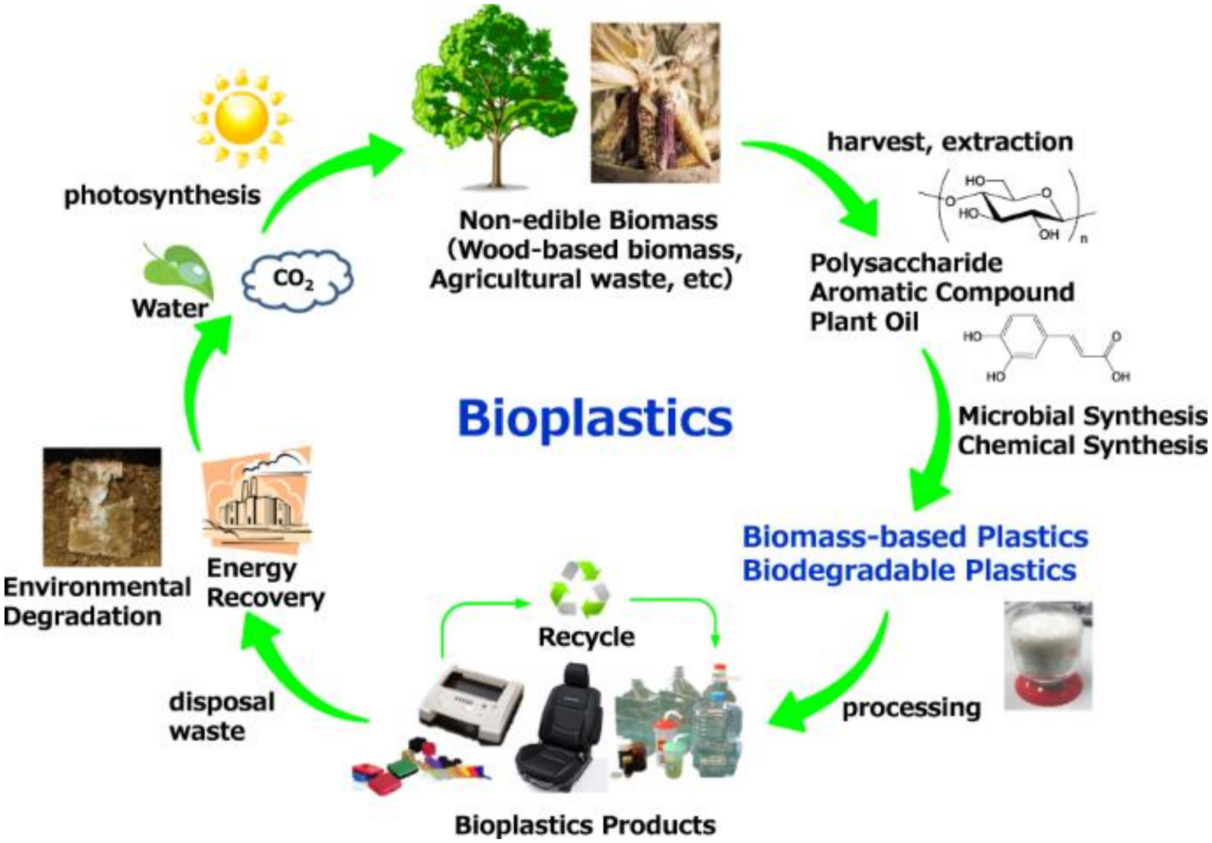
40 : 60
67% combined pure yield

Application of baker's yeast

Baker's yeast has been widely used as a biocatalyst in organic synthesis, primarily because it is inexpensive and readily available. The majority of studies on the biotransformation capability of yeast deal with reductions of carbonyl groups and carbon–carbon double bonds. Reactions involving carbon–carbon bond formation are of great interest in chemical synthesis. Most of these biocatalytic reactions have been carried out in aqueous media. The conversion of benzaldehyde and pyruvate to L-phenylacetyl carbinol was one of the first commercial processes to utilize an enzyme biotransformation step. During this biotransformation, a proportion of the benzaldehyde is also reduced to benzyl alcohol. Recent studies on biocatalysis of benzaldehyde and substituted benzaldehyde to benzyl alcohol by whole cells of wild-type and mutant strains of baker's yeast in nonconventional media have established the effects of organic solvents and substrate hydrophobicity on reaction performance.

MICROBIAL POLYESTERS SYNTHESIS

Production of microbial polyesters by fermentation and its complete carbon cycle. Microorganisms isolated from nature are metabolically engineered to accumulate a large amount of plastics with high yield and specific productivity . Biomass obtained from carbon dioxide and sunlight is converted to fermentable sugars, and used as a substrate for lab-scale fermentation for the examination of the performance and further strain optimization. Once a high performance microorganism is developed, industrial-scale fermentation, after process optimization to give the highest possible yield and productivity, is performed to produce large amounts of plastics. After fermentation, polymers inside cells are purified and used to make articles we use everyday. When they are disposed after use, they will be degraded to carbon dioxide (and methane under anaerobic condition). Thus, the carbon cycle becomes closed, providing environmentally friendly sustainable way of producing plastics without using fossil oil.



UNIT V

ALTERNATIVE SYNTHESIS,REAGENTS AND REACTION CONDITIONS

TWO MARKS

1.How does dimethyl carbonate act as a methylating agent?

2.What is super critical carbon dioxide?

3.Define green oxidants.

4. Write any two applications of green oxidants.

5.What do you mean by alternative synthesis?

6.Write Friedal crafts reaction.

7.What are the advantages of alternative synthesis?

8.` Which is involved in green synthesis?

9.Why green chemistry is needed?

10.How does green chemistry save money?

FIVE MARKS

1.Dimethyl Carbonate is used as a methylating agent.Justify.

2.Give the applications of super critical carbon dioxide in synthetic chemistry.

3.Descibe a photochemical alternative to Friedal-Crafts reactions.

4.How is super critical CO_2 used in synthetic chemistry?

5.Give their uses of green oxidants.

TEN MARKS

1.How are green oxidants designed and used in green chemistry?

2.Briefly,explain the photochemical alternative to Friedal – Craft reactions.

3.Describe the alternative methods for green synthesis.

GREEN SOLVENTS

The major application of solvents in human activities is in paints and coatings (46% of usage). Smaller volume applications include cleaning, de-greasing, adhesives, and in chemical synthesis Traditional solvents are often toxic or are chlorinated. Green solvents, on the other hand, are generally less harmful to health and the environment and preferably more sustainable. Ideally, solvents would be derived from renewable resources and biodegrade to innocuous, often a naturally occurring product. However, the manufacture of solvents from biomass can be more harmful to the environment than making the same solvents from fossil fuelsThus the environmental impact of solvent manufacture must be considered when a solvent is being selected for a product or process. Another factor to consider is the fate of the solvent after use. If the solvent is being used in an enclosed situation where solvent collection and recycling is feasible, then the energy cost and environmental harm associated with recycling should be considered; in such a situation water, which is energy-intensive to purify, may not be the greenest choice. On the other hand, a solvent contained in a consumer product is likely to be released into the environment upon use, and therefore the environmental impact of the solvent itself is more important than the energy cost and impact of solvent recycling; in such a case water is very likely to be a green choice. In short, the impact of the entire lifetime of the solvent, from cradle to grave (or cradle to cradle if recycled) must be considered. Thus the most comprehensive definition of a green solvent is the following: "*a green solvent is* the solvent that makes a product or process have the least environmental impact over its entire life cycle.

By definition, then, a solvent might be green for one application (because it results in less environmental harm than any other solvent that could be used for that application) and yet not be a green solvent for a different application. A classic example is water, which is a very green solvent for consumer products such as toilet bowl cleaner but is not a green solvent for the manufacture of polytetrafluoroethylene. For the production of that polymer, the use of water as solvent requires the addition of perfluorinated surfactants which are highly persistent. Instead, supercritical carbon dioxide seems to be the greenest solvent for that application because it performs well without any surfactant In summary, no solvent can be declared to be a "green solvent" unless the declaration is limited to a specific application.

Green chemistry addresses such challenges by inventing novel reactions that can maximize the desired products and minimize by-products, designing new **synthetic** schemes and apparatus that can simplify operations in **chemical** productions, and seeking greener solvents that are inherently environmentally and ecologically

Plants and animals suffer less harm from toxic **chemicals** in the environment. Lower potential for global warming, ozone depletion, and smog formation. Less **chemical** disruption of ecosystems. Less use of landfills, especially hazardous waste landfills.At the same time, **green chemistry can save** companies **money** by reducing the need for costly **chemicals**, reagents and solvents, lowering insurance and legal costs, reducing waste disposal costs .

ADVANTAGES OF GREENER CHEMISTRY

- — prevention of unnecessary wastes; the avoiding of unnecessary waste in organic synthesis can be reached by recyclability of most solvents, catalysts and reagents;
- — economy of matter (atoms): minimization of loss of precursors and intermediate compounds during synthesis of final material;
- — lower-hazard chemical reactions using little-toxic and safe chemical substances;
- — low-toxic and safe separation agents and solvents (water, natural compounds as, for example, plant extracts);
- — minimization of energy consumed (preferable/ideal conditions: normal pressure and room temperature);
- — renewable sources (raw materials);

- — minimization of reagents to avoid unnecessary wastes (lesser number of reaction steps and additional chemicals);
- — use of most selective catalysts, allowing higher yields of reaction products;
- — degradable reaction products, non-persisting in the environment;
- — contamination prevention via permanent (real-time) analysis of reaction intermediates when possible;
- — small quantities of reactants to prevent accidents (explosions, releases, fire);
- — green processes are cheaper and cost-effective, frequently resulting in products with a better quality; and
- — green reactions allow avoiding problems with many environmental regulations and laws.

ALTERNATIVE METHODS FOR SYNTHESIS

. Microwave irradiation

This is a green source of heating both in organic and inorganic synthesis, based on the conduction and dipolar polarization. A series of organic molecules have been reported as obtained this economic, efficient, fast and clean way, now recognized as a conventional synthetic chemistry tool, which has made a great contribution to organic synthesis . MW energy is *non-ionizing radiation*, which does not influence on the molecular structure of compounds. The MW coupling of a substance depends on its *dielectric constant*, so *N*,*N*-dimethylformamide (DMF), methanol, acetone, water is rapidly heated under MW irradiation, in a difference from CCl_4, toluene or aliphatic hydrocarbons. The electromagnetic energy, being transformed into heat, drives interactions between compounds. MW irradiation and reaction components are in a *direct* interaction, so a minimum of energy is needed for its heating, without expanding the process to the furnace material .That is why the temperature profiles of conventially and MW-heated simples are different (in the MW case, the interior is hotter and the surface is cooler). The heating is *uniform* and takes place *volumetrically*, in all the sample; the heat transfer requires lesser energy due to thermal conduction inside the sample. The MW heating is almost *instantaneous*, very fast, due to the fast transfer ‘MW energy—heat’, and can be stopped immediately by a simple turn-off of the MW equipment. In addition, the MW heating is *selective*, since reagents possess distinct capacity to be MW-heated, allowing, for example, the heating active points in a sample instead of heating an entire sample.

MW heating has the following *advantages*, among others, being compared with conventional heating: fast process speed, pure products, lesser heat loss, high heating efficiency, less waste, low cost of operations, lesser possibility of side products. *Solvent-*

free (dry media) conditions of MW-assisted reactions are preferable, to avoid fast uncontrolled solvent heating and violent explosions. Precursors can be adsorbed on *inorganic supports*, transparent for microwaves (montmorillonite clays, zeolites, ceramics, Al_2O_3, SiO_2) or, on the contrary, possessing strong MW-absorbance (for example, graphite). These supports can also contain additional reagents or catalysts. MW-assisted solvent-free reactions on inorganic supports at relatively low bulk temperature have shown certain advantages in the processes of reduction and oxidation, deprotection and protection, condensation, rearrangement, heterocyclic synthesis, etc. leading to important products such as HCN, imines, nitroalkenes, enamines, among others.

Modern apparatus for MW heating is well developed and covered in a comprehensive review a commercial example is a reactor Monowave 50 [26]. For simple experiments, modified domestic MW ovens are frequently used. Commercial equipment includes SMC (apparatus with single-mode cavity, 0.2–80 ml volume of sealed vessels), CEM MARS multimode MW reactor and Milestone Flowsynth continuous-flow reactor, all with maximum pressure of 300 psi and temperature 300°C. Sometimes, ultrasmall particles (5–10 nm) can be formed due to very rapid reaction time, although in some cases, *larger* particles can be also formed in comparison with conventional synthesis. Crystallinity, defect concentration and morphology can be different in MW-assisted and conventional synthesis. Shapes of products can depend on MW power and irradiation time, as, for example, in MoS_2 synthesis, where the layer-, nanotube- and fullerene-like forms were observed depending on the MW-treatment duration.

To carry out a successful MW-synthesis, all the reagents should ideally be *good absorbers*, otherwise, it is necessary to looking for another material acting as a heat source (susceptor) and converting MW energy to heat. The last case is not desirable at scaling up processes, since this additional material is a contamination source. Also, the substances, transparent for MW irradiation before certain temperature, can be conventionally heated to reach it and then the MW-assisted process starts. The use of MW-induced plasma, transferring energy between radiation and reagents and being, in some cases, a source of reactive species, is also possible.

Green solid- and liquid(solution)-state MW-synthesis of inorganics includes the formation of simple (in particular, yttria-stabilized ZrO_2, α-Fe_2O_3 thin films) and double oxides (i.e. Li, Cu, Co, Ni ferrites, $BaTiO_3$ (from TiO_2 and $BaCO_3$), $LaCrO_3$, $La_{1-x}Sr_xCoO_3$, among others) during some minutes; chalcogenides (ZnS, CuS, $Cu_{2-x}Te$, HgTe, Cu_2SnSe_4, Bi_2Se_3, CdSe, etc. sometimes from sulfates by carbothermal reduction, but generally from elemental powders in vacuum, avoiding chalcogene sublimation, without or with susceptors); borides (MgB_2, ZrB_2); carbides (SiC, $MgNi_3C$, CaC_2, Mo_2C, WC, etc. from metals or their oxides (Ta_2O_5 + C)); silicides ($Li_{21}Si_5$, $MoSi_2$, Mg_2Si, $CaAl_{1-x}Cu_xSi$, etc.); nitrides and other pnictides (TiN, Ta_2N, AlN, $LiSi_2N_3$, GaN, Li_3Bi, Li_3Sb); carbonitrides $V_{1-x}Ti_x$(C, N), and oxynitrides (β′-SiAlON).

Photocatalysis

Photochemical reactions under UV-irradiation are considered as green chemistry interactions and are based on the electronic excitation, which influences the chemical reactivity of reagents in organic synthesis. A recent review on photocatalysis describes generation of singlet oxygen and its role in the photo-oxygenation (incorporation of molecular oxygen into molecules), combination of photochemical processes with enzyme catalysis, application of continuous flows or microreactors for their optimization. Some examples of such reactions are the synthesis of N-containing heterocycles by photo-oxidation of furan derivatives, asymmetric oxidations catalysed with enzymes, and preparation of several F-organic compounds by photocatalysed trifluoromethylation of aromatics, using photocatalysis booth and reactors described .

Hydro(solvo)thermal synthesis

A solution reaction-based approach is applied to synthesize compounds, crystallize and grow single crystals and polycrystals at high pressures (normally up to 10 bar) and elevated temperatures (generally up to 300°C) in water or organic solvent media. The equipment for hydro(solvo)thermal technique consists of an autoclave (thick-walled steel cylinders, sometimes with protective inserts made of Teflon, platinum, titanium, quartz, gold, etc.), containing solvent (water) and dissolved/suspended precursors. For the past 20 years, a combined equipment ‘microwave-hydrothermal treatment’ has been frequently used in laboratories. The main advantage of the hydrothermal method is the possibility of the formation of crystalline phases, unstable at the melting point of the desired compound; the main disadvantage is the necessity to have expensive equipment. Morphology control and crystallinity for the formed materials can be made by changing pressure, temperature, solvent, reaction time or precursors' ratio. Hydrothermal reactions in water are considered as more suitable for green chemistry purposes, being environmentally friendly, and are widely applied to fabricate a variety of materials. This method allows minimum loss of reactants and frequently higher yields of products, being especially useful to obtain classic and less-common nanostructures with desired shape and size control: powders, films and especially one- to three-dimensional nanocrystals

Ultrasound-assisted (sonochemical) synthesis

Ultrasound-assisted (sonochemical) synthesis is only a solution-based approach (since cavitation occurs only in liquids) working as a result of the phenomenon of the acoustic cavitation (bubbles, appearing in a liquid, grow and implosively collapse, leading to extreme local pressures of 1000 atm and temperatures of 5000 K) in a liquid phase, without a direct affectation to the bond vibrational energy. Chemical reactions can be started or intensified in these conditions, additionally to the formation of free radicals and H_2O_2. Chemical composition, reactivity and surface morphology of materials (frequently increasing surface area) can be considerably changed as a result of these collisions. A variety of sonochemical reactions can be carried out in liquid systems, solid–liquid and liquid–liquid interfaces (as well as sonocatalysis), useful for the environment, for instance, destruction of halogenated aromatics. Ultrasound-mediated organic synthesis and preparation of functional materials are classic contributions, perfectly fitting to the green chemistry field, since they do not require large energy consumption and hazardous chemicals; additionally, the cost of equipment is normally low in the case of a simple ultrasonic cleaning bath (frequencies 20–40 kHz), with exception of high-power ultrasonic horns .

Magnetic field-assisted synthesis

Magnetic field-assisted synthesis is currently studied as an alternative to traditional methods. because some of the traditional methods require the use of toxic solvents or additional steps that need more energy and can generate unwanted residues. These extra steps can be omitted using magnetic fields during the synthesis of the desired material. The synthesis assisted by magnetic fields allows obtaining morphologies different from those prepared by traditional methods. In addition, it is possible to influence the orientations of the final product planes. Some synthesis techniques where the assistance of magnetic fields can be used are the methods of coprecipitation, solvothermal, electrospinning, etc. In addition, the magnetic field assistance can be implemented directly in the solution to influence the growth of the crystals of the desired material and can be applied for the formation of thin layers of some composites. The synthesis assisted with magnetic fields has numerous advantages due to its simplicity; however, it has some important limitations, derived from the foundation of the technique, because it can only be applied to materials whose reactants or products have magnetic properties; that is why the vast majority of reports in the literature use magnetic iron oxides.

Iron oxides such as Fe_3O_4 can adopt different assisted morphologies with magnetic field; for example, it is possible to obtain complex Fe_3O_4 nanorods by the solvothermal technique. This is possible because, during the formation of nanorods, the growth of the crystals of the metal oxide is oriented in a specific orientation due to the magnetic field . If the magnetic field is applied in the Fe_3O_4 synthesis by thermal decomposition, it is possible to obtain nanotubes of 250 nm, which are not formed in the absence of the magnetic field; besides, it was observed that the speed in which these nanoparticles of Fe_3O_4 are heated by hyperthermia is considerably higher in the oxides synthesized in the presence of the magnetic field . Another example that can be mentioned of the synthesis of Fe_3O_4 with the assistance of magnetic fields is a series of chains prepared at a temperature of 90°C. These particles had an average size of 150 nm. This was achieved due to the growth of the particles of uniaxial way by the influence of the magnetic field, and it was observed that the intensity of the magnetic field during the synthesis had a significant effect on the anisotropy of the resulting material .

The assisted syntheses with magnetic fields can also be applied to the synthesis of some composites, as long as they comply with the characteristics mentioned above. An example of this is the thin layers of reduced graphene oxide (rGO) with Fe_3O_4 nanocrystals. The synthesis of this composite is quite simple, based on taking advantage of the ferromagnetic characteristics of the nanocrystals of Fe_3O_4 that are adhered to the surface of sheets of rGO. When applying the magnetic field on this suspension, the particles agglomerate in one of the walls of the reactor and they adhere to each other by the electrostatic interactions between the GO and the nanocrystals of Fe_3O_4 . Such techniques can support the synthesis of flexible electrodes for batteries of new generation.

Some other materials reported to assist with magnetic fields are compounds containing nickel, cobalt, bismuth and some of their alloys. This is due to the fact that, as mentioned, it is necessary that the materials have ferromagnetic properties, this being their only limitation. Although it is true that there are reports of iron oxides in the literature, it is also possible to find reports, where assisted synthesis with electromagnetic field has been made using other materials and compounds containing nickel, cobalt, bismuth and some of their alloys with ferromagnetic properties . For example, the synthesis of cobalt and cobalt carbide nanowires is known, using magnetic field-assisted polyol synthesis. For comparison, both cobalt and cobalt carbide synthesized by traditional methods in the absence of magnetic fields usually have spherical morphologies . It is also possible to obtain thin films of cobalt nanosheets using magnetic fields during the reduction in solution of the Co^{2+}–EDTA complex, which opens a new methodology to create thin films of magnetic nanocrystals with anisotropic forms .

The synthesis of bismuth by the solvothermal method assisted with a magnetic field can also be used to generate nanowires . As it can be seen, the use of magnetic fields has a particular influence on the orientation in the case of the formation of crystals of ferromagnetic materials and in the order in which the composites assisted with magnetic fields are accommodated. The use of this technique depends on the method that is being complemented to be considered as a green synthesis. It is noteworthy that this technique reduces waste and synthesis, helping to make it more efficient; in addition, the application of the magnetic field does not generate any additional by-product to the main technique used.

Solvents and catalysis in green processes

For the organic synthesis, where hazardous solvents are mostly used, the 12 rules of green chemistry can be successfully applied maximal atom economy (avoiding by-products and wastes, in particular by solvent-less techniques, i.e. dry media), safe and non-hazardous chemical routes without harmful chemicals, use of renewable precursors (i.e. plants instead of fossil fuels), catalysts in small amounts (non-harmful and preferably solids in order to be renewable), safer chemicals and solvents (water, ILs) or better their absence, biodegradable substances, as well as avoiding energy waste, preventing pollution and minimizing possibility of accidents.

Solvents represent a major source (80–90%) of pollution in organic (and not only) chemical processes. Conventional organic solvents, derived from oil, are toxic and possess bad health, environmental and safety impacts. So, the solvents to be used as green media for organic synthesis need to possess biodegradability, low toxicity, high boiling point, easily recyclable and non-miscible with water. Upon these conditions, the water, ILs, polyethylene glycols (PEGs) and some SC fluids are most appropriate. In this respect, non-toxic and biodegradable glycerol, which is the principal side product in the fabrication of biodiesel, is quite suitable for green synthetic organic synthesis and even called ‘organic water’. Its advantages are great availability, biodegradability, low cost, low vapour pressure, high boiling point; in addition, glycerol is immiscible with aliphatic hydrocarbons, highly polar, capable to form hydrogen bonds and solubilizes both inorganic and organic compounds. The review describes a host of reaction schemes (metal-free, metal- and biocatalysed transformations) with glycerol use.

Supercritical green solvents

Among other greener solvents, non-flammable, non-toxic and environmentally friendly SC CO_2 is known from long ago as a good alternative solvent for the synthesis of polymers. SC water has been also used as a green solvent . Currently, the technologies based on the supercritical fluids (SCFs), in particular SC water or CO_2, contribute to the green chemistry in the nanomaterials synthesis (for example, in semiconductors' fabrication using SC CO_2), solving some environmental problems. The SCF technologies have been used in materials synthesis processes such as extraction, cleaning, fractionation, drying, polymerization, hydrothermal reactions, plating, biomass conversion, dyeing, among others, providing solvent-free media, simplicity and recyclability, high yields, absence of wastewater and secondary pollution, etc..

In the case of SC water (above critical pressure 22.1 MPa and critical temperature 646 K), it can be mixed with organic and inorganic substances forming homogeneous phase. The reactions in SC H_2O can occur by different routes due to the changes in thermal conductivity, diffusion coefficient, density of molecules and viscosity. Additionally, the dielectric constant of water (78 at room temperature (r.t.)) decreases to values typical for polar organic solvents around the critical point. Metal oxides can be hydrothermally produced in SC water, sometimes with H_2O_2 addition to create oxidizing atmosphere. A considerable decrease in their solubility near the critical point was observed and considered as a good advantage. Resulted green reactions have led to the fabrication of a variety of metal oxides, suitable for applications in the catalysis (for example, nanoparticles of TiO_2), as sensors, coatings, semiconductors, devices for solar energy and batteries (in that number, $LiMn_2O_4$, $LiFePO_4$ and $LiCoO_2$), ceramics, as well as for distinct medical applications. These methods are indeed green due to the use of water and especially because they lead to the fabrication of lower-cost sustainable nanomaterials. Metal oxide nanoparticles, modified with organic functionalities, can be also obtained in these conditions, providing good dispersibility in water or organic solvents. Other examples of SC-hydrothermally obtained materials are hybrid materials based on inorganic nanoparticles and polymers, possessing properties of both counterparts (high electrical resistance, mechanical strength, and thermal conductivity, light weight, etc.). Also, recycling materials (plastics) can also be made in SC water and EtOH; in these conditions, their decomposition or depolymerization occurs to form monomers. Recovery of materials from wastes is also available, in particular by hydrolysis of plastics in SC water or by SC oxidation of wastewater.

ILs, some of the best solvents after water for green chemistry goals, are indeed salts (ionic compounds, ‘constructed’ of ions and short-lived ion pairs), which are in a liquid state at 100°C and below (usually at room temperature). In their composition, mostly used cations are *N*-alkylpyridinium, 1-alkyl-3-methylimidazoium, PR_4^+, NR_4^+, typical anions are $[PF_6]^-$, $[BF_4^-]$, $[CF_3SO_3^-]$, tosylate, alkylsulfate, $[CH_3COO^-]$, NO_3^-, Cl^-, etc., common alkyl chains are ethyl, butyl, hexyl, octyl and decyl. IL molecules have a significantly lower symmetry in comparison with classic ionic compounds. In a difference with water, where hydrogen bonds act between molecules, and organic solvents with van der Waals interaction, in ILs, the Coulomb interactions are main forces. These solvents are generally thermally stable, electrically conducting fluids, highly viscous and highly powerful solvents with low vapour pressure (approx. 10^{-10} Pa at 25°C); some of them are magnetic, for instance 1-butyl-3-methylimidazolium tetrachloroferrate. The solubility of chemical compounds in ILs depends on the ability of hydrogen bonding and polarity. In addition to a solvent's role in chemical processes, ILs are used for gas handling, coal processing, fabrication of pharmaceuticals, nuclear fuel reprocessing and cellulose processing, among several other uses. Currently, about 1000 ILs are known, including 300 commercially available products.

The *catalysts* in organic synthesis are used in the homogeneous and heterogeneous catalysis, acting in the same (normally in liquid phase) or different phase (typically solid/gas, liquid/gas or solid/liquid) in the reaction mixture, respectively. In the first case, the active sites of catalysts are separated from each other. In the second case, phase separation 'product-catalyst' is easier, since no extraction or distillation is needed, thus contributing to the green chemistry. In addition, solid hazardous catalysts (for example, polluting and corrosive catalysts) can be substituted by greener zeolites or clays. *Catalyst-free* organic synthesis as the best greener alternative occurs for several reasons, limiting catalyst use, for instance, lower selectivity, longer synthesis duration, higher catalyst amounts, toxicity, insolubility, high cost, etc.

Dry media

In organic synthesis is obviously a great contribution to the green chemistry in the conditions of solvent-free interaction of reagents, which can react directly or be incorporated in alumina, silica, zeolites or clays. Physical treatments described above (heating, UV-irradiation, ultrasound or microwaves) can be also used in these reactions. The processes are shorter, with reduced contaminations, economic and frequently scalable.

As examples of replacing dangerous procedures with greener methods [50], we note, for example, use of Na_2CO_3 and Zn instead of fusing metallic Na with organic substances for organic qualitative analysis, use of LiOH instead of NaOH in the synthesis of dibenzalpropanone from acetone, benzaldehyde and EtOH, solvent(EtOH)-free preparation of benzylic acid, bromination of *trans*-stilbene in EtOH instead of chlorinated solvents, etc.

Biological methods

Biological methods, being compared with conventional chemical and physical methods, could be a preferable synthesis route due to environmentally friendly conditions, despite their lower speed of metal reduction. However, their studies are currently relatively limited, especially those establishing key factors of the biosynthesis, so this method is only developed in laboratory scale, although bacteria could be applied for industrial recovery of silver. The biological synthesis of nanoparticles does not require further stabilizing agents: the microorganisms or extracts themselves act as stabilizing and capping agents. Other advantages of the biological routes are no necessity of toxic chemicals and contaminants, possibility to control shapes and sizes, low cost, biocompatibility and numerous precursors (microorganisms and plants). So, biological methods perfectly fit to the green chemistry, in particular to nanochemistry, resulting in biologically produced nanoparticles, which are non-toxic, stable, environmentally friendly and cost effective. Frequently, the nanoparticles, prepared by biological methods, expose a higher antimicrobial activity (being compared with those synthesized by conventional chemical methods), related with the fact that the stabilization and capping by proteins is more effective. Main recent reviews in this area are described .

Biology-based green chemistry methods consist of the use of *bacteria, viruses, yeasts, plant extracts, fungi* and *algae*, among which we consider plant extracts as most frequent and popular green routes , as it will be shown below especially for the synthesis of nanoparticles, not only those of noble metals, but also carbon dots, metal sulfides, oxides, etc. This area, phytonanotechnology (use of plants) is scalable and medically applicable. Microorganisms represent natural nanofactories, capable to adsorb, accumulate and reduce toxicity of heavy metals, where enzymes are able to reduce metal ions to cero-valent nanoparticles. In the case of bacteria use for nanoparticle preparation, the techniques include the use of bacteria-containing biomass, as well as supernatant and derived components. Mycosynthesis (use of fungi) allows an easy, stable and possibly scaled-up biosynthesis of nanoparticles. Viruses, whose feature is dense and highly reactive surface (for instance, the surface of *tobacco mosaic* virus contains 2130 capsid protein molecules), were used to produce several inorganic nanoparticles, such as CdS, ZnS, Fe_2O_3 and SiO_2, important for semiconductor and quantum dot (QD) applications. In addition to conventional 0D nanoparticles, the nanotubes and nanowires can also be produced by virus action. The use of yeasts led the preparation of CdS and PbS QDs, Au and other metal nanoparticles. The use of algae is rare, generally for Au, Pd and Pt nanoparticles. Thus, in the case of algae use, the tetrahedral, decahedral and icosahedral Au nanoparticles, as well as bimetallic Ag/Ag nanoparticles, can be formed due to the action of proteins as stabilizing agent, shape-control modifier and reductant at the same time.

Inorganic micro- and nanosized materials can be prepared via *intracellular*- and *extracellular*-microorganism-assisted synthesis. The formation of nanoparticle is considered (but not yet fully understood) as a bottom-up process due to redox processes with participation of metal ions and biological molecules (proteins, sugars and enzymes), provided by the microorganism, whose interaction with metal ions depends on its type and can vary, also depending on temperature and pH (environmental factors), as well as metal salt concentration, leading to a particular morphology and size of nanoparticles. In the intracellular methods, several additional stages are needed, such as ultrasonication to destroy cell wall, washing, centrifugation, etc. which are absent in the extracellular techniques.

Biosynthesis processes of fabrication of homogeneous-size nanoparticles with certain reproducible morphology is carried out by size and shape control of *critical factors*, such as temperature (maximum possible for fast growth of microorganisms), pH (one of the most important factors, ranged generally from 3 to 10; acidic pH contributes to the agglomeration of nanoparticles due to the higher ion binding), salt concentration, choice of biological source, temperature, redox conditions, synthesis duration and incubation period, irradiation and aeration.

As it was noted, the use of plant extracts are common preparation procedures for a variety of nanoparticles of metals, non-metals and several of their compounds. Plant extracts contain polyphenols, terpenoids, proteins, enzymes, peptides, sugars, phenolic acids, bioactive alkaloids as a driving force for nanoparticle formation. Using plant extracts, the following nanoparticles have been obtained: Au, Ag (a host of reports), Cu, CuO, TiO_2, ZnO, In_2O_3, Fe, Fe_2O_3, Pb and Se. A large number of their final morphologies have been reported: spheres, triangles, cubes, pentagons, hexagons, wires, rods, etc., for example, Au triangles (reduction of $HAuCl_4$ with *Aloe vera*), Ag nanowires (reduction of Ag^+ with *Cassia fistula* leaf). Nanoparticle sizes can vary considerably, for example, CdS (from ultrasmall 2–5 nm to large 200 nm), Ag (5–400 nm), Au (5–85 nm) or magnetite (20–50 nm). Factors influencing their size and shape are as follows: plant extract and metal salt concentrations, temperature (25–95°C), pH (lower pH—larger particles), reaction time (normally from minutes to several hours).

Different metals have distinct capacity to be reduced by plant extracts; easiest processes correspond to noble metals, especially silver. Typical disadvantages in plant-assisted reduction of metals are difficulties in separation of formed metal nanoparticles from the biomass and accompanying putrification processes in reaction systems in the case of long-term reduction. So, the low or practically no cost of plant extracts can cause an imagination about apparent scalability for these processes; however, necessity of additional separation steps can result a negative conclusion on potential pilot-plant or major fabrication of metal nanoparticles.

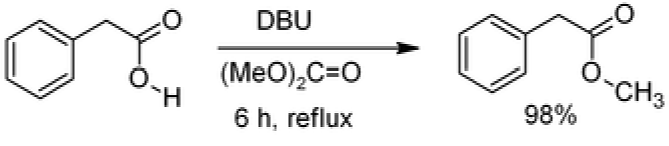
A huge number of reports are dedicated to Ag^0, Au^0 monometallic and Ag^0/Au^0 bimetallic nanoparticles, obtained by biological methods and reviewed in . Silver nanoparticles have been biologically obtained by all possible methods , including bacteria-assisted bioreduction (in particular, using *Escherichia coli*, *Bacillus licheniformis*, *B. subtilis*, among others), fungi (*Aspergillus fumigatus*, *Fusarium acumina-tum*, *Penicillium fellu-tanum*, among others), yeast (yeast strain) and numerous plant extracts containing polyphenols as reductants (pennyroyal—*Mentha pulegium* L., *Platanus orientalis*, thyme—*Thymus vulgaris* L. , *carum carvi* L. seeds , black and green tea, lemon grass, grape wastes, orange wastes, *Magnolia kobus*, marshmallow flower (*Althaea officinalis* L.), geranium, etc.). Au and Ag nanoparticles can be obtained with the use of actinomycetes (microorganisms with some properties of bacteria and fungi) and leaves of *Passiflora edulis* . Sometimes additional microwave treatment and capping agents were applied to complete metal formation process. Using microorganisms, metal ions (for instance, Au^+) can be reduced on cell membranes and walls in the intracellular reduction as a result of releasing enzymes from cell membrane. At the same time, the proteins can take a capping role. In the extracellular reduction, nitrate reductase enzyme can be a driving force for metal ion (Au^+, Ag^+) reduction according to the electron transfer mechanism and further stabilization by proteins.

DIMETHYL CARBONATE (DMC)

It is an organic compound with the formula $OC(OCH_3)_2$. It is a colourless, flammable liquid. It is classified as a carbonate ester. This compound has found use as a methylating agent and more recently as a solvent that is exempt from the restrictions placed on most volatile organic compounds (VOCs) . Dimethyl carbonate is often considered to be a green reagent.

Methylating agent

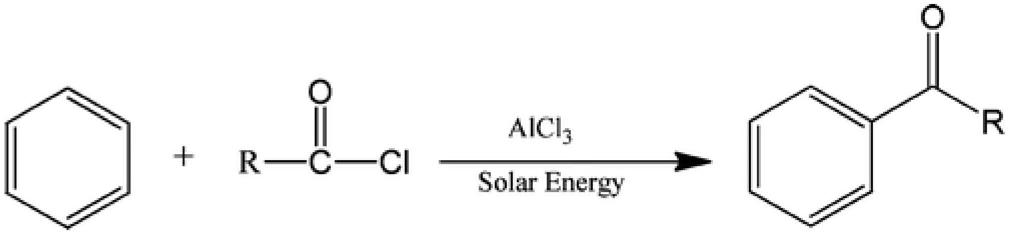
Dimethyl carbonate methylates anilines, phenols, and carboxylic acids, but many of these reactions require the use of an autoclave.



Dimethyl carbonate's main benefit over other methylating reagents such as iodomethane and dimethyl sulfate is its low toxicity. Additionally, it is biodegradable.Unfortunately, it is a relatively weak methylating agent compared to these traditional reagents.

FRIEDEL-CRAFTS REACTION

The Friedel-Crafts reaction, a widely used reaction in both industrial and academic laboratories, produces several byproducts which must be handled as pollutants. An alternative which involves the photochemically-mediated reaction of an aldehyde with a quinone is described..



SUPERCRITICAL CARBON DIOXIDE (SCO_2)

It is a fluid state of carbon dioxide where it is held at or above its critical temperature and critical pressure.

Carbon dioxide usually behaves as a gas in air at standard temperature and pressure (STP), or as a solid called dry ice when cooled and/or pressurised sufficiently. If the temperature and pressure are both increased from STP to be at or above the critical point for carbon dioxide, it can adopt properties midway between a gas and a liquid. More specifically, it behaves as a supercritical fluid above its critical temperature (304.13 K, 31.0 °C, 87.8 °F) and critical pressure (7.3773 MPa, 72.8 atm, 1,070 psi, 73.8 bar) expanding to fill its container like a gas but with a density like that of a liquid.

Supercritical CO_2 is becoming an important commercial and industrial solvent due to its role in chemical extraction in addition to its low toxicity and environmental impact. The relatively low temperature of the process and the stability of CO_2 also allows most compounds to be extracted with little damage or denaturing. In addition, the solubility of many extracted compounds in CO_2 varies with pressure permitting selective extractions.

USES OF SUPERCRITICAL CO_2