



CHHATRAPATI SHAHU JI MAHARAJ UNIVERSITY, KANPUR



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GREEN CHEMISTRY

M.Sc. IV SEM

Based On
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- Brief and Intensive Notes
- Multiple Choice Questions

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M. Sc. (IV) Semester CHEMISTRY

GREEN CHEMISTRY B021010T



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SYLLABUS

Unit 1: Introduction Principle and Concepts of green Chemistry

Need for green chemistry, Inception and evolution of green chemistry, Twelve principles of Green Chemistry with their explanation and examples, Designing a green synthesis using these principles, Green chemistry in day to day life.

Unit 2: Non Traditional Greener Alternative Approaches

Different approaches to green synthesis: Use of green reagents in organic synthesis-Dimethyl carbonate, Polymer supported reagents- Peracids and Chromic acids, Green Catalysis, role of catalysis in sustainable development, homogeneous and heterogeneous catalyst, Introduction, advantages and applications of Biocatalyst. and chlorine demand, purification and treatment of water.

Unit 3: Application of Non-conventional Energy Sources

Introduction of microwave induced synthesis: Microwave activation, equipment, time and energy benefits, limitations, Organic transformations under microwaves- Fries rearrangement, Diels-Alder reaction, Decarboxylation, saponification of ester.

Introduction of ultrasound assisted green synthesis: Instrumentation, Physical aspects, application in organic transformations.

Unit 4 Environmentally Benign Solutions to organic solvents:

Ionic liquids as green Solvents: Introduction, properties and types of ionic liquids, Synthetic applications- Diels-Alder reaction.

Aqueous phase reactions: Synthesis applications- 1,3- Dipolar Cycloadditions, Carbon-Carbon bondforming processes and bromination reactions. Role of supercritical Carbon dioxide in green chemistry, Ethyl lactate as a renewable green solvent: Properties and applications.

Unit 5: Synthesis of Nanomaterials:

Greener synthesis of Nanomaterials –Magnetic Nanoparticles, MW assisted nano catalysis in water, Synthesis of Nanoparticles using Bacteria, Yeast, Algae and Fungus

UNIT- 1

INTRODUCTION

Green chemistry (sometimes called sustainable chemistry) is the branch of chemistry that deals with designing and optimizing processes and products to lower or remove altogether the production and use of toxic substances. Green chemistry is not the same as environmental chemistry. Many chemical synthesis reactions carried out on an industrial scale require large amounts of chemical solvents. Furthermore, these solvents are also used industrially for degreasing and cleaning purposes. However, many traditional solvents used for such purposes in the past are known to be toxic to human beings. The advancement of green chemistry has brought many alternatives to these toxic solvents. The green solvents that are coming up as alternatives are known to be derived from renewable sources and are also known to be biodegradable. Thus, green chemistry has great potential to lower the toxicity of specific industrial environments by developing safer alternatives.

Inception and Evolution of Green Chemistry

Green chemistry, also known as sustainable chemistry, emerged as a scientific discipline in response to increasing environmental challenges and the growing need for sustainable industrial practices. It has since become a vital framework for designing eco-friendly processes and products.

Inception of Green Chemistry

1. Early Environmental Concerns

In the mid-20th century, rapid industrial growth led to significant environmental damage, including pollution, depletion of resources, and health hazards. Events such as oil spills, chemical disasters (e.g., Bhopal Gas Tragedy, 1984), and water contamination highlighted the urgent need for sustainable practices.

2. Legislative Push

The Pollution Prevention Act of 1990 (USA) marked a shift from pollution control to pollution prevention, emphasizing the reduction of hazardous substances at the source. It became clear that traditional end-of-pipe solutions (treating pollution after it is created) were insufficient to address growing environmental concerns.

3. Emergence of Green Chemistry

The term "green chemistry" was first popularized in the 1990s by chemists Paul T. Anastas and John C. Warner, who advocated for designing chemical processes that minimize environmental and health impacts. The U.S. Environmental Protection Agency (EPA) established the Green Chemistry Program in 1991, promoting research and application of sustainable chemical practices.

4. Publication of the 12 Principles

In 1998, Anastas and Warner formalized the framework of green chemistry in their book *Green Chemistry: Theory and Practice*. The **12 Principles of Green Chemistry** outlined practical strategies for reducing waste, energy use, and toxicity.

Evolution of Green Chemistry

1. Academic and Research Expansion

Universities and research institutions worldwide began incorporating green chemistry into their curricula and research agendas. The development of journals like *Green Chemistry* by the Royal Society of Chemistry provided a platform for disseminating innovations.

2. Industrial Adoption

Industries recognized the economic benefits of green chemistry, such as reduced waste management costs and enhanced process efficiency. Sectors like pharmaceuticals, agriculture, and energy began adopting green chemistry principles in their processes.

3. Technological Advances

Innovations such as catalysis, enzymatic reactions, green solvents, and renewable feedstocks emerged as key enablers of green chemistry. Tools like life cycle assessment (LCA) and real-time monitoring facilitated evaluating and optimizing sustainable processes.

4. Global Recognition and Awards

The Presidential Green Chemistry Challenge Awards (established in 1995) recognized groundbreaking achievements in sustainable chemistry. Green chemistry principles gained recognition in international agreements and initiatives like the

United Nations Sustainable Development Goals (SDGs).

Impact of Green Chemistry

1. Environmental Benefits

Reduced hazardous waste generation. Lower carbon emissions and energy consumption. Promotion of biodegradable and renewable materials.

2. Economic Advantages

Cost savings through efficient use of resources and energy. Reduced expenses for waste treatment and regulatory compliance. Increased marketability of green products.

3. Health and Safety Improvements

Minimized exposure to toxic substances for workers and consumers. Safer industrial processes with lower risks of accidents and disasters.

Principles of Green Chemistry

The twelve principles put forward by the American chemists Paul Anastas and John Warner in 1998 to lay the foundation for green chemistry are listed below.

Twelve Principles of Green Chemistry with detailed explanations and examples are given below:

1. Prevention

Explanation: It is better to prevent waste than to treat or clean up waste after it is formed. **Example:** In synthesizing ibuprofen using the BHC process, nearly all reactants are converted into the final product, reducing waste.

2. Atom Economy

Explanation: Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product. **Example:** The Diels-Alder reaction is a good example of a high atom economy, as it incorporates all reactants into the product.

3. Less Hazardous Chemical Syntheses

Explanation: Wherever possible, synthetic methods should be used to generate substances without toxicity to human health and the environment.

Example: Using hydrogen peroxide (H_2O_2) as an oxidizing agent instead of toxic reagents like chromium (VI) compounds.

4. Designing Safer Chemicals

Explanation: Chemical products should be designed to preserve their desired functionality while reducing toxicity. **Example:** Designing pesticides like Spinosad that are effective against pests but safe for humans and other non-target organisms.

5. Safer Solvents and Auxiliaries

Explanation: The use of auxiliary substances (e.g., solvents, separation agents) should be made unnecessary wherever possible, and when used, they should be innocuous. **Example:** Water can be used as a solvent instead of organic solvents in the Mannich reaction.

6. Energy Efficiency

Explanation: Energy requirements should be minimized. Reactions should be conducted at ambient temperature and pressure whenever possible. **Example:** Enzyme-catalysed reactions in biocatalysis operate efficiently at room temperature, reducing energy consumption.

7. Use of Renewable Feedstocks

Explanation: Raw materials should be renewable rather than depleting whenever technically and economically feasible. **Example:** Polylactic acid (PLA) plastics are produced from corn starch instead of petroleum-based polymers.

8. Reduce Derivatives

Explanation: Unnecessary derivatization (e.g., blocking groups, protection/deprotection steps) should be avoided as it requires additional reagents and generates waste. **Example:** Direct synthesis of esters using enzymes without protecting groups.

9. Catalysis

Explanation: Catalytic reagents (as selective as possible) are superior to stoichiometric reagents. **Example:** Palladium catalysts are used in cross-coupling reactions like the Suzuki coupling to create carbon-carbon bonds efficiently.

10. Design for Degradation

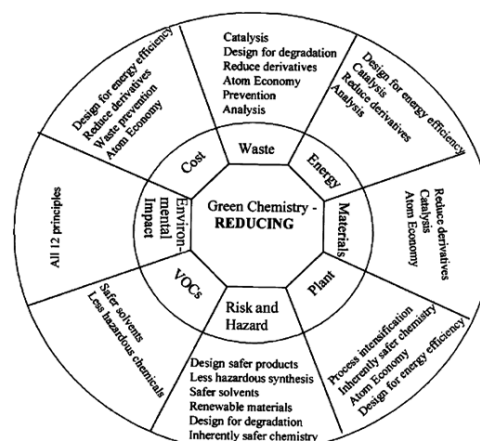
Explanation: Chemical products should be designed to break down into harmless substances after use to prevent environmental accumulation. **Example:** Biodegradable detergents and polymers like polyhydroxyalkanoates (PHAs) decompose naturally in the environment.

11. Real-Time Analysis for Pollution Prevention

Explanation: Analytical methods must be developed to allow for real-time monitoring and control of processes to minimize the formation of hazardous substances. **Example:** Using in-line spectroscopy to monitor pharmaceutical reactions and detect impurities immediately.

12. Inherently Safer Chemistry for Accident Prevention

Explanation: Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including explosions, fires, and environmental releases. **Example:** Replacing volatile organic solvents with ionic liquids, which are less flammable and safer to handle.



resources, improved atom efficiency, and the use of solvent-free or recyclable environmentally benign solvent systems.

Green Chemicals

The increasing local and global concern for environmental pollution offers an incentive to explore new green materials. They can be characterized in three parts:

I. Green Reagent, II. Green Catalyst, III. Green Solvent

I. Green Reagents

Green Reagents in Organic Synthesis: To transform selected feedstock into the target molecule, the criteria of efficiency, availability, and effect of the reagent must be kept in mind. Commonly used green reagents are: i) Dimethyl carbonate (DMC): DMC is also used to methylate active methylene compounds in which no inorganic salts are produced. ii) Polymer-supported reagents: Polymer-supported reagents are those in which ordinary reagents are bound to polymer support. e.g., polymer-supported peracid is used for epoxidation of alkenes

1. Dimethyl Carbonate (DMC)

Dimethyl carbonate is a versatile, eco-friendly reagent and solvent widely used in organic synthesis due to its non-toxic, biodegradable, and renewable nature. Molecular formula: $C_3H_6O_3$, Low toxicity and biodegradability. Acts as a carbonylation, methylation, and methoxy carbonylation agent.

Applications:

1-Carbonylation Reactions: DMC is a green alternative to phosgene for introducing carbonyl

UNIT -2

Non-Traditional Greener Alternative Approach

Different approaches to green synthesis:

Green synthesis produces nanoparticles that use biological materials and are more environmentally friendly than traditional chemical methods. Green synthesis emphasizes eco-friendly, sustainable methods for chemical and material production. Green chemistry aims to protect the environment not by cleaning up but by inventing new chemical processes that do not pollute the environment.

Due to increasing local and global concern for environmental pollution, green materials can be characterized in three parts: Green reagents (Dimethyl carbonate, Polymer supported reagents), Green catalysts (Acid Catalyst, Oxidation Catalyst, Basic Catalyst, Photocatalyst, Phase transfer Catalyst, Polymer supported catalyst, Biocatalyst) and green solvents (Supercritical CO_2 , Water, Ionic liquids). So, green chemistry is about minimizing waste resources, using catalysts instead of reagents, non-toxic reagents, renewable

groups. Used in the synthesis of carbamates and polycarbonates.

2-Methylation Reactions: Replaces toxic methyl halides or dimethyl sulfate for methylating alcohols, phenols, and amines.

3-Transesterification: Effective in synthesizing esters by reacting with alcohols. Applied in biodiesel production.

Solvent: DMC is a green solvent in reactions requiring minimal environmental impact.

2. Polymer-Supported Reagents

Polymer-supported reagents are functionalized polymers that facilitate reactions, particularly in heterogeneous systems. These reagents provide environmental and operational benefits, including easy separation and recyclability.

Key Features: Reduced waste generation (reagents are bound to a solid support). Ease of product purification (filtration instead of extraction). Compatibility with flow chemistry and automated synthesis.

Applications:

1-Catalysis: Polymer-supported catalysts, such as sulfonic acid resins, are used in esterification and hydrolysis.

2-Oxidation: Supported oxidizing agents like polymer-bound PCC (pyridinium chlorochromate) are employed for alcohol oxidation.

3-Scavenger Resins: These resins remove impurities or excess reagents in a reaction, simplifying product isolation.

4-Green Synthesis: Used in sustainable processes, including drug and acceptable chemical production.

Para-Acids

Para-acids refer to aromatic carboxylic acids, particularly those with para-position substitutions (e.g., p-toluene sulfonic acid, p-aminobenzoic acid).

Role in Synthesis:

1. **Catalysis:** p-Toluene sulfonic acid (p-TsOH) is a strong organic acid widely used as a catalyst in esterification and acetal formation.

2. **Precursor for Pharmaceuticals:** p-Aminobenzoic acid (PABA) is a key intermediate in drug synthesis, including folic acid derivatives.
3. **Environmental Impact:** Para-acids are generally safer and can be engineered for selective catalytic processes, reducing waste.

Chromic Acids

Chromic acid refers to a mixture of chromium trioxide (CrO_3) and sulfuric acid or other forms of chromium (VI) compounds used in organic oxidation reactions.

Applications: Oxidation of Alcohols: Chromic acid oxidizes primary alcohols to carboxylic acids and secondary alcohols to ketones. Widely applied in the preparation of carbonyl compounds. Chromic acid in acetone is used for selective oxidation of alcohols under mild conditions.

Environmental Concerns:

Toxicity: Chromium (VI) compounds are highly toxic and carcinogenic. **Alternatives:** Green alternatives, such as TEMPO, PCC, and polymer-supported oxidants, replace chromic acids in sustainable synthesis. Adoption minimizes environmental impact, improves safety, and enhances process efficiency, aligning with the principles of green chemistry.

Role of Catalysis in Sustainable Development

Catalysis addresses global challenges like climate change, resource scarcity, and pollution. The use of catalysts in chemical processes can have a profound impact on sustainability in several key ways:

Reducing energy consumption: Many chemical reactions are energy-intensive, requiring high temperatures and pressures. Catalysts can lower the activation energy required for these reactions, enabling them to occur in milder conditions. This reduces energy consumption and, by extension, greenhouse gas emissions.

Minimizing waste: Catalysts can selectively promote desired reactions while suppressing unwanted side reactions. This selectivity reduces waste product generation, increasing the desired product's overall yield. As a result, less material becomes waste, leading to a more sustainable process.

Enhancing resource efficiency: By making reactions more efficient, catalysts allow for the use of fewer raw materials. This reduces costs and conserves valuable resources, some of which may be finite or environmentally sensitive.

Enabling greener reagents: In some cases, catalysts can facilitate using greener reagents or solvents. For instance, they can make it possible to use water as a solvent instead of hazardous organic solvents, further reducing the environmental impact of a process. Extending the lifespan of equipment: Harsh reaction conditions can lead to equipment degradation and the need for frequent replacements. Catalysts that enable milder conditions can extend the lifespan of equipment, reducing maintenance costs and waste.

Real-World Examples The impact of catalysts on sustainability can be seen in various industries. Here are a few examples:

Catalytic converters in automobiles: One of the most well-known examples is the catalytic converter in cars. This device contains catalysts that convert harmful pollutants in exhaust gases, such as carbon monoxide and nitrogen oxides, into less harmful substances like carbon dioxide and nitrogen. Without catalytic converters, automobile emissions would be significantly more detrimental to air quality and public health.

Petrochemical industry: Catalysts are extensively used in the refining and petrochemical industries. They enable the production of cleaner fuels, converting crude oil into valuable products and reducing fuel sulfur content to meet environmental regulations.

Pharmaceutical manufacturing: The pharmaceutical industry relies on catalysts to streamline complex chemical reactions and improve the efficiency of drug synthesis. This reduces the cost of drug production and minimizes the generation of chemical byproducts.

I. Green Catalyst: Catalysts play a significant role in establishing the economic strength of the chemical industry and developing clean chemical processes and products. The following types of catalysts are used:

- i. Acid Catalyst
- ii. Oxidation Catalyst
- iii. Basic Catalyst
- iv. Photocatalyst
- v. Phase

- Transfer Catalyst, vi. Polymer-supported catalyst,
- vii. Biocatalyst

Principles:

Enhanced atom economy. Reduction of toxic by-products. Energy-efficient processes. Use of renewable feedstocks. Green Fuel Production: Enable the production of hydrogen and biofuels, reducing reliance on fossil fuels.

4. Homogeneous and Heterogeneous Catalysts

Homogeneous Catalysts:

Introduction: These catalysts exist in the same phase (usually liquid) as the reactants. They typically involve metal complexes or organometallic compounds. **Advantages:** High selectivity and efficiency. Better control over reaction conditions. Useful in fine chemical synthesis. **Challenges:** Difficult separation and recovery. Sensitivity to impurities. **Applications:** Hydroformylation in the production of aldehydes. Polymerization reactions.

Heterogeneous Catalysts:

Introduction: These catalysts exist in a different phase (usually solid) from the reactants. They often involve metal oxides or supported metals. **Advantages:** Easy separation and recovery. High stability and reusability. Operate under diverse conditions. **Challenges:** Lower selectivity compared to homogeneous catalysts. Susceptible to deactivation due to fouling. **Applications:** Haber-Bosch process for ammonia synthesis. Catalytic cracking in petroleum refining.

Biocatalysts

Introduction to Biocatalysts: Biocatalysts are enzymes or other biological molecules that accelerate chemical reactions in living organisms. These natural catalysts are particularly efficient and operate under mild conditions such as ambient temperature, pressure, and neutral pH. They play a critical role in biological processes like digestion, respiration, DNA replication, and industrial applications. Enzymes are the most common biocatalysts, made up of proteins or, in some cases, RNA molecules (ribozymes). Their specificity lies in their ability to target particular substrates, transforming them into desired products without producing unwanted byproducts. Biocatalysts are increasingly favored over traditional

chemical catalysts due to their eco-friendly and sustainable nature.

Advantages of Biocatalysts:

High Specificity

Biocatalysts are highly selective, acting on specific substrates and producing desired products with minimal side reactions. This reduces waste and enhances the efficiency of processes.

Eco-Friendly

They operate under mild conditions, reducing energy consumption and the need for hazardous chemicals. This aligns with green chemistry principles, minimizing environmental impact.

Renewability

Biocatalysts, derived from natural sources, are renewable and biodegradable, making them a sustainable alternative to synthetic catalysts.

Cost Efficiency

Despite high initial costs, biocatalysts can lower overall expenses by reducing energy and raw material requirements and waste disposal costs.

Operational Flexibility

Enzymes function effectively in various industrial setups, including aqueous and non-aqueous systems, enhancing their adaptability.

Improved Reaction Rates

Biocatalysts accelerate reaction rates significantly compared to uncatalyzed reactions, leading to higher productivity.

Applications of Biocatalysts

Pharmaceutical Industry Enzymes with high precision and purity synthesize drugs, such as antibiotics, anti-inflammatory agents, and antivirals.

Food and Beverage Industry

Applications include fermentation (e.g., brewing beer, baking bread), lactose hydrolysis in dairy, and enhancing flavors in processed foods.

Biofuel Production

Biocatalysts like cellulases and lipases convert biomass into biofuels and promote renewable energy sources.

Environmental Bioremediation

Biocatalysts aid in breaking down pollutants in soil and water, such as oil spills, pesticides, and heavy metals.

Agriculture

Enzymes enhance soil fertility, promote plant growth, and develop biopesticides and biofertilizers.

Textile Industry

Enzymes like amylases, cellulases, and proteases assist in fabric processing, such as bio-polishing and bio-scouring.

Chemical Synthesis

Biocatalysts facilitate the production of fine chemicals, such as flavors, fragrances, and specialty polymers.

Cosmetics Industry

Enzymes are used in formulations for skincare and haircare products to enhance their effectiveness and stability. Biocatalysts are a cornerstone of sustainable development, bridging biological processes with industrial applications. Their ability to combine efficiency, specificity, and environmental friendliness positions them as transformative agents in science and technology.

UNIT-3

Application of Non-Conventional Energy Sources

Introduction

Non-conventional energy sources, also known as renewable energy sources, are crucial for addressing the world's increasing energy demands while mitigating the adverse effects of fossil fuel usage. These sources include solar, wind, biomass, geothermal, and tidal. Their application spans numerous fields due to their eco-friendly nature, cost-effectiveness over time, and sustainability. Below is a detailed discussion of their applications:

1. Applications of Non-Conventional Energy Sources

Solar Energy- Power Generation: Solar photovoltaic (PV) cells convert sunlight into electricity for residential, commercial, and industrial use. **Solar Water Heating:** Utilized in domestic and industrial applications for heating purposes. **Agriculture:** Solar pumps for irrigation and drying of crops. **Lighting:** Solar-powered streetlights and household lighting systems.

Wind Energy- Electricity Production: Wind turbines convert wind energy into electrical energy, fed into grids, or used off-grid. **Water Pumping:** Windmills are used in remote areas to pump water. **Hybrid Systems:** Integrated with solar systems to power rural areas.

Biomass Energy- Biofuels: Production of ethanol and biodiesel for transportation. **Biogas:** Methane generated from organic waste for cooking and electricity generation. **Industrial Use:** Biomass as a feedstock in the chemical industry and for power plants.

Geothermal Energy- Heating and Cooling: Used for district heating systems and heat pumps. **Power Generation:** Convert geothermal heat into electricity in geothermal power plants.

Tidal and Wave Energy- Electricity Production: Tidal and wave energy converters harness the kinetic energy of ocean tides and waves.

Hydrogen Energy- Fuel Cells: Hydrogen is used in fuel cells to produce electricity for vehicles and stationary power systems. **Industrial Applications:** Hydrogen as a clean alternative in steel and chemical manufacturing.

Introduction to Microwave-Induced Synthesis

Microwave-induced synthesis is an innovative technique that leverages microwave energy to accelerate chemical reactions. It has gained significant attention in chemistry, materials science, and engineering due to its efficiency, speed, and eco-friendliness. This technique uses microwaves as an unconventional energy source for chemical transformations. It has many applications, including:

Organic synthesis

Microwave-assisted organic synthesis (MAOS) can accelerate reaction rates, reduce energy consumption, and eliminate the need for prolonged refluxing. It is also a green approach that can synthesize organic compounds.

Nanoparticle synthesis

Microwaves can homogeneously heat precursor materials, which helps synthesize nanoparticles. The process can be tuned to produce nanoparticles of the desired size and shape.

Polymer synthesis

Microwave irradiation (MWI) can produce polymers for organic solar cells, LEDs, OLEDs, and flexible OLEDs. MWI can also produce biodegradable nanoparticles and polymers. Here are some other advantages of microwave-induced synthesis: It can reduce environmental pollution, produce higher product yields with purity, reduce side reactions, and produce better products. Microwaves are electromagnetic radiation with wavelengths ranging from 1 mm to 1 m. They can penetrate solids and liquids, absorbing and transforming the electromagnetic energy into heat.

Principles of Microwave-Induced Synthesis

Microwave Heating:

Microwaves are electromagnetic waves with frequencies ranging from 300 MHz to 300 GHz. They interact with polar molecules and ionic species in the reaction medium, causing dipole rotation and ionic conduction. This generates heat directly within the material, leading to rapid and uniform temperature increases.

Non-Thermal Effects:

Microwaves also enhance reaction rates through specific interactions at the molecular level, sometimes bypassing conventional activation energy barriers. Microwave activation equipment can offer several benefits, including:

Energy efficiency: Microwaves can be more energy efficient than conventional cooking methods because they heat only the food, not the entire oven.

Faster cooking: Microwaves can cook food faster than conventional methods.

Uniform heating: Microwaves can distribute uniform energy, resulting in more uniform temperature and moisture profiles.

Reduced production run times: Microwaves can reduce production run times, cleaning times, and chemical costs.

Non-contact drying: Microwaves can be used as a non-contact drying technology.

Improved product performance: Microwaves can improve yields and enhance product performance.

Rapid volumetric heating: Microwaves can provide rapid volumetric heating.

Fast reaction rate: Microwaves can provide a fast reaction rate.

Low cost: Microwaves can be low cost.

Good product yield: Microwaves can provide good product yield. However, microwaves also have some limitations, including high installation costs, too much space, electromagnetic interference, dielectric changes due to temperature changes, and exposure to them for a prolonged period, which can cause severe burning.

Advantages

Faster Reaction Rates: Drastically reduces synthesis time compared to traditional methods.

Energy Efficiency: Direct heating minimizes energy wastage.

Selective Heating: Targets specific reactants or phases, reducing side reactions.

Eco-Friendliness: Reduces the need for solvents and energy-intensive steps.

Applications

Material Synthesis:

Production of nanomaterials, ceramics, and polymers. Fabrication of catalysts for industrial processes.

Pharmaceuticals:

Accelerated synthesis of drug compounds and active pharmaceutical ingredients.

Chemical Reactions:

Organic and inorganic reactions such as esterification, polymerization, and oxidation.

Environmental Applications:

Treatment of waste materials and synthesis of environmentally friendly products.

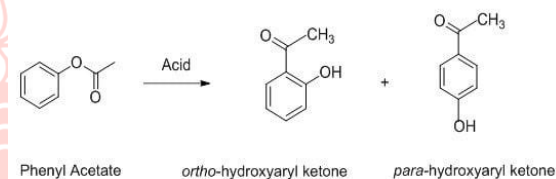
Energy Materials:

Development of batteries, supercapacitors, and solar cell materials.

Organic transformations under microwaves:

1- Fries rearrangement

Microwaves can perform the Fries rearrangement reaction, an organic reaction that converts phenolic esters into hydroxyaryl ketones: Microwave-enhanced thermal Fries rearrangement. A solvent-free, rapid, and cost-effective method for synthesizing para-amino aryl ketones



The Fries rearrangement reaction involves the following steps:

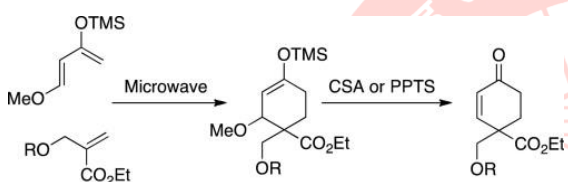
1. Heating a phenolic ester of a carboxylic acid
2. Adding a Lewis acid catalyst, such as AlCl_3 , HF , BF_3 , TiCl_4 , or SnCl_4
3. The acyl group of the phenolic ester migrates to the aryl ring

The Fries rearrangement is ortho and para selective, meaning the acyl group attaches to the ortho or para positions of the aryl ring. The reaction conditions, such as the temperature and solvent, can be modified to direct the selectivity. It involves the conversion of phenolic esters into hydroxyaryl ketones on heating in the presence of a catalyst. Suitable catalysts for this reaction are Brønsted or Lewis acids such as HF , AlCl_3 , BF_3 , TiCl_4 , or SnCl_4 . The Fries rearrangement reaction is an *ortho*, *para*-selective reaction used to

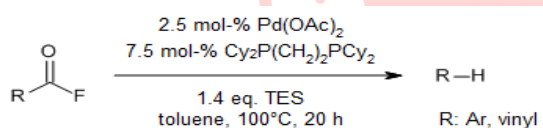
prepare acyl phenols.¹ This organic reaction has been named after German chemist Karl Theophil Fries.

2-Diels–Alder Reaction

The microwave heating drastically accelerates Diels–Alder cycloadditions between Danishefsky's diene and derivatives of ethyl α -(hydroxymethyl)acrylate whose hydroxyl group is protected with various protective groups to give previously unknown adducts, which are necessary as intermediates for the synthesis of a biotin conjugate of a monocyclic cyanoenone with high anti-inflammatory activity. The reaction time is only one hour, and the average yield is approximately 80%. Compared to the traditional thermal conditions, this method requires 1/48th to 1/14th of the time, and yields are 2–7 times higher.



3- Decarboxylation:



Microwave irradiation simplifies the decarboxylation reaction in the presence of a phase transfer catalyst, which affords a 90% yield. An effective protocol allows the smooth protodecarboxylation of diversely functionalized aromatic carboxylic acids within 5-15 min under microwave irradiation. In the presence of an inexpensive catalyst generated in situ from copper(I) oxide and 1,10-phenanthroline, even nonactivated benzoates were converted to high yields.

4. Saponification of Esters

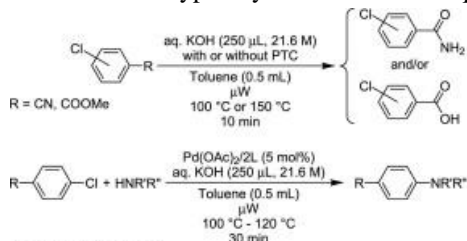
Saponification is the hydrolysis of esters to form alcohol and carboxylate salt in the presence of a base.

Microwave-assisted saponification

An example is the saponification of a sample using KOH in ethanol/water or methanol/water in a microwave vessel. The sample is heated to 90°C for 10 minutes under constant stirring.

Advantages: Reduced reaction times, especially for less reactive esters.

Conditions: Typically involves an aqueous or



R = CN, COOMe, C(O)Me
R'R'NH = morpholine, pyrrolidine, piperidine, 1-(3-methylphenyl)piperazine, BnNH₂, n-HexNH₂
alcoholic solution of a strong base (e.g., NaOH or KOH) under microwave irradiation.

General Benefits of Microwave-Assisted Organic Transformations:

Energy Efficiency: Microwaves selectively heat the reactants, solvents, or catalysts.

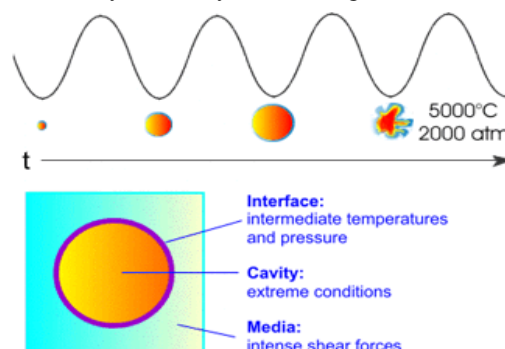
Shorter Reaction Times: Reactions typically take hours and can often be completed in minutes.

Environmentally Friendly: Potential to perform reactions under solvent-free or aqueous conditions.

Improved Yields and Selectivity: Rapid heating and uniform energy distribution minimize side reactions.

Introduction of Ultrasound-Assisted Green Synthesis

Ultrasound irradiation differs from conventional energy sources (such as heat, light, or ionizing radiation) in time, pressure, and energy per molecule. Using ultrasound waves in organic synthesis has attracted increasing interest over the last few years. Using ultrasound waves as an alternative energy source is very interesting in green and pharmaceutical chemistry. Sonochemistry involves the use of ultrasound techniques to promote chemical reactions. Sonochemistry is widely used in organic chemistry,



offering versatile and facile pathways for many syntheses. The study of sonochemistry is concerned with understanding the effect of sonic waves and wave properties of Sono chemical systems.

1. Instrumentation

Ultrasound-assisted synthesis relies on specialized equipment to generate and propagate ultrasonic waves into the reaction medium. Key components include:

Ultrasound Generators:

Convert electrical energy into mechanical vibrations. Operate at frequencies typically 20 kHz to 1 MHz, depending on the desired application.

Sonicator Types:

Probe Sonicator: A high-intensity device where the probe is directly immersed into the reaction medium, ensuring efficient energy transfer.

Bath Sonicator: Provides uniform ultrasonic waves within a tank; better for reactions requiring mild and even agitation.

Power Output: Adjustable from low (50 W) to high (up to several hundred watts), impacting cavitation intensity and reaction rates.

Reaction Vessel: Constructed from materials such as glass or stainless steel. Designed to withstand cavitation-induced stress and temperature fluctuations.

Cooling Systems: Necessary for exothermic reactions to maintain the stability of reactants and products. Integrated cooling jackets or external cooling baths are commonly used.

2. Physical Aspects: Ultrasound synthesis operates via acoustic cavitation, a phenomenon involving microbubbles' formation, growth, and collapse in a liquid medium. This process leads to several physical effects:

Cavitation Bubbles: Formed due to alternating high-pressure and low-pressure cycles in the liquid caused by ultrasonic waves. Using ultrasound in chemical reactions in solution provides specific activation based on a physical phenomenon: acoustic cavitation. Cavitation is a process in which mechanical activation destroys the attractive forces of molecules

in the liquid phase. Applying ultrasound, compression of the liquid is followed by rarefaction (expansion), in which sudden pressure drops form tiny, oscillating bubbles of gaseous substances. These bubbles expand with each cycle of the applied ultrasonic energy until they reach an unstable size; they can then collide and/or violently collapse.

For example, oncolysis of $\text{Fe}(\text{CO})_5$ in decane under argon produces amorphous iron upon decarbonylation instead of crystalline iron, which shows that both very high temperatures and rapid cooling rates ($\sim 10^6 \text{ K s}^{-1}$) are involved, the more volatile pentane yields $\text{Fe}_3(\text{CO})_{12}$, indicating a somewhat slower collapse. As these bubbles are tiny and rapidly collapse, they can be seen as microreactors that offer the opportunity to speed up specific reactions and allow mechanistically novel reactions to occur safely. The collapse of these bubbles generates localized "hot spots" with extremely high temperatures (5000 K) and pressures (up to 1000 atm).

Localized Energy:

Ultrasonic energy induces extreme conditions on a microscopic scale, enabling unique chemical transformations that are difficult to achieve under normal conditions.

Shear Forces: Cavitation creates strong mechanical forces that break down reactant molecules or promote mixing.

Non-thermal Effects: Cavitation-driven phenomena are distinct from bulk heating, making ultrasound efficient and energy-saving.

Physical Outcomes: Improved mass transfer and mixing. Reduction of particle size in heterogeneous systems. Formation of radicals that drive redox reactions.

Applications in Organic Transformations:

Ultrasound-assisted synthesis is widely applied in organic chemistry, offering significant advantages regarding reaction rates, yields, and environmental compatibility. Key applications include:

Green Chemistry: Reduces the need for hazardous solvents or reagents. Enhances reactions using environmentally benign conditions.

Organic Reactions:

Oxidation and Reduction: Ultrasound facilitates selective oxidation (e.g., alcohols to aldehydes) and reduction (e.g., nitro compounds to amines).

C-C Bond Formation: Efficient coupling reactions like Suzuki, Heck, and Sonogashira under milder conditions.

Esterification and Amidation: Speeds up ester and amide bond formation.

Hydrolysis: Promotes hydrolysis of esters and amides without requiring harsh conditions.

Catalysis: Improves the efficiency of heterogeneous catalysts by reducing particle size and increasing active surface area. Allows for the recycling of catalysts with minimal deactivation.

Nanomaterial Synthesis: Facilitates the green synthesis of nanoparticles, which serve as catalysts in various organic reactions.

Polymer Chemistry: Enhances the synthesis of biodegradable polymers, copolymers, and grafting processes.

Environmental Applications: Enables degradation of toxic organic pollutants. Supports the synthesis of bio-based chemicals and fuels.

Advantages of Ultrasound in Green Synthesis

Reduces reaction time significantly. Improves atom economy and reaction selectivity. Minimizes the use of toxic reagents and solvents. Enhances process safety by reducing temperature and pressure requirements. By leveraging ultrasound's unique physical effects, it has become an indispensable tool for sustainable and innovative organic synthesis, aligning with the principles of green chemistry.

UNIT-4

Environmentally Benign Solutions to organic solvents

Ionic Liquids as Green Solvents

Introduction: One of the most important areas of green chemistry is the application of environmentally friendly solvents in catalysis and synthesis.

Conventional organic solvents threaten the environment due to their volatility, high flammability, toxicity, and carcinogenic properties. The recently emerged room temperature ionic liquids (RTILs) are promising green solvent alternatives to the volatile organic solvents due to their ease of reuse, non-volatility, thermal stability, and ability to dissolve various organic and organometallic compounds. The properties of ILs and their use as solvents for chemical reactions have been reviewed extensively in recent years. "Ideal" solvent requirements may include low toxicity, low cost, high solute selectivity, inertness to materials, non-flammability, high solute capacity, low carrier selectivity, and moderate interfacial tension. Toxicity and recycling. The use of ILs, particularly in extracting and isolating plant constituents such as flavonoids, phenolic compounds, glycosides, alkaloids, aromatic compounds, and essential oils. The application of ILs in the extraction of bioactive compounds from herbal and vegetative plants is likely to be a predominant field of study. This is because herbs are widely consumed and applied by humankind for therapeutic and nutritional benefits.

Ionic liquids are salts in the liquid state, typically composed of organic cations and inorganic or organic anions, with melting points below 100°C. While ordinary liquids such as water and gasoline are predominantly electrically neutral molecules, ionic liquids are primarily made of ions. These substances are liquid electrolytes, ionic melts, fluids, fused salts, liquid salts, or glasses. The ionic bond is usually more substantial than the Van der Waals forces between the molecules of ordinary liquids. Because of these strong interactions, salts tend to have high lattice energies, manifested in high melting points. Some salts, especially those with organic cations, have low lattice energies and thus are liquid at or below room temperature. Examples include compounds based on the 1-ethyl-3-methylimidazolium (EMIM) cation and include EMIM: Cl, EMIMAc (acetate anion), EMIM dicyanamide, 1-butyl-3,5-dimethylpyridinium bromide which becomes a glass below -24 °C (-11 °F).

Significance: Their unique properties make them suitable for various applications as environmentally benign alternatives to conventional organic solvents.

Properties of Ionic Liquids

Low Volatility: Ionic liquids have negligible vapor pressure, minimizing emissions and reducing air pollution.

Thermal Stability: They are thermally stable over various temperatures, enabling use in high-temperature reactions.

Non-flammability: Most ionic liquids are non-flammable, enhancing safety in industrial processes.

High Solubility: They dissolve various compounds, including organic, inorganic, and polymeric materials.

Design Flexibility: Ionic liquids can be tailored by modifying their cations and anions, allowing customization for specific applications.

High Ionic Conductivity: Suitable for electrochemical applications due to their high ionic conductivity.

Types of Ionic Liquids

Based on Cation Type

Imidazolium-based ILs: Most studied due to their high stability and wide solubility range.

Pyridinium-based ILs: Useful in organic synthesis and catalysis.

Ammonium-based ILs: Lower cost, used in extraction and separation processes.

Phosphonium-based ILs have high thermal stability and are suitable for high-temperature applications.

Examples: Room-temperature ionic liquids (RTILs) are dominated by salts derived from 1-methylimidazole, i.e., 1-alkyl-3-methylimidazolium. Examples derived from pyridine 4-methyl-N-butylpyridinium (MBPy) and N-octylpyridinium (C8Py). Conventional quaternary ammonium cations also form ILs, e.g., tetraethylammonium (TEA) and tetrabutylammonium (TBA).

Based on Anion Type

Halide-based ILs: Widely used but sometimes corrosive.

Tetrafluoroborate ($[\text{BF}_4^-]$) ILs: Known for their thermal and chemical stability.

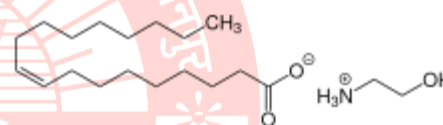
Hexafluorophosphate ($[\text{PF}_6^-]$) ILs: Low viscosity and stability.

Examples: Typical anions in ionic liquids include the following: tetrafluoroborate (BF_4), hexafluorophosphate (PF_6), bis(trifluoromethanesulfonyl)imide (NTf_2), trifluoromethanesulfonate (OTf), dicyanamide ($\text{N}(\text{C}\text{N})_2$), hydrogensulfate (HSO_4), and ethyl sulfate (EtOSO_3).

Organic anion-based ILs: Biodegradable, reducing environmental concerns.

Protic ILs: Contain a transferable proton, suitable for acid-catalyzed reactions.

A **protic ionic liquid** is an ionic liquid formed via proton transfer from a Bronsted acid to a Bronsted base. Unlike many other ionic liquids, which are formed through a series of synthesis steps, protic ionic liquids are easier to create because the acid and base must be mixed.



Monoethanolamine oleate is a typical protic ionic liquid.

Aprotic ILs: Lack of a transferable proton, offering a wider range of chemical inertness.

Task-Specific Ionic Liquids (TSILs): Designed for CO_2 capture, biomass processing, or catalytic processes. ILs and amines have been investigated for capturing carbon dioxide CO_2 and purifying natural gas.

Applications of Ionic Liquids as Green Solvents

Enhance reaction rates, selectivity, and yield while reducing by-products. ILs improve the catalytic performance of palladium nanoparticles. Furthermore, ionic liquids can be used as pre-catalysts for chemical transformations. In this regard, dialkyl imidazolium, such as $[\text{EMIM}]\text{Ac}$, has been combined with a base to generate N-heterocyclic carbenes (NHCs). These imidazolium-based NHCs catalyze several transformations, such as the benzoin condensation and the OTHO reaction.

2-Dispersing agent: ILs can act as dispersing agents in paints to enhance finish, appearance, and

drying properties. ILs disperse nanomaterials at IOLITEC (Ionic Liquid Technologies GmbH).

3-Biomass Processing: Effective in dissolving cellulose and lignocellulosic materials for biofuel production. NMMO monohydrate is used as a solvent in the lyocell process to produce lyocell Fiber. Another use of NMMO is in the dissolution of scleroprotein (found in animal tissue). This dissolution occurs in the crystal areas, which contain more glycine and alanine residues with a small number of other residues. NMMO can break the hydrogen bond of the amides.

4-Electrochemistry: Utilized in batteries, fuel cells, and supercapacitors due to their high ionic conductivity. ILs can replace water as the electrolyte in metal-air batteries. ILs are attractive because of their low vapor pressure. Furthermore, ILs have an electrochemical window of up to six volts, supporting more energy-dense metals. Energy densities from 900 to 1600 watt-hours per kilogram appear possible.

5-Pharmaceuticals: Act as solvents or co-solvents in drug synthesis and delivery. Recognizing that approximately 50% of commercial pharmaceuticals are salts, ionic liquid forms of several pharmaceuticals have been investigated. Combining a pharmaceutically active cation with a pharmaceutically active anion leads to a dual-active ionic liquid in which the actions of two drugs are combined.

6- Nuclear fuel reprocessing: The IL 1-butyl-3-methylimidazolium chloride has been investigated to recover uranium and other metals from spent nuclear fuel and other sources.

7-Solar thermal energy: ILs are potential heat transfer and storage media in solar thermal energy systems. Concentrating solar thermal facilities such as parabolic troughs and solar power towers focus the sun's energy onto a receiver, generating temperatures around 600 °C (1,112 °F). This heat can then generate electricity in a steam or other cycle. Ionic liquids such as [C₄mim] [BF₄] have more favorable liquid-phase temperature ranges (-75 to 459 °C) and could, therefore, be excellent liquid thermal storage media and heat transfer fluids.

Environmental Benefits: Reduction in volatile organic compound (VOC) emissions. Minimal

contribution to ozone depletion and global warming. Recyclable and reusable, reducing waste generation.

Challenges and Future Directions

Cost: High production costs limit widespread use.

Toxicity: Some ionic liquids exhibit toxicity, requiring careful design for specific applications.

Biodegradability: Developing biodegradable ionic liquids is critical for truly sustainable solutions.

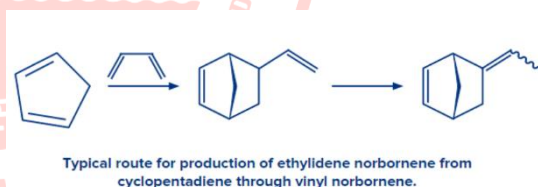
Synthetic Applications of Diels-Alder Reaction:

The Diels-Alder reaction is a [4+2] cycloaddition reaction between a conjugated diene and a dienophile (an alkene or alkyne) to form a six-membered ring. It is a cornerstone of synthetic organic chemistry due to its ability to construct cyclic compounds with high regio- and stereoselectivity. Below are detailed notes on its synthetic applications:

Key Features of the Diels-Alder Reaction

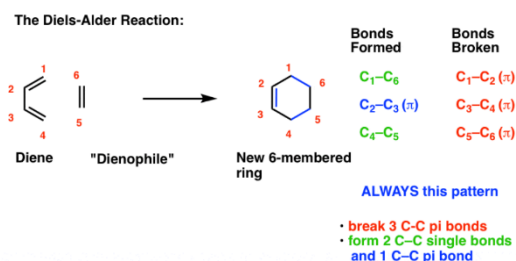
Concerted Mechanism:

The reaction occurs in a single step without intermediates. Bonds form simultaneously between the diene and dienophile.



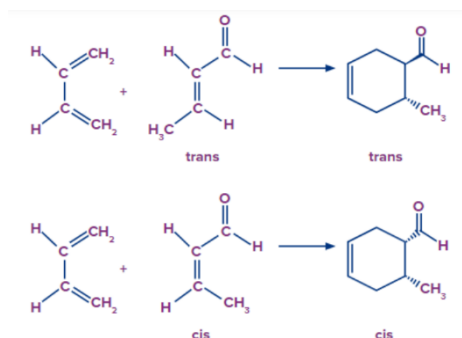
Regioselectivity:

Substituents on the diene and dienophile dictate the orientation of the reaction.



Stereoselectivity:

The reaction is stereospecific: cis dienophiles yield cis products, and trans dienophiles yield trans products.



Thermodynamic Favorability:

Typically, it is exothermic due to strong σ -bonds forming from weaker π -bonds.

Synthetic Applications

1. Construction of Six-Membered Rings: The Diels-Alder reaction is the most efficient method for synthesizing six-membered rings, ubiquitous in natural products and pharmaceuticals. Example: Synthesis of cyclohexenes and derivatives.

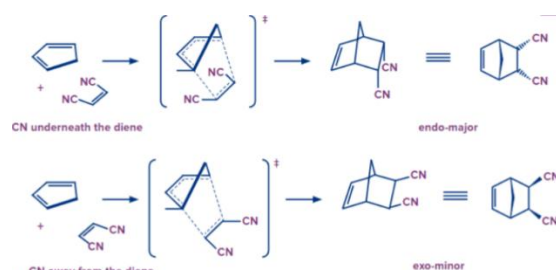
2. Functional Group Compatibility: Functional groups such as electron-withdrawing groups (EWGs) on the dienophile (e.g., $-\text{CN}$, $-\text{COOR}$) and electron-donating groups (EDGs) on the diene enhance reactivity. Example: Acrylonitrile, as a dienophile, reacts efficiently with butadiene.

3. Total Synthesis of Natural Products: Used extensively in synthesizing complex natural products containing cyclic frameworks. Example: Vitamin D synthesis, where a Diels-Alder reaction constructs part of the steroid framework.

4. Endo and Exo Selectivity: The reaction favors the endo product due to secondary orbital interactions, which help synthesize specific stereoisomers.

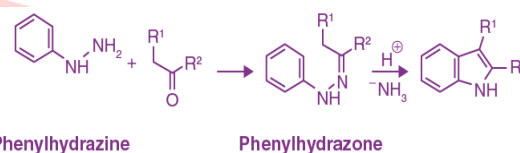
Example: In the synthesis of bridged bicyclic compounds like norbornene derivatives.

5. Cycloaddition in Polycyclic Systems: The key to creating fused and bridged polycyclic systems. Example: Synthesis of tetrahydronaphthalene frameworks in aromatic



6. Synthesis of Aromatic Compounds: A retro-Diels-Alder reaction or subsequent aromatization can yield aromatic products. Example: Anthracene derivatives.

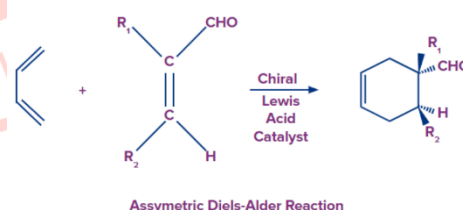
7. Asymmetric Synthesis: Chiral catalysts and auxiliaries enable enantioselective Diels-Alder reactions. Example: Synthesis of enantiomerically pure intermediates for pharmaceuticals.



8. Polymer Chemistry: Utilized in synthesizing cross-linked polymers and thermosetting materials. Example: Maleimide-based dienophiles in creating robust polymer networks.

Advanced Techniques in Diels-Alder Reactions

Catalysis: Lewis acids (e.g., AlCl_3 , TiCl_4) increase the electrophilicity of dienophiles, enhancing reaction rates and selectivity.



Organocatalysts and enzymatic approaches for greener synthesis.

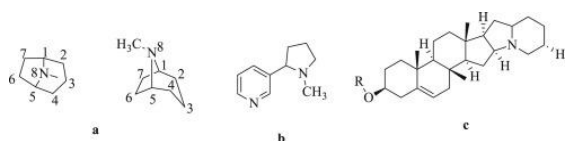
High-Pressure or Microwave Assistance: High pressure can drive less favorable reactions. Microwave irradiation accelerates the reaction and enhances yields.

Hetero-Diels-Alder Reaction: Reactions involving heteroatom-containing dienophiles or dienes. Example: Synthesis of pyran or furan derivatives.

Intramolecular Diels-Alder Reaction (IMDA):

Builds complex polycyclic structures in a single step.

Example: Synthesis of steroids and alkaloids.



The structure of tropane (a), nicotine (b), and solanidine derivatives (c).

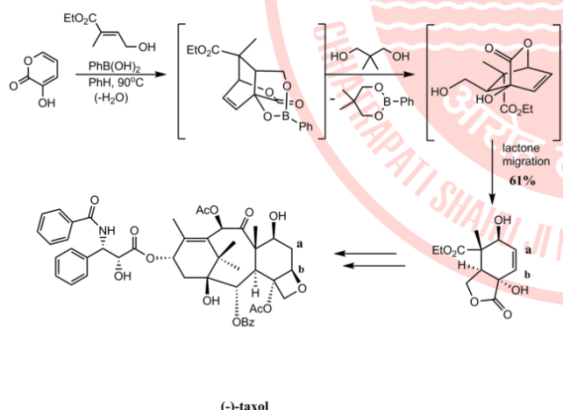
Challenges and Limitations

Steric Hindrance: Bulky substituents can reduce reaction rates.

Thermal Requirements: Some reactions require high temperatures, which may not be compatible with sensitive substrates.

Selectivity Issues: Regio- and stereoselectivity may require careful tuning of reactants and conditions.

Synthesis of Taxol: Diels-Alder of the pyranone was similarly used as the dienophile in the Taxol. Stereocenters that were carried



Cyclopentadiene and Maleic Anhydride: Model reaction illustrating regio- and stereoselectivity.

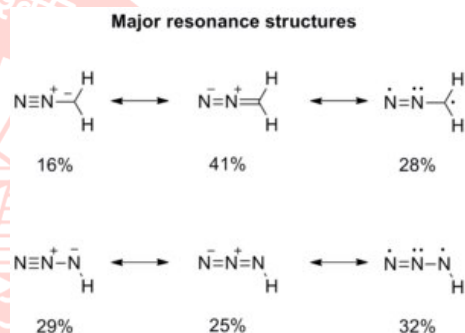
Fischer Indole Synthesis: A modified Diels-Alder pathway. The Fischer indole synthesis reaction is given below.

Aqueous Phase Reactions: General Overview

Reactions in water (aqueous phase) leverage water's unique properties, including high polarity, hydrogen bonding, and environmental friendliness. The 1,3-dipolar cycloaddition methodology applied to aqueous media has produced several heterocyclic

compounds, usually with a regio- and stereoselectivity peculiarity. These heterocycles include triazoles, tetrazoles, pyrazoles, isoxazoles, isoxazolidines, pyrroles, and pyrrolidines.

The superiority of copper(I) catalysis in the azide-alkyne cycloaddition (Huisgen cycloaddition) in water is endorsed by several examples. Nowadays, it is known that water was already the medium employed in synthesis more than a century ago. However, water was promptly dismissed once the organic solvents emerged and exhibited better performance because of the miscibility of the reaction components, that is, homogeneity. Indeed, a better substitute to water was highly polar organic solvents such as dimethyl formamide (DMF), dimethyl acetamide (DMAc), and dimethyl sulfoxide (DMSO).



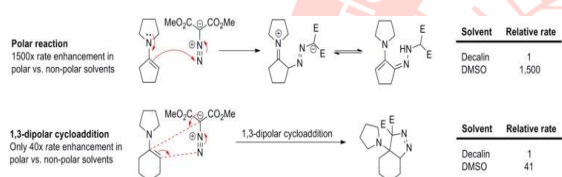
The 1,3-dipolar cycloaddition is a chemical reaction between a 1,3-dipole and a dipolarophile to form a five-membered ring. The 1,3-dipolar cycloaddition between an organic azide and an alkyne to generate 1,2,3-triazole). 1,3-dipolar cycloaddition is an important route to the regio- and stereoselective synthesis of five-membered heterocycles and their ring-opened acyclic derivatives. The dipolarophile is typically an alkene or alkyne but can be other pi systems. When the dipolarophile is an alkyne, aromatic rings are generally produced.

1,3-Dipole: Structure and nomenclature of all second-row 1,3-dipoles consisting of carbon, nitrogen, and oxygen centers. The dipoles are categorized as allyl-type or propargyl/allenyl-type based on the geometry of the central atom. A 1,3-dipole is an organic molecule representing either an allyl-type or a propargyl/allenyl-type zwitterionic octet/sextet structure. Both types of 1,3-dipoles share four electrons in the π -system over three atoms. The allyl type is bent, whereas the propargyl/allenyl type is linear in geometry. 1,3-

Dipoles containing higher-row elements such as sulfur or phosphorus are also known but are utilized less routinely.

Consequently, this ambivalence means that the ends of a 1,3-dipole can be treated as both nucleophilic and electrophilic at the same time. The extent of nucleophilicity and electrophilicity at each end can be evaluated using the frontier molecular orbitals, which can be obtained computationally. In general, the atom that carries the most significant orbital coefficient in the HOMO acts as the nucleophile, whereas that in the LUMO acts as the electrophile. The most nucleophilic atom is usually, but not consistently, the most electron-rich atom. In 1,3-dipolar cycloadditions, the identity of the dipole-dipolarophile pair determines whether the HOMO or the LUMO character of the 1,3-dipole will dominate

Dipolarophile



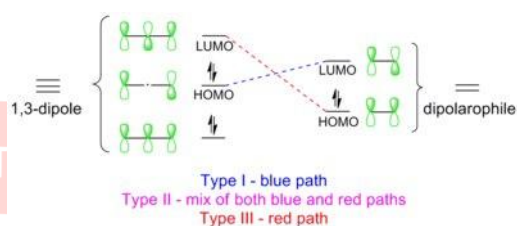
The most used dipolarophiles are alkenes and alkynes. Heteroatom-containing dipolarophiles such as carbonyls and imines can also undergo 1,3-dipolar cycloaddition. Other examples of dipolarophiles include fullerenes and nanotubes, which can undergo 1,3-dipolar cycloaddition with azomethine ylide in the Prato reaction.

Solvent effects 1,3-Dipolar cycloadditions experience minimal solvent effect because the reactants and the transition states are generally non-polar. For example, the reaction rate between phenyl diazomethane and ethyl acrylate or norbornene (see scheme below) changes slightly upon varying solvents from cyclohexane to methanol.

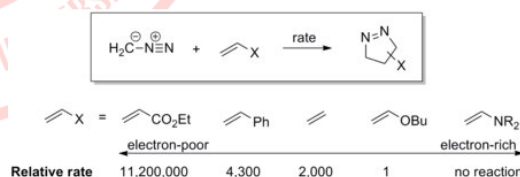
	Solvent	Ph ⁻ N ₂ + CH ₂ =CHCO ₂ Et	Ph ⁻ N ₂ + Norbornene
		relative k ₁	relative k ₂
non-polar	cyclohexane	1	1
	dioxane	1.48	0.82
	DMF	3.16	1.06
polar	methanol	5.34	0.98

The lack of solvent effects in 1,3-dipolar cycloaddition is demonstrated in the reaction between enamines and dimethyl diazomalonate (see scheme below). The polar reaction, N-cyclopentenyl pyrrolidine nucleophilic addition to the diazo compound, proceeds 1,500 times faster in polar DMSO than non-polar decalin. On the other hand, a close analog of this reaction, N-cyclohexenyl pyrrolidine 1,3-dipolar cycloaddition to dimethyl diazo malonate, is sped up only 41-fold in DMSO relative to decalin.

Frontier molecular orbital theory



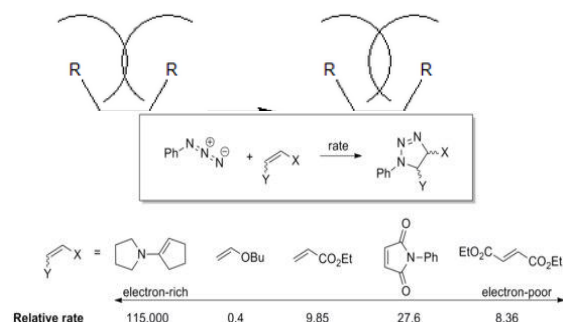
The Woodward-Hoffmann rules. In the Dewar-Zimmerman treatment, the reaction proceeds through a 5-center 1,3-Dipolar cycloaddition are pericyclic reactions, which obey the Dewar-Zimmerman rules and zero-node, 6-electron Hückel transition state for this particular molecular orbital diagram. However, each orbital can be randomly assigned a sign to arrive at the same result. In the Woodward-Hoffmann treatment, frontier molecular orbitals (FMO) of the 1,3-dipole and the dipolarophile overlap in the symmetry-allowed $\pi 4_s + \pi 2_s$ manner. Such orbital overlap can be achieved in types I, II,



and III. The dominant pathway is the one that possesses the smallest HOMO-LUMO energy gap.

Type I: The dipole has a high-lying HOMO, which overlaps with the LUMO of the dipolarophile. A dipole of this class is referred to as a **HOMO-controlled dipole** or a **nucleophilic dipole**, which includes azomethine ylide, carbonyl ylide, nitrite ylide, azomethine imine, carbonyl imine and diazoalkane. This type resembles the normal-electron-demand Diels-Alder reaction, in which the diene HOMO combines with the dienophile LUMO.

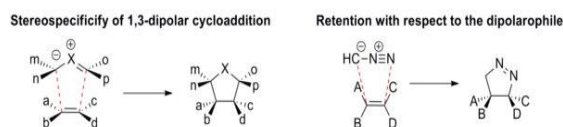
Type II: HOMO of the dipole can pair with LUMO of the dipolarophile; alternatively, HOMO of the dipolarophile can pair with LUMO of the dipole. This



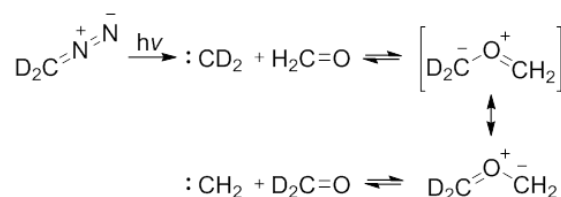
two-way interaction arises because the energy gap in either direction is similar. A dipole of this class is called a HOMO-LUMO-controlled dipole or an amphiphilic dipole, which includes nitrile imide, nitron, carbonyl oxide, nitrile oxide, and azide. For example, azides react with electron-rich and electron-poor dipolarophiles with similar reactivities (see reactivity scale below).

Type III: The dipole has a low-lying LUMO which overlaps with the HOMO of the dipolarophile (indicated by red dashed lines in the diagram). A dipole of this class is referred to as a **LUMO-controlled dipole** or an **electrophilic dipole**, which includes nitrous oxide and ozone. This type resembles the inverse electron-demand Diels-Alder reaction, in which the diene LUMO combines with the dienophile HOMO.

Isomerism of the dipolarophile affects the reaction rate due to sterics. *Trans*-isomers are more reactive (*trans*-stilbene will add diphenyl (nitrile imide) 27 times faster than *cis*-stilbene) because, during the reaction, the 120° bond angle shrinks to 109°, bringing eclipsing *cis*-substituents towards each other for increased steric clash. *Cis*-substituents on the dipolarophilic alkene end up *cis*, and *trans*-substituents end up *trans* in the resulting five-membered cyclic compound (see scheme below).



Synthetic applications: 1,3-dipolar cycloadditions are important ways to synthesize many important 5-membered heterocycles such as triazoles, furans, isoxazoles, pyrrolidines, etc.



Nitrile oxides: 1,3-dipolar cycloaddition with nitrile oxides is a widely used masked-aldol reaction. Cycloaddition between a nitrile oxide and an alkene yields the cyclic isoxazoline product, whereas the reaction with an alkyne yields the isoxazole. Both isoxazolines and isoxazoles can be cleaved by hydrogenation to reveal aldol-type β -hydroxycarbonyl or Claisen-type β -dicarbonyl products, respectively.

Carbonyl ylides: 1,3-dipolar cycloaddition reactions have emerged as powerful tools in synthesizing complex cyclic scaffolds and molecules for medicinal, biological, and mechanistic studies. Among them, [3+2] cycloaddition reactions involving carbonyl ylides have extensively been employed to generate oxygen-containing five-membered cyclic molecules.

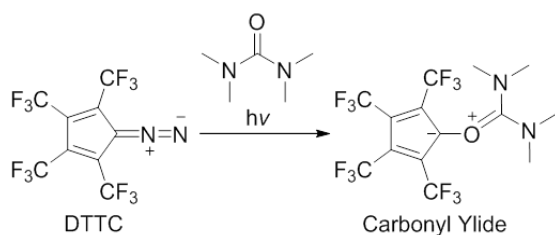
Preparation of carbonyl ylides for 1,3-dipolar cycloaddition reactions

Ylides are regarded as positively charged heteroatoms connected to negatively charged carbon atoms, which include ylides of sulfonium, thiocarbonyl, oxonium, nitrogen, and carbonyl. Several methods exist for generating carbonyl ylides, necessary intermediates for generating oxygen-containing five-membered ring structures, for [3+2] cycloaddition reactions.

Synthesis of carbonyl ylides from diazomethane derivatives by photocatalysis

One of the earliest examples of carbonyl ylide synthesis involves photocatalysis.

Photolysis of diazo-tetrakis (trifluoromethyl)cyclopentadiene (DTTC) in the presence of tetramethyl urea can generate the carbonyl ylide by an intermolecular nucleophilic attack and subsequent aromatization of the DTTC moiety.



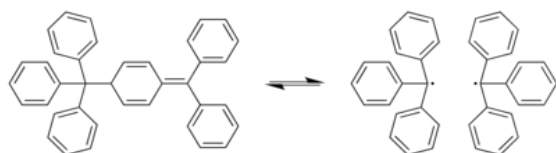
Stable carbonyl ylide dipoles can be used in [3+2] cycloaddition reactions with dipolarophiles.

Another early example of carbonyl ylide synthesis by photocatalysis, Dideuteriodiazomethane, was photolyzed in the presence of formaldehyde to generate the dideuterioformaldehyde carbonyl ylide.

Carbon-Carbon Bond Forming Reactions Processes

Chains and branching: Carbon is one of the few elements that can form long chains of its atoms, a property called catenation. This, coupled with the strength of the carbon-carbon bond, gives rise to an enormous number of molecular forms, many of which are important structural elements of life, so carbon compounds have their field of study: organic chemistry. Some examples of reactions that form carbon-carbon bonds are the aldol reaction, Diels-Alder reaction, Grignard reaction, cross-coupling reaction, the Michael reaction and the Wittig reaction.

Bond strengths and lengths: The carbon-carbon single bond is weaker than C-H, O-H, N-H, H-H, H-Cl, C-F, and many double or triple bonds and comparable in strength to C-O, Si-O, P-O, and S-H bonds but is commonly considered as strong. The values above represent C-C bond dissociation energies commonly encountered; occasionally, outliers may deviate drastically from this range.



Long, weak C-C single bonds

Various extreme cases have been identified where the C-C bond is elongated. In the even more congested molecule hexakis(3,5-di-*tert*-butylphenyl)ethane, the

bond dissociation energy to form the stabilized triarylmethyl radical is only 8 kcal/mol.

Twisted, weak C-C double bonds

The structure of tetrakis(dimethylamino)ethylene (TDAE) is highly distorted. The dihedral angle for the two N_2C ends is 28° , although the C=C distance is expected at 135 pm.

Short, strong C-C triple bonds

Conversely, the central carbon-carbon single bond of diacetylene is very strong at 160 kcal/mol, as the single bond joins two carbons of sp hybridization. Carbon-carbon multiple bonds are generally more substantial; the double bond of ethylene and triple bond of acetylene have been determined to have bond dissociation energies of 174 and 230 kcal/mol, respectively. Carbon-carbon bond-forming reactions are organic reactions forming a new carbon-carbon bond.

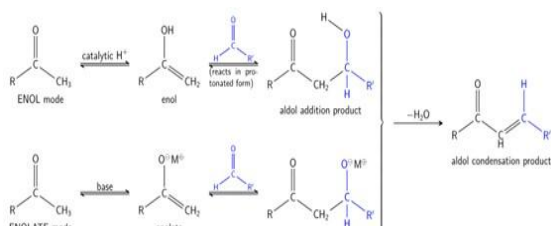
General Importance



Carbon-carbon (C-C) bond formation is foundational in organic synthesis, enabling the construction of complex molecules from simpler precursors. They are important in producing many man-made chemicals, such as pharmaceuticals and plastics. Some examples of reactions that form carbon-carbon bonds are aldol reactions, Diels-Alder reactions, adding a Grignard reagent to a carbonyl group, a Heck reaction, a Michael reaction, and a Wittig reaction.

Aldol reaction

An aldol is a molecule that is both an aldehyde and an alcohol (this is the reason for the name). It is a hydroxy ketone or aldehyde. The aldol reaction happens between two carbonyl compounds to form a new β -hydroxy carbonyl compound. The aldol reaction may proceed by two different mechanisms. Carbonyl compounds, such as aldehydes and ketones, can exist as enols or enolates.



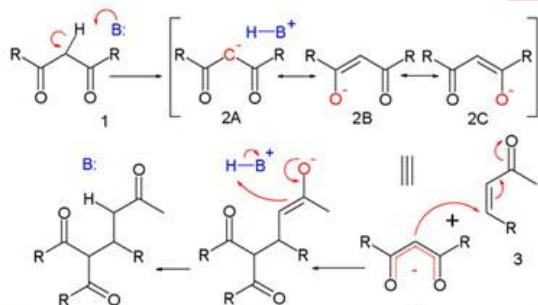
Enols are nucleophilic at the α -carbon, so they can attack carbonyls (when protonated). This is the 'enol mechanism'. Enolates form if a carbonyl is deprotonated. They are much more nucleophilic than enols or enol ethers and can attack electrophiles directly. The usual electrophile is an aldehyde since ketones are much less reactive. This is the 'enolate mechanism'.

Diels-Alder reaction

Diels-Alder reactions occur between a diene and a conjugated alkene. They are cycloadditions, chemical reactions in which two or more unsaturated molecules combine to form a cyclic adduct. In this process, bond multiplicity is reduced: from 3 double bonds, only one remains in the product. The others are spent to form a ring. Two sigma bonds are formed in one concerted step. Diels-Alder products can be easily recognized since six-membered rings constitute them with a double bond inside the ring and a conjugating group outside the ring on the opposite side of the double bond.

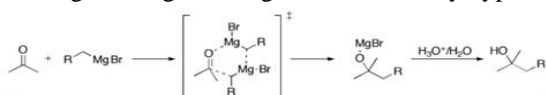
Addition of a Grignard reagent to a carbonyl group

In this reaction, an alkyl is added to a carbonyl, using a Grignard reagent in the transition state. Grignard reagents are compounds formed by the reaction of



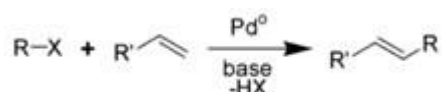
magnesium metal with alkyl or alkenyl halides. They are good nucleophiles and very strong bases.

The Grignard reagent (nucleophile) attacks the electrophilic carbon atom of a carbonyl group. Adding the Grignard reagent to the carbonyl typically

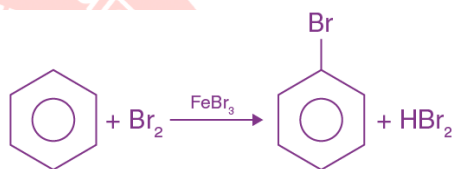


proceeds through a six-membered ring transition state. Organometallics are very powerful nucleophiles and can attack the carbonyl group to form alcohols. The reactions from Grignard organometallic reagents with carbonyl compounds are among the most important ways of making carbon-carbon bonds.

Heck reaction: The Heck reaction (also called the Mizoroki-Heck reaction) is a reaction where a substituted alkene is formed from an unsaturated halide (or triflate) and an alkene. The reaction needs



a catalyst, usually a palladium nanomaterial-based catalyst. It is a carbon-carbon bond-forming reaction of great importance, allowing one to do substitution reactions on planar sp^2 -hybridized carbon atoms.



Michael reaction

The Michael reaction or Michael addition is the nucleophilic addition of a carbanion or another nucleophile to an α , β -unsaturated carbonyl compound. This is one of the most valuable methods for forming C-C bonds. Many variants exist. In every Michael reaction, there are Michael donors, electron-withdrawing groups such as acyl and cyano, and a Michael acceptor, usually a ketone. R and R' substituents are Michael donors, making the methylene hydrogen acidic. Structures between parentheses are three resonance structures, two of which have enolate ions. This can react with the electrophilic alkene 3.

Wittig reaction

The Wittig reaction or Wittig olefination involves an aldehyde or ketone with a triphenyl phosphonium ylide (often called a Wittig reagent) to form an alkene and triphenylphosphine oxide.



This reaction is widely used to prepare alkenes.

Bromination Reaction

Bromination is a chemical reaction involving the reaction of a compound, and bromine results in adding bromine to the compound. The product formed after bromination will exhibit new properties from the initial reactant.

Types of Bromination

Bromination can occur in different ways, depending on the reactant. 1-A saturated compound undergoes bromination via a free radical mechanism. 2-An unsaturated hydrocarbon undergoes bromination via an addition reaction. 3-An aromatic compound undergoes bromination via an electrophilic substitution mechanism.

We will now briefly discuss types of bromination in detail.

Bromination via a Free Radical Mechanism

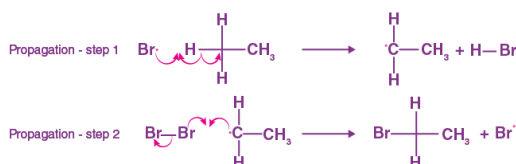
This type of reaction occurs in the saturated compound. The mechanism for the reaction takes place in the following steps.

Initiation Step

The Br-Br bond of elemental bromine undergoes homolytic fission when irradiated under UV rays, yielding two bromine radicals.

Propagation Step

A bromine radical abstracts a hydrogen atom from ethane to produce the ethyl radical. In turn, the ethyl radical abstracts a bromine atom from a bromine molecule, forming bromoethane. The second step also regenerates a bromine atom. These steps repeat many times until termination occurs.



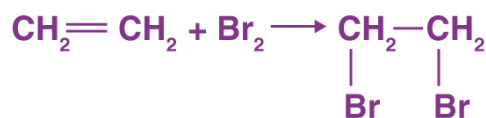
Termination Step

Termination takes place when A bromine atom reacts with another bromine atom to generate Br₂. A bromine atom reacts with ethyl radical to form

bromoethane. Two ethyl radicals can also combine to produce butane.

Bromination via an Addition Reaction

This type of reaction occurs in the unsaturated compound. Bromination in unsaturated compounds proceeds through a bromonium ion intermediate.



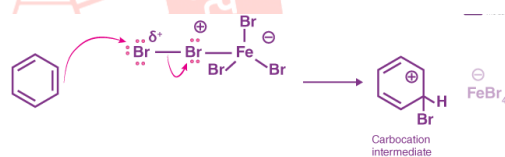
© By

This reaction is also used to check unsaturation.

Bromination via an Electrophilic Substitution Mechanism

Benzene reacts with bromine in Lewis acid-like FeBr₃ to form aryl bromide. This reaction is known as the bromination of benzene.

Activation of Bromine by Lewis Acid



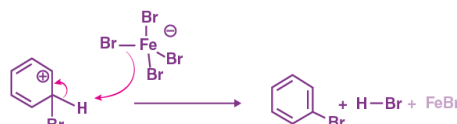
Bromine reacts with Lewis acid FeBr₃ to form a complex that makes the bromine more electrophilic.

Attack of Benzene

Benzene, being electron-rich, attacks electrophilic bromine. This step produces a cyclohexadienyl cation intermediate, destroying the aromaticity of benzene.

Deprotonation to generate Aromatic Ring

Proton is removed from sp³ Carbon bearing a Bromo group. Aromaticity is retained.



Importance of Bromination: Bromination is used in many chemical industries as a suitable building block for numerous syntheses. Bromination is used in agriculture, pharmaceuticals, and chemical intermediates.

Radical Bromination: Preferred for alkanes or allylic positions.

Mechanism:

Initiation: Homolytic cleavage of Br_2 using heat or UV light.

Propagation: Hydrogen abstraction and bromine addition.

Termination: Radical recombination.

Highly selective for the most stable radical (e.g., tertiary radicals).

Anti-Addition Bromination

Typical for alkenes and alkynes.

Mechanism:

Formation of a bromonium ion intermediate.

Nucleophilic attack of bromide ion from the opposite side.

Product: Vicinal dibromides (anti-configuration).

Applications

Synthesis of brominated intermediates for further functionalization. Selective halogenation in retrosynthetic strategies. Preparation of flame retardants, pharmaceuticals, and agrochemicals.

Regioselectivity and Stereoselectivity

Regioselectivity: Controlled by substituents or the stability of intermediates (e.g., radical stability in free radical bromination).

Stereoselectivity: Anti-addition in alkenes and alkynes ensures defined stereochemical outcomes.

Reagents

Br_2 : Standard brominating agent for most reactions.

N-Bromo succinimide (NBS): Used for allylic or benzylic bromination.

Pyridinium Tribromide: A mild brominating agent.

Environmental and Safety Concerns

Bromine and brominated by-products can be hazardous.

Proper disposal and use of alternative green reagents (e.g., NBS) are encouraged.

Role of Supercritical Carbon Dioxide (scCO_2) in Green Chemistry

Supercritical carbon dioxide (scCO_2) is a substance that exhibits unique properties when carbon dioxide is heated and pressurized above its critical temperature (31.1°C) and pressure (73.8 bar). In this state, scCO_2 behaves as both a gas and a liquid, which makes it a versatile medium for various applications in green chemistry. Its role can be summarized as follows:

1. Environmentally Friendly Solvent

Non-toxic and Non-flammable: scCO_2 is a safer alternative to traditional organic solvents, which are often volatile, toxic, and flammable.

Low Environmental Impact: Carbon dioxide is abundant, inexpensive, and often sourced as a byproduct of industrial processes, minimizing its carbon footprint. Environmentally beneficial, low-cost substitutes for rigid thermoplastic and fired ceramic use scCO_2 as a chemical reagent. The scCO_2 in these processes is reacted with the alkaline components of fully hardened hydraulic cement or gypsum plaster to form various carbonates. The primary byproduct is water.

Solubility: scCO_2 can dissolve non-polar and some polar substances, making it a flexible medium for various reactions and separations. Supercritical carbon dioxide is used as the extraction solvent to create essential oils and other herbal distillates. Its main advantages over solvents such as hexane and acetone in this process are that it is non-flammable and does not leave toxic residue.

2. Replacement for Volatile Organic Compounds (VOCs)

Minimizing Pollution: By replacing VOCs in industrial applications, scCO_2 helps reduce air pollution and the associated health hazards.

Regulatory Compliance: Its use can help industries comply with strict environmental regulations concerning solvent emissions.

3. Applications in Extraction Processes

Food and Pharmaceuticals: scCO₂ is widely used to extract bioactive compounds, such as caffeine (decaffeination of coffee and tea), essential oils, and nutraceuticals.

scCO₂ is forced through green coffee beans sprayed with water at high pressure to remove the caffeine. The caffeine can then be isolated for resale (e.g., to pharmaceutical or beverage manufacturers) by passing the water through an activated charcoal filter or by distillation, crystallization, or reverse osmosis.

Supercritical CO₂ is an alternative for thermal sterilization of biological materials and medical devices with a combination of the additive peracetic acid (PAA). Supercritical CO₂ does not sterilize the media because it does not kill the spores of microorganisms. Moreover, this process is gentle, as the inactivated microbes' morphology, ultrastructure, and protein profiles are preserved.

Selective Extraction: Its tunable solvating properties allow selective extraction of target compounds, enhancing efficiency and reducing waste. In laboratories, scCO₂ is used as an extraction solvent, for example, for determining total recoverable hydrocarbons from soils, sediments, fly ash, and other media and for determining polycyclic aromatic hydrocarbons in soil and solid wastes. Supercritical fluid extraction has been used to determine hydrocarbon components in water.

4. Reaction Medium for Green Synthesis

Catalysis: scCO₂ often enhances reaction rates and selectivity in catalytic processes. It acts as a medium for homogeneous and heterogeneous catalysis.

Reduced Side Reactions: Its unique properties can suppress undesired side reactions.

Applications: Synthesis of polymers, organic reactions (e.g., hydrogenation, oxidation), and pharmaceutical intermediates.

5. Polymer Processing

Foaming Agent: scCO₂ is used as a blowing agent in polymer foaming processes, eliminating the need for harmful chemical foaming agents. Supercritical carbon dioxide can saturate the polymer with solvent. The carbon dioxide rapidly expands upon depressurization and heating, causing voids within the polymer matrix, i.e., creating a foam.

Plasticization: It can temporarily plasticize polymers, aiding in their processing and reducing the use of toxic additives.

6. Carbon Capture and Utilization

Sequestration: scCO₂ can capture and sequester carbon dioxide from industrial emissions, turning it into a helpful resource.

Chemical Feedstock: It is used as a raw material in processes that convert CO₂ into valuable chemicals and fuels.

7. Energy Efficiency

Mild Conditions: Many processes using scCO₂ can operate at relatively mild temperatures, reducing energy consumption.

Reuse and Recycling: scCO₂ can be easily recycled in a closed-loop system, minimizing waste and operational costs.

8. Waste Minimization

Clean Processing: scCO₂-based methods generate minimal hazardous waste, contributing to cleaner production. Supercritical carbon dioxide can be used as a solvent in dry cleaning.

Degradable Products: Residual CO₂ from processes efficiently dissipates, unlike persistent solvents.

9. Applications in Analytical Chemistry

Chromatography: scCO₂ is employed in supercritical fluid chromatography (SFC) for high-resolution and rapid separation of complex mixtures.

Purity Analysis: Its inert nature makes it ideal for handling sensitive analytes without degradation.

10. Limitations and Challenges

High Initial Costs: Equipment and infrastructure for handling scCO₂ require significant investment.

Pressure Requirements: The need for high-pressure systems can pose safety and operational challenges.

Solubility Constraints: While scCO₂ is versatile, it may not dissolve all types of compounds efficiently.

Ethyl Lactate: A Renewable Green Solvent

Ethyl lactate, an ester of lactic acid and ethanol, is a biodegradable, environmentally friendly solvent derived from renewable resources such as corn or sugarcane. Favorable properties and diverse applications make it an important compound in green chemistry.

Properties of Ethyl Lactate

Chemical Structure:

Formula: $C_5H_{10}O_3$, Molar Mass: 118.13 g/mol, IUPAC Name: Ethyl 2-hydroxy-propanoate

1-Physical Properties:

Appearance: Colorless liquid with a mild, sweet odor. Density: $\sim 1.03 \text{ g/cm}^3$ at 20°C ., Boiling Point: $\sim 154^\circ\text{C}$., Flash Point: $\sim 46^\circ\text{C}$ (closed cup)., Miscibility: Soluble in water and most organic solvents.

2-Chemical Properties:

Biodegradability: Readily breaks down into lactic acid and ethanol in the environment. Non-toxic: Considered safe compared to traditional organic solvents. Stability: Stable under standard conditions but hydrolyzes in the presence of strong acids or bases.

3-Environmental Profile:

Air pollution: Traditional solvents are quite volatile and pose significant air pollution risk, mainly since most are used under reflux conditions. In contrast, the volatility of ethyl lactate is comparatively much lower, and since it is used under ambient conditions, it has less chance of escaping into the atmosphere, thereby decreasing the risk of air pollution.

Low Volatile Organic Compound (VOC) content.

Renewable Source: Produced from fermentation processes.

Feedstock type: Many traditional solvents originate from petrochemical (nonrenewable) resources (toluene, benzene). Ethyl lactate is a renewable feedstock.

Human toxicity: Traditional solvents (toluene, benzene, dichloromethane, ethanol, methanol) used for imine synthesis are known or suspected to be carcinogenic, mutagenic, and/or teratogenic according to their MSDS (Material Safety Data

Sheet) information. In contrast, ethyl lactate is benign enough to be approved by the FDA as a food additive. Since it is used in lower volume under ambient conditions, it poses a minimal inhalation hazard.

No ozone depletion or global warming potential.

Applications of Ethyl Lactate

Industrial Applications:

Cleaning Agents: These are used in electronics, optics, and precision instruments due to their high solvency and low residue.

Degreasing: Removes oils, greases, and other contaminants effectively.

Paints and Coatings: A solvent in formulations for lacquers, varnishes, and inks.

Pharmaceutical and Cosmetic Industry:

Drug Delivery: Acts as a solvent for active pharmaceutical ingredients (APIs).

Personal Care: Used in creams, lotions, and fragrances as a solvent or stabilizer.

Food Industry:

Food-Grade Solvent: Employed for flavor extraction and decaffeination processes.

Biotechnology and Green Chemistry:

Reaction Medium: Used in enzymatic reactions and biocatalysis, especially in processes requiring a low-toxicity environment.

Alternative to Halogenated Solvents: Replaces harmful solvents in synthesis and extraction processes.

Environmental Cleanup:

Oil Spills and Soil Remediation: Helps dissolve hydrocarbons for easier removal.

Printing Industry:

Ink Solvent: Offers superior solvency for resins and dyes in printing inks.

Advantages of Ethyl Lactate: Eco-Friendly: Derived from renewable resources and fully biodegradable.

Non-toxic: Safer for human health and the environment than traditional solvents like acetone or toluene. Most traditional solvents (toluene, benzene, ethanol, methanol) are highly flammable. While ethyl lactate is also quite flammable, it is generally used in much lower quantities and never heated during reactions, thus minimizing the potential for fires or explosions.

High Solvency Power: Dissolves a wide range of polar and non-polar substances.

Versatility: Compatible with many industries due to its diverse chemical and physical properties.

Limitations

Hydrolysis Sensitivity: Susceptible to breakdown in the presence of moisture, limiting some applications.

Cost: Slightly more expensive than conventional solvents, though its environmental benefits offset this.

UNIT-V

Synthesis of Nanomaterials:

Greener Synthesis of Nanomaterials

Nanomaterial synthesis can be subdivided into two main categories: traditional methods and green methods. Green synthesis employs a clean, safe, cost-effective, and environmentally friendly process of constructing nanomaterials. Microorganisms such as bacteria, yeast, fungi, algal species, and certain plants act as substrates for the green synthesis of nanomaterials. The part of the green species utilized in synthesizing nanomaterials often consists of specific enzymes, amino acid groups, proteins, or chemical structures. Synthesis of nanomaterials via environmentally friendly approaches aims to minimize the use of hazardous substances, reduce energy consumption, and lower manufacturing processes' environmental footprint. This approach aligns with the principles of green chemistry and sustainable development.

Two approaches can be used to generate nanoparticles

“Top-down” approach: In which nanoparticles are produced using physical techniques such as grinding or abrasion of a material.

“Bottom-up” approach: Where nanoparticles are generated from “building blocks” of atoms or molecules, resulting in more complex assemblies. Three alternatives are identified using this approach.

1-Chemical synthesis: Producing molecules or particles by reacting to substances used as raw materials.

2-Self-assembly: A technique in which atoms or molecules self-order through physical and/or chemical interactions.

3-Positional assembly: The atoms, molecules, and aggregates are deliberately manipulated and positioned individually. However, this method is highly laborious and unsuitable for industrial applications.

The “bottom-up” approach is preferred over the “top-down” approach because specialized equipment is not required, and the time to obtain nanoparticles is shorter. Using plant species, algae, or microorganisms such as bacteria or fungi is one of the most used resources for this procedure. Various compounds from plants or microorganisms, including terpenes, polyphenols, alkaloids, carbohydrates, proteins, and genetic materials, play an important role in the synthesis of nanoparticles by acting together.

In addition to the biological resources used to perform the synthesis (plants, algae, or microorganisms), other factors influence the shape and size of nanoparticles, such as the concentration of the metal ion, pH, reaction time, and temperature. In general, the phases for the green synthesis of nanoparticles include. Initial phase: Obtaining the reaction medium, the aqueous extract of one or several parts of the plant species, or the culture media for the growth of microorganisms, in addition to the precursor salt, the source of metal ions. Activation phase: Chemical reduction of metal ions and generation of nucleation centers occur where nanoparticles emerge and grow. Growth phase: Small adjacent nanoparticles spontaneously fuse into larger particles, forming aggregates, which are influenced by temperature, concentration, type of compounds, pH, and reaction time. Termination phase: The final shape of the nanoparticles is determined, and the compounds that participate in the reaction help stabilize and enhance their properties.

Biological resources for the green synthesis of nanoparticles:

Synthesis Numerous nanoparticle synthesis techniques have been developed; however, these may involve toxic compounds and high-energy physical processes. An alternative is the use of biological methods to circumvent these obstacles. Bacteria, fungi, algae, and plant species are some of the most used biological resources for the nanoparticles. Biological resources and compounds used for the green synthesis of nanoparticles and some of their applications

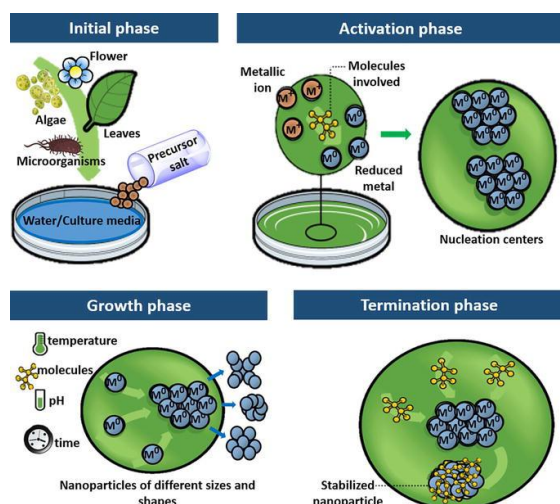
Bacteria: Nanoparticle synthesis using bacteria is performed both extracellularly and intracellularly.

Intracellular: The synthesis is carried out inside the living microorganism, using its growth conditions to favor synthesis, known as “nanoparticle micro-factories.” To recover nanoparticles, bacteria must be destroyed.

Extracellular: The components released by the bacteria after lysis are used. The synthesis is performed by adding a metal salt precursor to the medium in which these components are located. Extracellular synthesis has the advantage of being faster because it does not require additional steps to recover nanoparticles from microorganisms.

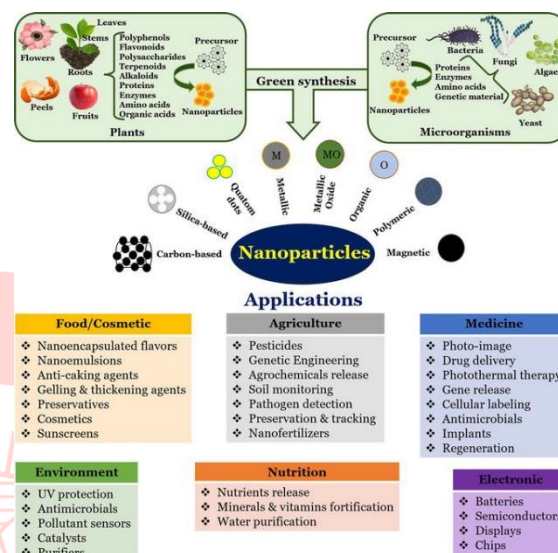
Enzymes, such as reductases, which catalyze the reduction of metal ions into nanoparticles, participate in the synthesis. Even components of the genetic material participate in this process.

Fungi: Fungi contain active biomolecules, such as proteins or enzymes, that participate in nanoparticle synthesis, improving their yields and stability. For



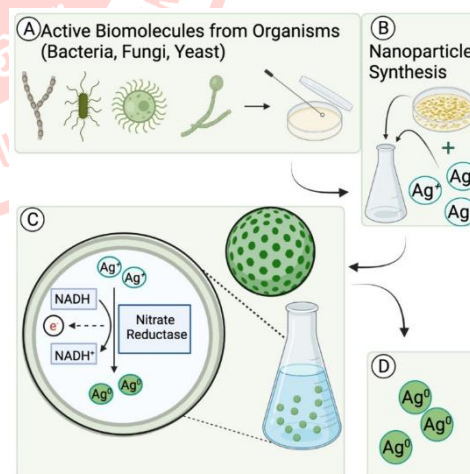
example, glutamic and aspartic acids on the surface of yeast or the reductase enzyme in the cytosol of fungi reduce metal ions to form nanoparticles.

Algae: Algae are used in nanotechnology because of their low toxicity and ability to bioaccumulate and reduce metal compounds such as polysaccharides, proteins, and pigments that direct the reduction of metal ions and coat the newly formed nanoparticles.



Plant species

Plants are one of the most widely used methods for nanoparticle synthesis because of their environmentally friendly nature, as they avoid using



toxic or harmful substances.

Plants contain several compounds (terpenes, flavonoids, polyphenols, alkaloids, proteins, etc.) that reduce metal ions and stabilize the resulting nanoparticles. This type of synthesis can be performed using intracellular, extracellular, and phytochemical-mediated methods.

Intracellular: The synthesis is carried out inside the plant cell, and the nanoparticles are recovered by breaking down the structure, which is very similar to the intracellular method using microorganisms. Control of the growth factors of plant species is required so that they do not interfere with synthesis.

Extracellular: This method is the most used because of its ease and speed. The process begins by obtaining a plant extract, which is generally water-based, to which a metal salt precursor is added.

Phytochemically mediated: This is based on the extracellular method, but with the difference that isolated phytochemical compounds are used, and other substances are added to stabilize the nanoparticles.

Factors involved in the green synthesis of nanoparticles

Temperature: This is one of the most influential factors, as the shape (spherical, prismatic, flakes, triangular, octahedral, etc.), size, and synthesis depend on temperature. Different temperatures promote different reactant interactions, giving rise to various shapes. The more significant the temperature increase, the larger the size of the nanoparticles will be.

pH: This influences the nucleation centers, generating more centers at higher pH values. Another important influence of pH is that some nanoparticles can only be synthesized in acidic or alkaline media.

Time: This parameter plays an important role in defining the size of the nanoparticles. It has been observed that longer reaction times favor an increase in the size of the nanoparticles and higher yields.

The mechanism involved in the green synthesis of nanoparticles

The plant extract or organism used for the synthesis is an important factor that influences the morphology and size of nanoparticles because different concentrations of metabolites or cellular components give rise to differences in the nanoparticles.

Proteins and enzymes facilitate the formation of nanoparticles from metal ions. Because of their high reducing activity, proteins and enzymes can attract metal ions to specific regions of a molecule responsible for reduction, facilitating the formation

of nanoparticles; however, their chelating activity is not excessive.

The amino acids of a protein can significantly influence the size, morphology, and quantity of nanoparticles generated, thus playing a significant role in determining their shape and yield.

The mechanism of green synthesis of nanoparticles has been associated with the action of polyphenols, which act as ligands. Metal ions form coordination compounds, in which the fundamental structural unit is the central metal ion surrounded by coordinated groups arranged spatially at the corners of a regular tetrahedron. The aromatic hydroxyl groups in polyphenols bind to metal ions and form stable coordinated complexes. This system undergoes direct decomposition at high temperatures, releasing nanoparticles from the complex system. Flavonoids, amino acids, proteins, terpenoids, tannins, and reducing sugars have hydroxyl groups surrounding the metal ions to form complexes. After this process, the hydroxyl ions are oxidized to carbonyl groups, stabilizing the nanoparticles. Synthesis is favored if the participating molecules have at least two hydroxyl groups at the ortho- and para-positions. Flavonoids, amino acids, proteins, terpenoids, tannins, and reducing sugars have hydroxyl groups surrounding the metal ions to form complexes. After this process, the hydroxyl ions are oxidized to carbonyl groups, stabilizing the nanoparticles. Synthesis is favored if the participating molecules have at least two hydroxyl groups at the ortho- and para-positions. Amino acids influence the size, morphology, and yield of nanoparticles generated, depending on the specific amino acids present in the extract and their concentration, along with the reaction conditions that give rise to nanoparticles with different shapes.

Advantages of Greener Synthesis

Nanoparticles have many potential benefits for the environment. For example, nanoparticles can be used to improve the efficiency of water treatment, air filtration, and soil remediation, reduce pollution, and develop new types of renewable energy technologies. In medicine, nanoparticles have shown potential for drug delivery, imaging, and cancer therapy.

Challenges and Limitations

Scalability: Transitioning from lab-scale to industrial-scale production can be difficult.

Reproducibility: Biological methods may show variability due to changes in biomass composition.

Purity and Yield: Ensuring high purity and adequate yield remains a challenge.

Optimization: Balancing green synthesis principles with nanoparticles' desired physical and chemical properties.

Applications of Green-Synthesized Nanomaterials

Medicine: Drug delivery systems. Antimicrobial agents.

Environmental Remediation:

Water purification and pollutant removal. Catalysts for degradation of organic contaminants.

Energy:

Green batteries and solar cells.

Agriculture:

Nano-fertilizers and pesticides for sustainable farming.

Magnetic Nanoparticles:

Magnetic nanoparticles are a class of nanoparticles that can be manipulated using magnetic fields. Such particles commonly consist of two components, typically composed of magnetic materials such as **iron oxide (Fe_3O_4 or $\gamma\text{-Fe}_2\text{O}_3$)**, cobalt, nickel, or their alloys and a chemical component that has functionality, frequently with (bio) catalytic or biorecognition properties. Magnetic nanoparticles have been the focus of much research recently because they possess attractive properties that could see potential use in catalysis, including nanomaterial-based catalysts, biomedicine, tissue-specific targeting, magnetically tunable colloidal photonic crystals, microfluidics, magnetic resonance imaging, magnetic particle imaging, data storage, environmental remediation, nanofluids, optical filters, defect sensor, magnetic cooling, and cation sensors. The physical and chemical properties of magnetic nanoparticles largely depend on the synthesis method and chemical structure. In most cases, the particles range from 1 to 100 nm in size and may display superparamagnetism.

A **core**: Magnetic material providing magnetic properties.

A **coating or shell**: Stabilizes the particle, prevents agglomeration, and can provide functional groups for specific applications (e.g., silica, polymers, or surfactants).

2. Magnetic Properties:

Iron, cobalt, nickel, silver, and gold are some examples of standard magnetic nanoparticles. Metallic oxide nanoparticles primarily include iron oxides ($\gamma\text{-Fe}_2\text{O}_3$ and Fe_3O_4) and ferrites (CoFe_2O_4 and $\text{MnO.6ZnO.4Fe}_2\text{O}_4$), while FeCo , FePt, and others fall under metallic alloy nanoparticles. Among these, the most widely used magnetic nanoparticles are metal oxide Fe_2O_3 and Fe_3O_4 magnetic nanoparticles. To fabricate a variety of ferrite nanoparticles ($\text{Mn}_3\text{Zn}_7\text{Fe}_2\text{O}_4$, $\text{MnO.6ZnO.4Fe}_2\text{O}_4$, and others). Some metal elements, such as zinc (Zn) and manganese (Mn), might be added to the nanoscale structure of iron oxide. Hence, they are used in magnetic resonance imaging (MRI)

Superparamagnetism: The particles lose their magnetism when removing the external magnetic field, preventing agglomeration. High coercivity and saturation magnetization depend on size, shape, and material. They can also be used as a vector after surface functionalization in chemotherapy and colon cancer.

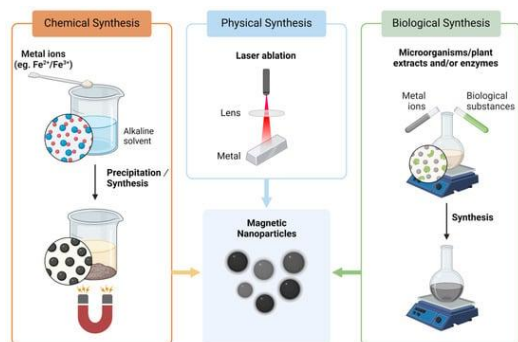
Magnetocaloric Effect:

Some magnetic materials heat up when placed in a magnetic field and cool down when removed from a magnetic field, defined as the magnetocaloric effect (MCE). Magnetic nanoparticles provide a promising alternative to conventional bulk materials because of their particle size-dependent superparamagnetic features.

Synthesis Techniques

The methods encompassed in this study are ball milling, laser ablation, other physical techniques, coprecipitation, thermal decomposition, hydrothermal synthesis, microemulsion, and the sol-gel technique. Other non-thermal and biological synthesis methods are also mentioned. Each of methods

possesses distinct mechanisms and circumstances for generating MNPs, customized to meet certain requirements and applications.



Methods of Synthesis

1-Co-precipitation:

Principle: Co-precipitation involves the simultaneous precipitation of Fe²⁺ and Fe³⁺ salts in an alkaline medium.

Procedure:

Dissolve iron salts (e.g., FeCl₂ and FeCl₃) in water. Add a strong base (e.g., NH₄OH or NaOH) under an inert atmosphere (to prevent oxidation). Stir the solution at elevated temperatures (~80°C). Separate the black precipitate (magnetite, Fe₃O₄) using a magnet and wash it with deionized water.

Advantages: Simple, cost-effective, scalable.

Limitations: Limited control over size and shape.

2-Thermal Decomposition:

Principle: High-temperature decomposition of organometallic precursors in the presence of surfactants.

Procedure:

Use iron precursors like iron acetylacetonate (Fe(acac)₃) and dissolve in organic solvents (e.g., octadecene). Add surfactants (e.g., oleic acid, oleylamine) to stabilize nanoparticles. Heat the mixture to temperatures (200–300°C) under an inert atmosphere.

Advantages: Produces monodisperse particles.

Limitations: Requires expensive precursors and surfactants.

3-Hydrothermal/Solvothermal Method:

Principle: High-pressure and high-temperature synthesis in a sealed autoclave.

Procedure:

Dissolve iron salts in water (hydrothermal) or organic solvents (solvothermal). Seal the mixture in an autoclave and heat to 150–300°C for several hours.

Advantages: High crystallinity and uniform size distribution.

Limitations: Long reaction times.

4-Microemulsion Method:

Principle: Synthesis occurs within water-in-oil microemulsion droplets.

Procedure:

Prepare a microemulsion system using surfactants, oil, and water. Add iron salts to the aqueous phase and precipitate MNPs using a base.

Advantages: Good control over particle size.

Limitations: Low yield and scalability issues.

5-Sol-Gel Method:

Precursor materials undergo hydrolysis and condensation to form MNPs. Offers control over morphology but requires precise process control.

Functionalization of Magnetic Nanoparticles

Objectives of Functionalization

1. Enhance stability in aqueous and biological environments.
2. Prevent agglomeration through surface coating.
3. Add specific functionalities for targeted applications (e.g., biocompatibility, drug conjugation).

Strategies for Functionalization

Polymer Coating:

Use polymers like polyethylene glycol (PEG), polyvinyl alcohol (PVA), or chitosan. Benefits: Improved hydrophilicity, biocompatibility, and prolonged circulation time in vivo.

Silica Coating:

Coat MNPs with a silica shell using precursors like tetraethyl orthosilicate (TEOS) in a sol-gel process. Benefits: Chemically inert surface, easy functionalization with biomolecules or dyes.

Organic Ligand Functionalization:

Use surfactants (e.g., oleic acid) or small molecules (e.g., dopamine). Benefits: Provides a reactive surface for further modification.

Biomolecule Conjugation:

Attach biomolecules like antibodies, peptides, or DNA using covalent coupling or affinity interactions.

Inorganic Shells:

Coat MNPs with gold or other metals. Benefits: Enhances chemical stability and enables plasmonic properties.

Parameters Affecting MNP Synthesis and Functionalization

Reaction Parameters:

Precursor concentration, temperature, pH, and reaction time affect size and magnetic properties.

Surface Chemistry:

Functional groups, on the surface, dictate the interaction of MNPs with their environment.

Magnetic Properties:

Superparamagnetic behavior is ideal for many biomedical applications.

5. Characterization Techniques

Structural Analysis:

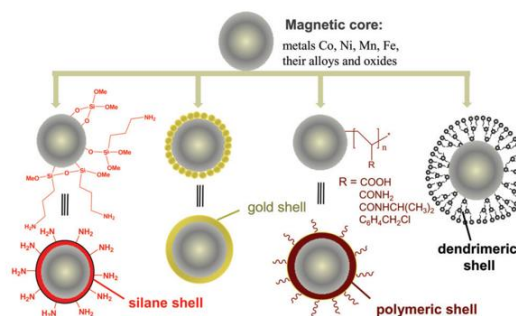
X-ray diffraction (XRD) for crystal structure. Transmission electron microscopy (TEM) for size and morphology.

Magnetic Properties:

Vibrating sample magnetometry (VSM) or superconducting quantum interference device (SQUID).

Surface Chemistry:

Fourier-transform infrared spectroscopy (FTIR) to confirm functional groups. X-ray photoelectron spectroscopy (XPS) for elemental analysis.



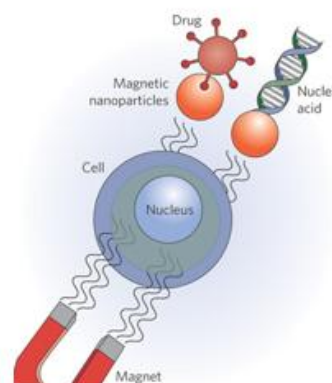
Hydrodynamic Size and Stability:

Dynamic light scattering (DLS) for particle size in solution. Zeta potential for surface charge.

5. Applications

Biomedical Applications

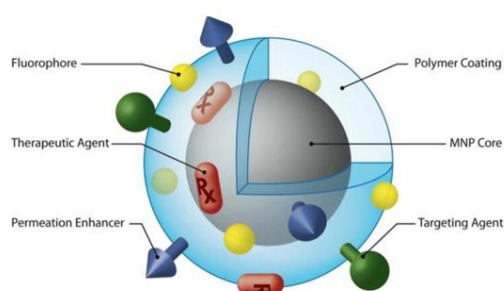
1- Magnetic separation: the biological molecules are labeled by magnetic nanoparticle colloids and then subjected to separation by an external magnetic field, which may be applied for cell isolation, protein purification, RNA/DNA extraction, and immunoprecipitation. Magnetic nanoparticle particles such as beads have been extensively used to separate and purify cells and biomolecules due to their small size, promising separation mood, and



good dispersibility. One of the trends in this subject area is magnetic separation, which uses antibodies conjugated with beads to provide highly accurate

antibodies that can specifically bind to their matching antigens on the surface of the targeted sites.

2-Hyperthermia Therapy: In addition, the large surface area in magnetic nanoparticles has the potential to provide better heat exchange with the surrounding environment. By carefully designing core-shell structures, it would be possible to control the heat exchange between the magnetic nanoparticles and the surrounding matrix, which provides a way to improve therapy technologies, such as hyperthermia.



3. Diagnostics

Non-invasive imaging methods have been developed by labeling stem cells using magnetic nanoparticles. Among them, Magnetic Resonance Imaging (MRI) is widely used as a diagnostic tool to present a high spatial resolution and great anatomical detail to visualize the structure and function of tissues. Several kinds of magnetic nanoparticles have been developed to improve contrast agents in MRI imaging, with significant benefits of improved sensitivity, good biocompatibility, and ready detection at moderate concentrations.

4. Sensors

Many magnetic nanoparticle-based biosensors have been surface functionalized to recognize specific molecular targets due to their unique magnetic properties not found in biological systems. Due to their different compositions, sizes, and magnetic properties, magnetic nanoparticles can be used in a variety of instruments and formats for biosensing, enhancing sensitivity and stability.

5. Drug delivery

Magnetic nanoparticles have been developed and applied in localized drug delivery to tumors. The magnetic nanoparticles first act as a carrier of the drug, which are attached to its outer surface or dissolve in the coating. Once the drug-coated

particles have been introduced into the patient's bloodstream, a strong permanent magnet creates a magnetic field gradient to retain the particles at the targeted region. Moreover, magnetic nanoparticles coated with a drug could be injected intravenously, transported, and retained at targeted sites, which makes them a highly promising system for drug delivery.

5. Therapy

Magnetic nanoparticles have been explored as a technique for targeted therapeutic heating of tumors, called hyperthermia. Various superparamagnetic nanoparticles with different coatings and targeting agents are used for specific tumor sites. Magnetic particle heating can be accomplished at depths necessary to treat tumors virtually anywhere in the human body. In addition, magnetic nanoparticle hyperthermia can also be used as an adjuvant to conventional chemotherapy and radiation therapy, which shows great potential.

Environmental Remediation: Removal of heavy metals and pollutants from water. Oil spill cleanup.

Energy and Catalysis: Catalysts for chemical reactions. Components in energy storage systems.

Data Storage: Used in magnetic recording media due to high coercivity.

Analytical Chemistry: Magnetic separation techniques for purification.

Microwave-Assisted Nanocatalysis in Water:

In recent years, more and more attention has been focused on advanced catalytic oxidation technology. It utilizes electricity, light, ultrasound, etc., to induce catalysts and/or oxidants to produce free radicals with high oxidizing activity, such as hydroxyl radicals ($\text{OH}\cdot$), superoxide anion radicals ($\text{O}_2^{\cdot-}$), and sulfate radicals ($\text{SO}_4^{\cdot-}$). These free radicals can produce extensive destruction of the covalent bonds in refractory contaminants and can repeatedly cycle or react with the parent and intermediate substrates, leading to extensive degradation or mineralization of contaminants. Generally, advanced catalytic oxidation methods have made remarkable progress in wastewater treatment. In actual wastewater treatment processes, however, the requirements for reaction conditions are relatively high, and the investment and operation costs are very prominent. Thus, researchers

have started to explore and study better catalytic technology, such as introducing superior heating methods. Studies have shown that applying microwave (MW) technology could solve this problem.

Compared to traditional wastewater treatment methods mentioned above, MW-assisted catalytic technology can avoid the problems of sludge bulking, high capital expenditure, difficult disposal of surplus sludge, secondary pollution, membrane fouling, etc. Besides, the advantages of fast processing speed, complete degradation, low infrastructure, operating costs, etc., emerge naturally due to the MW effect and advanced catalytic oxidation combination. Thus, MW-assisted catalytic technology may show a superior development prospect in wastewater treatment compared with other advanced catalysts.

1. Introduction to Nanocatalysis: Nanocatalysis involves using nanoparticles (NPs) as catalysts to enhance chemical reactions. Their high surface area-to-volume ratio, tunable surface properties, and quantum effects make them highly efficient compared to traditional bulk catalysts.

2. Role of Microwaves (MW) in Catalysis: Microwaves provide energy to chemical reactions via electromagnetic radiation (frequency range: 300 MHz to 300 GHz). Their use in nanocatalysis introduces several advantages:

Selective Heating: Direct interaction with polar molecules or ionic species.

Rapid Heating: Reduces reaction times significantly compared to conventional methods.

Non-uniform heating ("Hot Spots"): Generates localized regions of high temperature, enhancing reaction rates.

Green Chemistry Alignment: Often reduces the need for harsh reagents or solvents. Water is an ideal solvent for MW-assisted nanocatalysis due to its high dielectric constant and ability to absorb microwave radiation efficiently. Additional benefits include:

Sustainability: Water is a green, non-toxic, and abundant solvent. **Polar Nature:** Promotes solubility of ionic species and interacts effectively with MWs.

Facilitates Biomimetic Reactions: Mimics natural enzymatic processes.

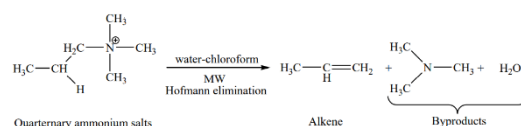
4. Mechanism of MW-Assisted Nanocatalysis

- Microwave Absorption:** Water and polar molecules absorb microwave energy, converting it to heat.
- Nanoparticle Activation:** Rapid heating activates nanoparticles, enhancing their catalytic properties.
- Localized Hot Spots:** Non-uniform heating creates zones of higher reactivity around the nanoparticles.
- Reaction Acceleration:** Enhanced energy input reduces activation energy and increases reaction rates.

Microwave-Assisted Reactions in Water:

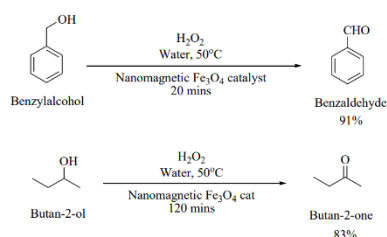
1- Hofmann Elimination Reaction:

In this method, quaternary ammonium salts are heated at high temperature and the yield of the product is low. However, use of microwave irradiation in water-chloroform system gives high yielding synthesis of a thermally unstable Hofmann elimination product.



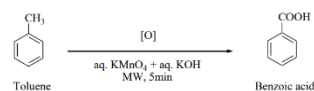
2-Oxidation of Alcohol:

Magnetically nano Fe_3O_4 efficiently catalyzes green oxidation of primary and secondary benzylic and aliphatic alcohols to give the corresponding carbonyl products in good yields. The reactions were carried out in an aqueous medium in the presence of hydrogen peroxide as an oxidant at 50°C .



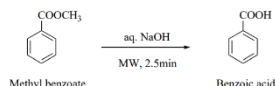
3-Oxidation of Toluene:

Oxidation of toluene with KMnO_4 under normal condition of refluxing takes 10-12 hr. compared to reaction in microwave conditions, which takes only 5 min and the yield is 40%.



4-Hydrolysis of Methyl Benzoate to Benzoic Acid (Saponification):

Saponification of methyl benzoate in aqueous sodium hydroxide under microwave irradiation takes only 2.4 min and gives 84% yield of benzoic acid.



5. Organic Synthesis

Synthesis of fine chemicals and pharmaceuticals. E.g., MW-assisted Suzuki coupling reactions in water using palladium NPs.

Environmental Applications

Degradation of pollutants. For example, MW-assisted Fenton-like processes are used for wastewater treatment.

Energy Applications

Hydrogen production from water splitting. Biodiesel production using metal oxide NPs under MW irradiation.

Biomimetic Reactions

Enzyme-like catalysis for peptide bond formation or hydrolysis.

6. Advantages of MW-Assisted Nanocatalysis

Enhanced Reaction Rates: Reduces reaction times drastically.

High Selectivity and Yield: Reduces side products.

Energy Efficiency: Focused energy delivery minimizes waste.

Scalability: Suitable for industrial applications with continuous flow reactors.

7. Challenges and Limitations

Non-Uniform Heating: This can lead to incomplete reactions or degradation of sensitive compounds.

Cost of MW Systems: Initial investment in MW reactors can be high.

Scaling Up: Uniform MW penetration is more brutal in large-scale systems.

Nanoparticle Stability: Prolonged MW exposure may alter nanoparticle structure or activity.

8. Recent Advances and Innovations

Hybrid Nanocatalysts: Combining metal NPs with metal oxides or carbon-based materials (e.g., graphene).

Continuous Flow Reactors: Overcoming scale-up challenges by integrating MW-assisted catalysis in flow systems.

Biosynthesis of NPs through bacterial, yeast, algae and fungus:

The biosynthesis of nanoparticles (NPs) is an eco-friendly, cost-effective, and sustainable approach that utilizes microorganisms such as bacteria, yeast, algae, and fungi. These microorganisms act as biological factories for synthesizing metallic or non-metallic nanoparticles, with diverse applications in medicine, agriculture, environmental science, and industry. Below are the key points on biosynthesis using different microorganisms.

Bacteria

Mechanism:

Bacteria reduce metal ions to nanoparticles through enzymatic processes and metabolic pathways.

Enzymes: nitrate reductase, hydrogenase, and electron transport chains.

Types of Nanoparticles: Silver (Ag), Gold (Au), Iron oxide (Fe₃O₄), Zinc oxide (ZnO), Titanium dioxide (TiO₂).

Advantages:

High growth rate and scalability. Intracellular and extracellular synthesis. Can operate under extreme conditions (temperature, pH, salinity). Easy to manipulate genetically for optimizing nanoparticle production.

Examples:

Pseudomonas aeruginosa: Silver and gold nanoparticles.

Bacillus subtilis: Iron oxide nanoparticles.

Yeast

Mechanism:

Yeast cells can sequester and reduce metal ions using intracellular and extracellular enzymes. Functional biomolecules (e.g., proteins, peptides) stabilize the nanoparticles.

Types of Nanoparticles: Silver (Ag), Cadmium sulfide (CdS), Selenium (Se).

Advantages:

Ability to tolerate high metal concentrations. Production of monodisperse nanoparticles. Intracellular synthesis allows high stability of nanoparticles.

Examples:

Saccharomyces cerevisiae: Silver and selenium nanoparticles.

Pichia pastoris: Cadmium sulfide nanoparticles.

Fungus

Mechanism:

Fungi secrete extracellular enzymes and secondary metabolites that facilitate the reduction of metal ions. High production of biomass aids in large-scale synthesis. Types of Nanoparticles: Silver (Ag), Gold (Au), Zinc oxide (ZnO), Selenium (Se).

Advantages:

Ability to produce large amounts of nanoparticles. Fungal proteins act as stabilizers and reducers. Large-scale production is possible. Stabilization of nanoparticles using fungal proteins. **Examples:**

Aspergillus Niger: Silver nanoparticles.

Fusarium oxysporum: Gold and zinc oxide nanoparticles.

Many fungi, including *Fusarium oxysporum*, *Verticillium luteolbum*, *Trichothecium species*, *Colletotrichum species*, *Aspergillus Oryza*, etc., have been found to create NPs of various shapes and sizes.

Algae

Mechanism:

Algae synthesize nanoparticles through photosynthetic pathways and the release of bioactive compounds (e.g., polysaccharides and proteins).

Metal ions are trapped and reduced on the cell surface or intracellularly.

Types of Nanoparticles:

Gold (Au), Silver (Ag), Platinum (Pt), Iron oxide (Fe₃O₄).

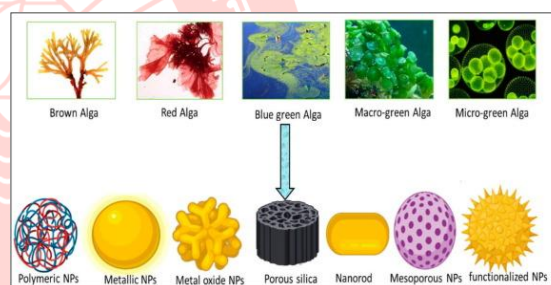
Advantages:

Abundant biomass and ease of cultivation. Natural production of capping agents for stability. Wide range of bioactive compounds for reducing metal ions. High biomass production potential. Can utilize sunlight for synthesis.

Examples:

Chlorella vulgaris: Gold and silver nanoparticles.

Spirulina platensis: Iron oxide nanoparticles.



Several algae species are used for the synthesis of nanoparticles

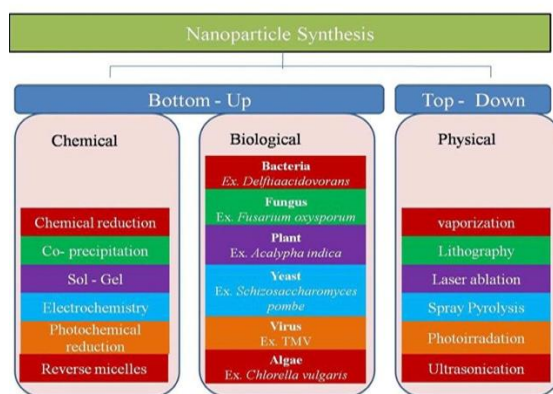
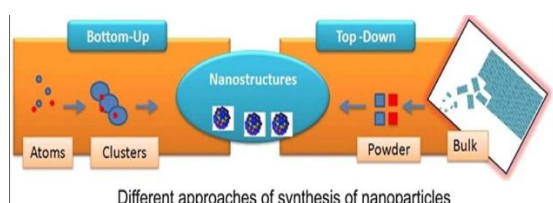
Mechanisms of Nanoparticle Synthesis

The synthesis of nanoparticles using microorganisms such as bacteria, yeast, algae, and fungi is an emerging field in nanotechnology known as **biological or green synthesis of nanoparticles**. These organisms can act as biological factories to produce nanoparticles, offering eco-friendly, cost-effective, and sustainable alternatives to chemical and physical methods.

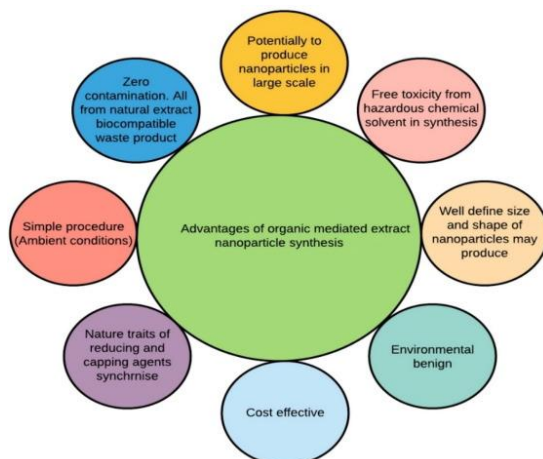
The 'top-down' and 'bottom-up' techniques to nanoparticle synthesis are shown in fig given below. Nanoparticles are made by dissolving bulk materials into small particles in the top-down technique such as lithography, sputtering, mechanical [e.g., milling, grinding], chemical etching, thermal evaporation, pulsed laser ablation, and photo reduction. The main advantages of top-

down approach are the cost and controlled shape and size of the product.

Top-down approaches are good for producing structures with long-range order and for making macroscopic connections. The top-down technique, on the other hand, has a key flaw i.e., surface structure is incomplete. In the bottom-up approach, wet-chemical processes [e.g., chemical reduction or oxidation of metals ion] solid-gel chemistry, co-precipitation, microemulsion, chemical vapour deposition [CVD], hydrothermal, pyrolysis, radiation induced, solvothermal, and electrodeposition procedures are used



Factors and increasing awareness of biosynthesis's significance have been lauded as auspicious eco-friendly alternatives that seem to provide the finest



methodology or outputs among core green chemistry

approaches. Plants, algae, fungi, yeast, and bacteria are a few biological agents. The nature of biological entities significantly determines the structure and appearance of synthesized nanoparticles. The diverse spectrum of biological entities has resulted in a fascinating array of nanoparticle shapes and sizes, with the entities serving as a blueprint for nanoparticle development, as given below. Biogenic synthesis is ideal due to its numerous biomolecules, cost-effectiveness, good stability, lack of toxic chemicals, and simple and safe operation procedures.

Advantages of Biosynthesis of Nanoparticles (NPs):

Sustainable and Eco-friendly Approach:

Biosynthesis of nanoparticles (NPs) using biological entities like plants, fungi, bacteria, and algae provides a more sustainable alternative to chemical and physical synthesis methods. It reduces hazardous chemicals and energy-intensive processes, aligning with eco-friendly practices.

Cost-effectiveness:

The biological synthesis of NPs often leverages readily available and inexpensive biomaterials, minimizing costs associated with precursor chemicals and energy consumption.

Scalability and Feasibility:

Though promising, the scalability of biosynthetic methods requires optimization. Issues like batch-to-batch variability and control over nanoparticle size, shape, and yield remain challenges that must be addressed for industrial applications.

Versatility in Applications:

Biosynthesized nanoparticles exhibit unique properties like biocompatibility, enhanced surface reactivity, and reduced toxicity, making them suitable for diverse applications in medicine, agriculture, environmental remediation, and electronics.

Challenges in Consistency and Characterization:

Ensuring uniformity in particle size, shape, and distribution is a challenge in biosynthesis. Advanced

characterization techniques are essential to understand and control these parameters effectively.

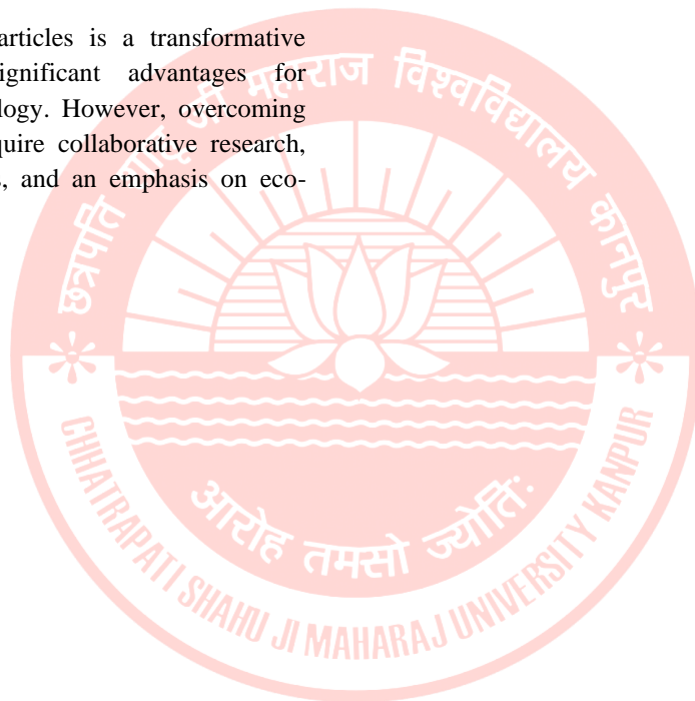
Potential for Functionalization:

Biosynthesized nanoparticles are often functionalized with bioactive molecules from the biological source, offering enhanced bioactivity for specific applications like antimicrobial agents, drug delivery systems, and cancer therapy.

Interdisciplinary Opportunities:

The biosynthesis of nanoparticles lies at the intersection of microbiology, nanotechnology, chemistry, and material science, fostering interdisciplinary research and innovation.

Biosynthesis of nanoparticles is a transformative approach, offering significant advantages for sustainable nanotechnology. However, overcoming the limitations will require collaborative research, innovative technologies, and an emphasis on eco-friendly practices.



MCQs

TOPIC – 1

1. Which of the following is not a principle of green chemistry?

- a) Prevention
- b) Atom economy
- c) Hazardous waste production
- d) Safer chemicals

2. Green chemistry aims to:

- a) Maximize the use of non-renewable resources
- b) Eliminate pollution entirely
- c) Use hazardous chemicals more cautiously
- d) Balance economic growth with environmental concerns

3. What does "atom economy" measure in green chemistry?

- a) Efficiency of resource utilization
- b) Reduction in hazardous waste
- c) Amount of waste produced per reaction
- d) Percentage of reactant atoms that end up in the desired product

4. Which is an example of a green solvent?

- a) Acetone
- b) Dichloromethane
- c) Water
- d) Toluene

5. The principle of "benign synthesis" refers to:

- a) Synthesis of less hazardous chemicals
- b) Chemical reactions that produce minimal waste
- c) Using benign catalysts in chemical reactions
- d) Eliminating toxic reagents from reactions

6. In green chemistry, the term "E-factor" refers to:

- a) Efficiency factor
- b) Environmental factor
- c) Ecological factor
- d) Environmental impact factor

7. Which is an example of a green engineering principle?

- a) Recycling waste materials
- b) Increasing energy consumption
- c) Using complex chemical processes
- d) Maximizing resource depletion

8. Which is an example of a green catalyst?

- a) Lead
- b) Palladium
- c) Mercury
- d) Chromium

9. The concept of "renewable feedstocks" in green chemistry refers to:

a) Non-renewable resources used in chemical processes

b) Raw materials derived from fossil fuels

c) Feedstocks that are produced in large quantities

d) Raw materials derived from renewable resources

10. Green chemistry focuses on minimizing:

- a) Economic growth
- b) Toxicity of chemicals
- c) Energy efficiency
- d) All of the above

11. The principle of "safety" in green chemistry refers to:

- a) Proper disposal of chemicals
- b) Minimizing the hazards of chemicals used
- c) Reducing chemical production
- d) Using fewer chemicals in processes

12. Which of the following is an example of a green product?

- a) Aerosol spray containing CFCs
- b) Non-biodegradable plastic bags
- c) Bio-based detergent with minimal toxicity
- d) Conventional batteries with heavy metal content

13. Green chemistry emphasizes the use of _____ as energy sources.

- a) Non-renewable resources
- b) Coal and petroleum
- c) Fossil fuels
- d) Renewable resources

14. Which principle of green chemistry involves designing chemicals to degrade after use?

- a) Atom economy
- b) Design for degradation
- c) Use of renewable feedstocks
- d) Pollution prevention

15. The primary goal of green chemistry is to:

- a) Increase chemical waste
- b) Reduce environmental impact
- c) Use more hazardous chemicals
- d) Maximize energy consumption

16. The Twelve Principles of Green Chemistry were formulated by:

- a) Environmental Protection Agency (EPA)
- b) Greenpeace
- c) American Chemical Society (ACS)
- d) Anastas and Warner

17. Which of the following is a characteristic of a green solvent?

- a) High toxicity
- b) Low volatility
- c) Poor biodegradability
- d) Non-renewable source

18. Green chemistry principles aim to improve:

- a) Environmental and economic sustainability
b) Chemical industry profits only
c) Government regulations
d) Chemical synthesis complexity
19. Which principle of green chemistry involves minimizing the number of steps in a synthetic route?
a) Atom economy
b) Design for energy efficiency
c) Use of renewable feedstocks
d) Simplification
20. Green chemistry encourages the use of _____ in chemical processes.
a) High temperatures and pressures
b) Strong acids and bases
c) Safer and less toxic reagents
d) Non-renewable energy sources
21. The concept of "green chemistry" was first introduced in the early:
a) 1970s
b) 1980s
c) 1990s
d) 2000s
22. Which principle of green chemistry involves designing chemical syntheses to prevent waste generation?
a) Atom economy
b) Pollution prevention
c) Use of renewable feedstocks
d) Safer chemicals
23. Green chemistry principles are relevant to which industries?
a) Chemical industry only
b) Oil and gas industry only
c) Pharmaceutical, agricultural, and chemical industries
d) Renewable energy industry only
24. Green chemistry focuses on the development of:
a) Hazardous chemicals
b) Safer alternatives
c) Non-renewable resources
d) Toxic waste management
25. The principle of "catalysis" in green chemistry emphasizes the use of:
a) Toxic catalysts
b) Renewable catalysts
c) Catalysts that promote waste generation
d) Expensive catalysts
26. Which of the following is a key aspect of green chemistry education?
a) Ignoring environmental concerns
b) Emphasizing economic profits
c) Teaching sustainable practices
d) Using only traditional chemical methods
27. Green chemistry principles can contribute to:
a) Increased environmental pollution
b) Higher energy consumption
c) Sustainable development
d) Reduced safety standards
28. Which principle of green chemistry involves using chemicals in their safest form?
a) Prevention
b) Design for energy efficiency
c) Safer chemicals
d) Atom economy
29. Green chemistry aims to _____ the use of hazardous chemicals.
a) Increase
b) Minimize
c) Maximize
d) Monitor
30. The concept of "benign solvents" in green chemistry refers to solvents that are:
a) Highly toxic
b) Not biodegradable
c) Renewable
d) Non-renewable
31. Which of the following is an example of a green chemistry innovation?
a) Increased use of persistent organic pollutants
b) Development of biodegradable plastics
c) Disposal of hazardous waste in landfills
d) Use of non-renewable resources
32. Green chemistry principles prioritize the use of _____ resources.
a) Limited
b) Finite
c) Renewable
d) Non-renewable
33. The concept of "life-cycle assessment" in green chemistry evaluates:
a) Only economic factors
b) Only environmental factors
c) Both environmental and economic impacts
d) Social impacts only
34. Which of the following is a challenge in implementing green chemistry principles?
a) Increasing pollution levels
b) Cost-effectiveness of green technologies
c) Minimizing regulatory compliance
d) Using toxic chemicals
35. Green chemistry promotes the use of _____ in chemical reactions.
a) Hazardous materials

- b) Low-energy processes
 - c) Toxic by-products
 - d) Non-renewable resources
36. The principle of "renewable feedstocks" encourages the use of raw materials that are:
- a) Only available in small quantities
 - b) Derived from fossil fuels
 - c) Biodegradable
 - d) Derived from renewable resources
37. Which of the following is a benefit of green chemistry?
- a) Increased pollution
 - b) Reduced environmental impact
 - c) Higher toxicity in products
 - d) Decreased energy efficiency
38. The principle of "inherently safer chemistry" aims to:
- a) Increase chemical hazards
 - b) Design safer chemicals and processes
 - c) Ignore potential risks
 - d) Minimize chemical synthesis
39. Green chemistry principles support the development of ____ chemicals.
- a) Hazardous
 - b) Non-biodegradable
 - c) Safer
 - d) High-energy
40. Which of the following is an example of green chemistry application?
- a) Developing persistent organic pollutants
 - b) Using non-renewable energy sources
 - c) Creating biofuels from renewable resources
 - d) Increasing waste generation
- 18. a) Environmental and economic sustainability
 - 19. d) Simplification
 - 20. c) Safer and less toxic reagents
 - 21. c) 1990s
 - 22. b) Pollution prevention
 - 23. c) Pharmaceutical, agricultural, and chemical industries
 - 24. b) Safer alternatives
 - 25. b) Renewable catalysts
 - 26. c) Teaching sustainable practices
 - 27. c) Sustainable development
 - 28. c) Safer chemicals
 - 29. b) Minimize
 - 30. c) Renewable
 - 31. b) Development of biodegradable plastics
 - 32. c) Renewable
 - 33. c) Both environmental and economic impacts
 - 34. b) Cost-effectiveness of green technologies
 - 35. b) Low-energy processes
 - 36. d) Derived from renewable resources
 - 37. b) Reduced environmental impact
 - 38. b) Design safer chemicals and processes
 - 39. c) Safer
 - 40. c) Creating biofuels from renewable resources
- XX

Answers

- 1. c) Hazardous waste production
- 2. d) Balance economic growth with environmental concerns
- 3. d) Percentage of reactant atoms that end up in the desired product
- 4. c) Water
- 5. a) Synthesis of less hazardous chemicals
- 6. b) Environmental factor
- 7. a) Recycling waste materials
- 8. b) Palladium
- 9. d) Raw materials derived from renewable resources
- 10. b) Toxicity of chemicals
- 11. b) Minimizing the hazards of chemicals used
- 12. c) Bio-based detergent with minimal toxicity
- 13. d) Renewable resources
- 14. b) Design for degradation
- 15. b) Reduce environmental impact
- 16. d) Anastas and Warner
- 17. b) Low volatility

TOPIC – 2

1. Which of the following principles of green chemistry focuses on maximizing the incorporation of all materials used in the process into the final product?

- a) Design for degradation
- b) Atom economy
- c) Safer solvents
- d) Use of renewable feedstocks

2. When designing a green synthesis, which principle encourages the reduction of hazardous substances in chemical reactions?

- a) Prevention
- b) Inherently safer chemistry
- c) Real-time analysis
- d) Catalysis

3. The principle of "design for energy efficiency" aims to:

- a) Reduce the number of steps in a synthesis
- b) Minimize energy consumption
- c) Use renewable feedstocks
- d) Enhance the biodegradability of products

4. According to green chemistry principles, what type of solvents should be used in a green synthesis?

- a) Highly volatile organic solvents
- b) Non-renewable solvents
- c) Safer, environmentally benign solvents
- d) Chlorinated solvents

5. Which principle involves designing chemical products that are fully effective yet have little or no toxicity?

- a) Design for degradation
- b) Safer chemicals
- c) Prevention
- d) Real-time analysis

6. In a green synthesis, which principle is applied to ensure that chemical reactions produce minimal waste?

- a) Prevention
- b) Atom economy
- c) Use of renewable feedstocks
- d) Catalysis

7. The use of catalysts in a green synthesis aligns with which principle of green chemistry?

- a) Real-time analysis
- b) Design for degradation
- c) Catalysis
- d) Inherently safer chemistry

8. Which principle focuses on using raw materials that are renewable rather than depleting natural resources?

- a) Atom economy
- b) Use of renewable feedstocks
- c) Safer solvents
- d) Prevention

9. Designing products that break down into harmless substances after use aligns with which principle?

- a) Design for degradation
- b) Inherently safer chemistry
- c) Catalysis
- d) Real-time analysis

10. When implementing green synthesis, real-time analysis for pollution prevention is important because it:

- a) Ensures that products are biodegradable
- b) Helps in monitoring and controlling the formation of hazardous substances during the process
- c) Reduces the energy consumption of the process
- d) Encourages the use of renewable feedstocks

Answers:

- 1. b) Atom economy
- 2. b) Inherently safer chemistry
- 3. b) Minimize energy consumption
- 4. c) Safer, environmentally benign solvents
- 5. b) Safer chemicals
- 6. b) Atom economy
- 7. c) Catalysis
- 8. b) Use of renewable feedstocks
- 9. a) Design for degradation
- 10. b) Helps in monitoring and controlling the formation of hazardous substances during the process

XX

TOPIC – 3

1. The primary need for green chemistry arose due to concerns about:
 - a) Increased production costs
 - b) Environmental pollution and human health risks
 - c) Decreasing demand for chemical products
 - d) Lack of scientific research
2. The inception of green chemistry is most closely associated with which decade?
 - a) 1970s
 - b) 1980s
 - c) 1990s
 - d) 2000s
3. Who are considered the founding figures of green chemistry?
 - a) Paul Anastas and John Warner
 - b) Marie Curie and Dmitri Mendeleev
 - c) Linus Pauling and Robert Hooke
 - d) Rachel Carson and Al Gore
4. The Pollution Prevention Act, which influenced the development of green chemistry, was enacted in:
 - a) 1976
 - b) 1980
 - c) 1990
 - d) 2000
5. Which organization played a significant role in the formalization of green chemistry principles?
 - a) Greenpeace
 - b) World Health Organization
 - c) Environmental Protection Agency (EPA)
 - d) United Nations
6. The term "green chemistry" emphasizes:
 - a) Economic growth
 - b) Chemical weapon development
 - c) Sustainable and environmentally friendly chemical practices
 - d) Traditional chemical methods
7. The evolution of green chemistry has led to increased focus on:
 - a) Using more toxic solvents
 - b) Minimizing waste and energy use
 - c) Enhancing fossil fuel extraction
 - d) Increasing industrial emissions
8. The principles of green chemistry aim to:
 - a) Eliminate chemical industry
 - b) Maximize the efficiency and safety of chemical processes
 - c) Increase the use of hazardous materials
 - d) Reduce research and development in chemistry
9. Which of the following books is co-authored by Paul Anastas and John Warner and outlines the principles of green chemistry?
 - a) "Silent Spring"
 - b) "Green Chemistry: Theory and Practice"
 - c) "The Limits to Growth"
 - d) "Our Common Future"
10. The need for green chemistry was highlighted by which environmental disaster?
 - a) The Deepwater Horizon oil spill
 - b) The Bhopal gas tragedy
 - c) The Chernobyl nuclear disaster
 - d) The Great Smog of London
11. Green chemistry contributes to the development of:
 - a) Non-renewable resources
 - b) Renewable energy sources and sustainable materials
 - c) Higher carbon emissions
 - d) Traditional manufacturing processes
12. The evolution of green chemistry includes the development of:
 - a) Persistent organic pollutants
 - b) Biodegradable polymers
 - c) Non-biodegradable plastics
 - d) Toxic pesticides
13. One of the key motivations for green chemistry is to:
 - a) Decrease the lifespan of chemical products
 - b) Reduce the environmental impact of chemical manufacturing
 - c) Increase the use of non-renewable resources
 - d) Eliminate the need for chemical safety regulations
14. The principle of "prevention" in green chemistry emphasizes:
 - a) Treating waste after it is created
 - b) Preventing waste and pollution at the source
 - c) Increasing the complexity of chemical processes
 - d) Maximizing the use of hazardous chemicals
15. The evolution of green chemistry has led to the development of:
 - a) Safer and more sustainable chemical processes
 - b) More hazardous waste
 - c) Higher energy consumption in chemical processes
 - d) Increased reliance on non-renewable resources
16. The Green Chemistry Challenge Awards were established by:
 - a) United Nations
 - b) Environmental Protection Agency (EPA)
 - c) World Wildlife Fund
 - d) American Chemical Society (ACS)

17. One of the earliest examples of green chemistry is the replacement of CFCs in:

- a) Pharmaceuticals
- b) Refrigerants and aerosols
- c) Agricultural fertilizers
- d) Industrial solvents

18. The need for green chemistry is driven by:

- a) The goal to increase chemical production
- b) The need to address climate change and resource depletion
- c) The desire to use more toxic chemicals
- d) Economic recession

19. The evolution of green chemistry has encouraged the use of:

- a) Fossil fuels
- b) Renewable feedstocks
- c) Heavy metals
- d) Persistent organic pollutants

20. Green chemistry aims to design products that:

- a) Have a long-lasting negative environmental impact
- b) Are less effective but more profitable
- c) Degrade into harmless substances after use
- d) Require extensive hazardous waste management

Answers:

- 1. b) Environmental pollution and human health risks
- 2. c) 1990s
- 3. a) Paul Anastas and John Warner
- 4. c) 1990
- 5. c) Environmental Protection Agency (EPA)
- 6. c) Sustainable and environmentally friendly chemical practices
- 7. b) Minimizing waste and energy use
- 8. b) Maximize the efficiency and safety of chemical processes
- 9. b) "Green Chemistry: Theory and Practice"
- 10. b) The Bhopal gas tragedy
- 11. b) Renewable energy sources and sustainable materials
- 12. b) Biodegradable polymers
- 13. b) Reduce the environmental impact of chemical manufacturing
- 14. b) Preventing waste and pollution at the source
- 15. a) Safer and more sustainable chemical processes
- 16. b) Environmental Protection Agency (EPA)
- 17. b) Refrigerants and aerosols
- 18. b) The need to address climate change and resource depletion
- 19. b) Renewable feedstocks
- 20. c) Degrade into harmless substances after use

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TOPIC – 4

1. Which of the following everyday products is commonly produced using green chemistry principles?

- a) Non-biodegradable plastic bags
- b) Bio-based detergents
- c) Pesticides with high toxicity
- d) Aerosol sprays with CFCs

2. Green chemistry has led to the development of biodegradable plastics. These plastics are primarily made from:

- a) Petroleum-based products
- b) Renewable biological sources
- c) Heavy metals
- d) Non-renewable resources

3. A common application of green chemistry in household cleaning products involves the use of:

- a) Chlorinated solvents
- b) Phosphates
- c) Natural enzymes and biodegradable surfactants
- d) Synthetic dyes and fragrances

4. Green chemistry can reduce the environmental impact of packaging by promoting the use of:

- a) Non-recyclable materials
- b) Excessive packaging
- c) Recyclable and compostable materials
- d) Heavy metals in packaging

5. In personal care products, green chemistry focuses on using ingredients that are:

- a) Synthetic and non-biodegradable
- b) Derived from petrochemicals
- c) Natural, renewable, and biodegradable
- d) Toxic and persistent in the environment

6. Green chemistry principles are applied in agriculture to develop:

- a) Chemical fertilizers with high toxicity
- b) Biopesticides and biofertilizers
- c) Pesticides with long environmental persistence
- d) Synthetic growth hormones

7. Which of the following is a benefit of using green chemistry in pharmaceuticals?

- a) Increased production of hazardous waste
- b) Higher levels of environmental pollution
- c) Reduced use of toxic solvents and reagents
- d) Longer drug development times

8. Green chemistry in the textile industry promotes the use of:

- a) Synthetic dyes with high environmental impact
- b) Natural dyes and environmentally friendly processing methods
- c) Non-renewable resources for fabric production

d) Chlorinated bleaching agents

9. In the food industry, green chemistry has contributed to the development of:

- a) Non-biodegradable packaging
- b) Natural preservatives and food additives
- c) Synthetic flavor enhancers
- d) Chemical pesticides

10. One of the most significant benefits of applying green chemistry in day-to-day life is:

- a) Increased reliance on hazardous materials
- b) Reduction in energy consumption and waste generation
- c) Greater use of fossil fuels
- d) Enhanced production of non-renewable resources

Here are the answers for the above questions:

- 1. b) Bio-based detergents
- 2. b) Renewable biological sources
- 3. c) Natural enzymes and biodegradable surfactants
- 4. c) Recyclable and compostable materials
- 5. c) Natural, renewable, and biodegradable
- 6. b) Biopesticides and biofertilizers
- 7. c) Reduced use of toxic solvents and reagents
- 8. b) Natural dyes and environmentally friendly processing methods
- 9. b) Natural preservatives and food additives
- 10. b) Reduction in energy consumption and waste generation

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TOPIC – 5

1. Which of the following is a green reagent used for oxidation reactions in organic synthesis?

- a) Chromic acid
- b) Potassium permanganate
- c) Hydrogen peroxide
- d) Osmium tetroxide

2. A common green catalyst used in organic synthesis is:

- a) Aluminum chloride
- b) Palladium on carbon
- c) Iron(III) chloride
- d) Tungsten hexachloride

3. Which green reagent is often used as a reducing agent in organic synthesis?

- a) Lithium aluminum hydride
- b) Sodium borohydride
- c) Hydrogen gas
- d) Hydrazine

4. Which of the following is considered a green solvent in organic synthesis?

- a) Benzene
- b) Dichloromethane
- c) Ethyl acetate
- d) Chloroform

5. Supercritical carbon dioxide (scCO₂) is used as a green solvent because it:

- a) Is highly toxic
- b) Requires high temperatures to use
- c) Is non-flammable and environmentally benign
- d) Is expensive and difficult to obtain

6. Which green reagent is used for the epoxidation of alkenes?

- a) Peracetic acid
- b) m-chloroperoxybenzoic acid (MCPBA)
- c) Hydrogen peroxide
- d) Sodium periodate

7. Ionic liquids are considered green solvents because they:

- a) Have high volatility
- b) Are derived from petroleum
- c) Have low volatility and can be recycled
- d) Are highly toxic

8. A green reagent commonly used in the Wittig reaction is:

- a) Triphenylphosphine
- b) Butyllithium
- c) Sodium hydride
- d) Potassium tert-butoxide

9. Which green reagent is used in the Suzuki coupling reaction?

- a) Pd(OAc)₂
- b) BF₃·OEt₂
- c) AlCl₃
- d) TiCl₄

10. For green chemistry, which reagent is preferred for alkylation reactions?

- a) Methyl iodide
- b) Dimethyl sulfate
- c) Ethyl chloride
- d) Dimethyl carbonate

11. A green reagent used in the Baeyer-Villiger oxidation is:

- a) Peracetic acid
- b) meta-chloroperoxybenzoic acid
- c) Hydrogen peroxide
- d) Sodium dichromate

12. Which green reagent is often used in the synthesis of esters?

- a) Thionyl chloride
- b) Sodium hydroxide
- c) Sulfuric acid
- d) Enzymes (lipases)

13. For greener nitration reactions, which reagent can be used?

- a) Nitric acid and sulfuric acid
- b) Acetyl nitrate
- c) Nitrogen dioxide
- d) Solid-supported nitrite

14. Which green reagent can be used for the oxidation of alcohols to aldehydes?

- a) Potassium permanganate
- b) Pyridinium chlorochromate (PCC)
- c) TEMPO with bleach (sodium hypochlorite)
- d) Jones reagent

15. In green chemistry, a common reagent for the cleavage of ethers is:

- a) Hydrobromic acid
- b) Boron tribromide
- c) Sodium periodate
- d) Hydrogen bromide in acetic acid

16. Which of the following is a green reagent for the synthesis of amides?

- a) Thionyl chloride
- b) Phosphorus pentachloride
- c) Ethyl chloroformate
- d) Carbodiimides

17. A green reagent used for the synthesis of cyclic carbonates from epoxides and CO₂ is:

- a) Boron trifluoride
- b) Tetrabutylammonium bromide (TBAB)

TOPIC – 6

18. Which green reagent is used for oxidative cleavage of olefins to carbonyl compounds?

- a) Ozone
b) Potassium permanganate
c) Sodium periodate
d) Osmium tetroxide

19. Which green reagent is used for the synthesis of quinolines from anilines and ketones?

- Sulfuric acid
- Polyphosphoric acid
- Ionic liquids
- Boron trifluoride

20. In green chemistry, which reagent is used for the catalytic hydrogenation of alkenes?

- Platinum on carbon
- Nickel
- Palladium on carbon
- Raney nickel

Answers:

1. c) Hydrogen peroxide
2. b) Palladium on carbon
3. c) Hydrogen gas
4. c) Ethyl acetate
5. c) Is non-flammable and environmentally benign
6. c) Hydrogen peroxide
7. c) Have low volatility and can be recycled
8. a) Triphenylphosphine
9. a) $\text{Pd}(\text{OAc})_2$
10. d) Dimethyl carbonate
11. c) Hydrogen peroxide
12. d) Enzymes (lipases)
13. d) Solid-supported nitrite
14. c) TEMPO with bleach (sodium hypochlorite)
15. c) Sodium periodate
16. d) Carbodiimides
17. b) Tetrabutylammonium bromide (TBAB)
18. c) Sodium periodate
19. c) Ionic liquids
20. c) Palladium on carbon

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1. Dimethyl carbonate (DMC) is considered a green reagent because it is:

- a) Toxic
- b) Non-renewable
- c) Biodegradable and less toxic
- d) Expensive to produce

2. In organic synthesis, DMC is commonly used as a:

- a) Reducing agent
b) Oxidizing agent
c) Methylating agent
d) Polymerization catalyst

3. Which reaction type is DMC often used for in green synthesis?

- a) Nitration
b) Esterification
c) Hydrogenation
d) Sulfonation

4. Compared to traditional methylating agents like methyl iodide, DMC is preferred because it:

- a) Is more toxic
- b) Generates fewer hazardous byproducts
- c) Requires higher temperatures
- d) Produces more waste

5. DMC can replace phosgene in the synthesis of:

- a) Amines
- b) Urethanes
- c) Alcohols
- d) Alkenes

6. A significant advantage of using DMC in transesterification reactions is that it:

- a) Produces toxic byproducts
- b) Requires harsh conditions
- c) Generates methanol as a byproduct, which is easily recoverable
- d) Is not readily available

7. Which of the following is NOT a property of dimethyl carbonate?

- a) Low toxicity
- b) High boiling point
- c) Biodegradability
- d) Non-flammability

8. In the synthesis of polycarbonates, DMC is often used as a safer alternative to:

- a) Benzene
b) Formaldehyde
c) Phosgene
d) Acetone

9. DMC is often used in the methylation of:

- a) Alcohols

- b) Alkanes
c) Alkenes
d) Alkynes
10. The use of DMC in organic synthesis aligns with which principle of green chemistry?
a) Design for degradation
b) Increase in atom economy
c) Avoiding the use of derivatives
d) Use of renewable feedstocks
11. Peracids are commonly used as:
a) Reducing agents
b) Oxidizing agents
c) Dehydrating agents
d) Solvents
12. Which of the following peracid is commonly used in epoxidation reactions?
a) Peracetic acid
b) Perbenzoic acid
c) Meta-chloroperoxybenzoic acid (MCPBA)
d) Perpropionic acid
13. The use of peracids in oxidation reactions is considered green because:
a) They produce highly toxic byproducts
b) They operate under harsh conditions
c) They can often be performed under mild conditions
d) They are non-selective
14. Peracetic acid is often used as a green alternative to:
a) Chromic acid
b) Sodium dichromate
c) Osmium tetroxide
d) Nitric acid
15. Which peracid is known for its stability and ease of handling?
a) Peracetic acid
b) Perbenzoic acid
c) Meta-chloroperoxybenzoic acid (MCPBA)
d) Perpropionic acid
16. In organic synthesis, peracids are typically used to:
a) Reduce alkenes to alkanes
b) Oxidize alkenes to epoxides
c) Dehydrate alcohols to alkenes
d) Halogenate alkanes
17. The oxidation of sulfides to sulfoxides can be efficiently carried out using:
a) Peracetic acid
b) Meta-chloroperoxybenzoic acid (MCPBA)
c) Perbenzoic acid
d) Perpropionic acid
18. Peracids are preferred in green synthesis because they:
a) Are highly volatile
b) Produce fewer harmful byproducts
c) Are highly toxic
d) Require very high temperatures
19. A key advantage of using peracids over traditional oxidizing agents is:
a) Higher selectivity and mild reaction conditions
b) Lower reactivity
c) Higher toxicity
d) Increased cost
20. Which of the following reactions commonly employs peracids?
a) Hydrogenation
b) Epoxidation
c) Nitration
d) Hydrolysis
21. Chromic acid is considered less green due to its:
a) Low efficiency
b) High cost
c) High toxicity and hazardous waste production
d) Poor availability
22. In green synthesis, chromic acid can often be replaced by:
a) Sodium dichromate
b) Potassium permanganate
c) Hydrogen peroxide
d) Phosphoric acid
23. A common use of chromic acid in organic synthesis is the oxidation of:
a) Alkenes to alkanes
b) Alcohols to aldehydes or ketones
c) Ketones to alcohols
d) Alkanes to alkenes
24. The use of chromic acid is declining in favor of more environmentally friendly alternatives because it:
a) Is expensive
b) Requires high temperatures
c) Generates toxic chromium waste
d) Is inefficient
25. Which of the following is a green alternative to chromic acid for alcohol oxidation?
a) Potassium permanganate
b) Meta-chloroperoxybenzoic acid (MCPBA)
c) TEMPO with bleach (sodium hypochlorite)
d) Osmium tetroxide
26. Chromic acid is typically prepared using:
a) Sodium hydroxide and chlorine
b) Sulfuric acid and sodium dichromate
c) Hydrochloric acid and potassium permanganate

- d) Nitric acid and silver nitrate
27. The hazards associated with chromic acid include:
- Low reactivity
 - Corrosiveness and carcinogenicity
 - High volatility
 - Low toxicity
28. A major disadvantage of using chromic acid in green chemistry is that it:
- Is not readily available
 - Requires very high pressures
 - Produces hazardous chromium(VI) waste
 - Is not effective at low temperatures
29. In green synthesis, the preferred method for the oxidation of primary alcohols to carboxylic acids often avoids using chromic acid because it:
- Is too slow
 - Is too selective
 - Is too mild
 - Generates harmful byproducts
30. A sustainable and green oxidation method for secondary alcohols to ketones that avoids chromic acid uses:
- Potassium dichromate in acidic medium
 - Sodium periodate
 - TEMPO and bleach (sodium hypochlorite)
 - Pyridinium chlorochromate (PCC)
25. c) TEMPO with bleach (sodium hypochlorite)
26. b) Sulfuric acid and sodium dichromate
27. b) Corrosiveness and carcinogenicity
28. c) Produces hazardous chromium(VI) waste
29. d) Generates harmful byproducts
30. c) TEMPO and bleach (sodium hypochlorite)
- XX

Answers

- c) Biodegradable and less toxic
- c) Methylating agent
- b) Esterification
- b) Generates fewer hazardous byproducts
- b) Urethanes
- c) Generates methanol as a byproduct, which is easily recoverable
- d) Non-flammability
- c) Phosgene
- a) Alcohols
- b) Increase in atom economy
- b) Oxidizing agents
- c) Meta-chloroperoxybenzoic acid (MCPBA)
- c) They can often be performed under mild conditions
- a) Chromic acid
- c) Meta-chloroperoxybenzoic acid (MCPBA)
- b) Oxidize alkenes to epoxides
- b) Meta-chloroperoxybenzoic acid (MCPBA)
- b) Produce fewer harmful byproducts
- a) Higher selectivity and mild reaction conditions
- b) Epoxidation
- c) High toxicity and hazardous waste production
- c) Hydrogen peroxide
- b) Alcohols to aldehydes or ketones
- c) Generates toxic chromium waste

TOPIC – 7

1. What is a primary goal of green catalysis in chemical processes?

- a) Increase toxicity
- b) Increase reaction time
- c) Reduce energy consumption and waste
- d) Use non-renewable resources

2. Which of the following is a characteristic of a green catalyst?

- a) High toxicity
- b) High selectivity
- c) High cost
- d) High energy requirement

3. In green catalysis, which type of catalysts are often preferred due to their ability to be reused?

- a) Homogeneous catalysts
- b) Heterogeneous catalysts
- c) Toxic catalysts
- d) Expensive catalysts

4. An example of a green catalyst used in oxidation reactions is:

- a) Osmium tetroxide
- b) Palladium on carbon
- c) Iron(III) chloride
- d) Hydrogen peroxide

5. What is the role of a catalyst in a chemical reaction?

- a) It increases the reaction rate without being consumed
- b) It decreases the yield of the reaction
- c) It changes the products of the reaction
- d) It increases the energy requirement

6. Which metal is commonly used in green catalysis for cross-coupling reactions?

- a) Mercury
- b) Lead
- c) Palladium
- d) Cadmium

7. Green catalysts aim to minimize the production of:

- a) By-products and waste
- b) Desired products
- c) Reactants
- d) Catalysts

8. Which green catalyst is widely used in the hydrogenation of alkenes?

- a) Nickel
- b) Platinum on carbon
- c) Palladium on carbon
- d) Iron(III) chloride

9. An enzyme that acts as a green catalyst in biological systems is:

- a) Lipase
- b) Iron(III) oxide
- c) Aluminum chloride
- d) Calcium carbonate

10. Which of the following is a benefit of using green catalysts in industrial processes?

- a) Higher operational costs
- b) Increased environmental pollution
- c) Reduced energy and resource consumption
- d) Longer reaction times

11. A green catalyst often used in oxidation reactions involving alcohols is:

- a) Chromium trioxide
- b) TEMPO (2,2,6,6-Tetramethylpiperidine 1-oxyl)
- c) Sodium dichromate
- d) Lead tetraacetate

12. Which type of green catalyst is known for being biodegradable and derived from natural sources?

- a) Metal oxides
- b) Organometallic complexes
- c) Enzymes
- d) Peroxides

13. One advantage of using green catalysis over traditional methods is:

- a) Increased toxicity
- b) Higher energy consumption
- c) Reduced environmental impact
- d) Higher costs

14. In the context of green catalysis, what is meant by "atom economy"?

- a) Maximizing the use of all atoms in the starting materials
- b) Increasing the number of steps in a reaction
- c) Using more reagents than necessary
- d) Increasing waste production

15. A green catalyst used for the synthesis of biodiesel is:

- a) Sulfuric acid
- b) Sodium hydroxide
- c) Calcium oxide
- d) Hydrochloric acid

16. Which green catalyst is commonly used in the epoxidation of alkenes?

- a) Osmium tetroxide
- b) Meta-chloroperoxybenzoic acid (MCPBA)
- c) Chromium trioxide
- d) Palladium chloride

17. In green catalysis, what is the benefit of using water as a solvent?

- a) It is expensive
- b) It is non-toxic and environmentally benign
- c) It is non-renewable

TOPIC – 8

18. The use of microwaves in green catalysis is beneficial because it:

- a) Decreases reaction rate
- b) Increases energy consumption
- c) Reduces reaction times and energy usage
- d) Increases waste production

19. Which type of green catalysis involves the use of light to drive chemical reactions?

- a) Biocatalysis
- b) Electrocatalysis
- c) Photocatalysis
- d) Homogeneous catalysis

20. Green catalysts can often be supported on solid materials for ease of recovery and reuse. An example of such a support material is:

- 11
a) Sodium chloride
b) Silica gel
c) Mercury
d) Lead oxide

Answers

1. c) Reduce energy consumption and waste
2. b) High selectivity
3. b) Heterogeneous catalysts
4. d) Hydrogen peroxide
5. a) It increases the reaction rate without being consumed
6. c) Palladium
7. a) By-products and waste
8. c) Palladium on carbon
9. a) Lipase
10. c) Reduced energy and resource consumption
11. b) TEMPO (2,2,6,6-Tetramethylpiperidine 1-oxyl)
12. c) Enzymes
13. c) Reduced environmental impact
14. a) Maximizing the use of all atoms in the starting materials
15. c) Calcium oxide
16. b) Meta-chloroperoxybenzoic acid (MCPBA)
17. b) It is non-toxic and environmentally benign
18. c) Reduces reaction times and energy usage
19. c) Photocatalysis
20. b) Silica gel

[illegible]

1. What is a biocatalyst in the context of green chemistry?

- a) Synthetic catalyst
- b) Chemical reactor
- c) Enzyme or microorganism
- d) Photocatalyst

2. Biocatalysts are advantageous in green chemistry because they:

- a) Are highly toxic
- b) Require high temperatures
- c) Are biodegradable and specific
- d) Produce large amounts of waste

3. Enzymes, as biocatalysts, are made up of:

- a) Inorganic metals
- b) Organic polymers
- c) Amino acids
- d) Nucleic acids

4. Which of the following is a characteristic of enzymes used as biocatalysts?

- a) Low specificity
- b) High toxicity
- c) Non-renewable
- d) High selectivity

5. Biocatalysts promote green chemistry principles by:

- a) Increasing energy consumption
- b) Producing hazardous byproducts
- c) Operating under mild conditions
- d) Using non-renewable resources

6. A common example of a biocatalyst used in the synthesis of pharmaceuticals is:

- a) Palladium on carbon
b) Lipase
c) Silver nanoparticles
d) Aluminum chloride

7. Enzymes used in biocatalysis are often derived from:

- a) Synthetic polymers
- b) Microorganisms or plants
- c) Inorganic compounds
- d) Noble metals

8. Which enzyme is commonly used in the production of biodiesel?

- a) Lipase
- b) Pepsin
- c) Amylase
- d) Catalase

9. Biocatalysts operate under which type of reaction conditions?

- a) Extreme pH and temperature

TOPIC – 9

1. Microwave-induced synthesis in green chemistry is advantageous primarily because it:

- a) Reduces reaction efficiency
- b) Requires higher reaction temperatures
- c) Increases energy consumption
- d) Decreases reaction times and energy usage

2. The use of microwaves in organic synthesis is particularly effective for:

- a) Slow reactions
- b) Reactions requiring high pressure
- c) Stereoselective transformations
- d) Reactions with long reaction times

3. Which of the following is a key benefit of microwave-assisted reactions in green chemistry?

- a) Increased waste production
- b) Enhanced selectivity
- c) Reduced yield
- d) Longer reaction times

4. Microwave irradiation in green chemistry typically results in:

- a) Lower product purity
- b) Higher energy consumption
- c) Improved reaction selectivity
- d) Increased solvent usage

5. One advantage of microwave heating in organic synthesis is its ability to:

- a) Use toxic solvents effectively
- b) Facilitate controlled heating of reaction mixtures
- c) Generate toxic byproducts
- d) Decrease reaction rates

6. Which type of reactions benefit most from microwave-assisted techniques in green chemistry?

- a) Reactions requiring extreme pH conditions
- b) Heterogeneous catalytic reactions
- c) Aqueous-phase reactions
- d) Aromatic substitution reactions

7. Microwave-assisted reactions are known for their ability to:

- a) Increase the use of non-renewable resources
- b) Improve reaction kinetics and yield
- c) Produce hazardous intermediates
- d) Reduce product diversity

8. In microwave-induced synthesis, the dielectric heating effect primarily influences:

- a) Solid-phase reactions
- b) Liquid-phase reactions
- c) Gas-phase reactions
- d) Aqueous-phase reactions

9. Which aspect of microwave-assisted synthesis contributes significantly to its green chemistry profile?

- a) Use of toxic reagents
- b) Requirement for extreme reaction conditions
- c) Reduction of reaction times and energy usage
- d) Generation of non-biodegradable waste

10. The adoption of microwave irradiation in green chemistry aligns with which principle of sustainable chemistry?

- a) Use of non-renewable feedstocks
- b) Maximization of waste production
- c) Reduction of environmental impact
- d) Minimization of reaction efficiency

Answers

1. d) Decreases reaction times and energy usage

2. c) Stereoselective transformations

3. b) Enhanced selectivity

4. c) Improved reaction selectivity

5. b) Facilitate controlled heating of reaction mixtures

6. d) Aromatic substitution reactions

7. b) Improve reaction kinetics and yield

8. b) Liquid-phase reactions

9. c) Reduction of reaction times and energy usage

10. c) Reduction of environmental impact

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TOPIC – 10

1. The Fries rearrangement is typically used to:

- a) Reduce aromatic compounds
- b) Oxidize alcohols
- c) Rearrange acyl esters
- d) Hydrolyze amides

2. Under microwave conditions, the Fries rearrangement is favored because it:

- a) Requires longer reaction times
- b) Enhances product selectivity
- c) Produces toxic intermediates
- d) Reduces yield

3. Which of the following reagents is commonly used in the Fries rearrangement?

- a) Zinc dust
- b) Aluminum chloride
- c) Trifluoroacetic acid
- d) Chlorosulfonic acid

4. The Fries rearrangement involves the migration of an acyl group to:

- a) An alcohol
- b) A carbonyl group
- c) An aromatic ring
- d) An amine

5. Microwave-assisted Fries rearrangement reactions often lead to:

- a) Decreased reaction rates
- b) Increased reaction temperature requirements
- c) Improved reaction selectivity
- d) Higher solvent consumption

6. The product of the Fries rearrangement of phenyl acetate is:

- a) Phenol
- b) Benzoic acid
- c) Acetophenone
- d) Anisole

7. In the Fries rearrangement, the migration of the acyl group occurs via:

- a) Electrophilic aromatic substitution
- b) Nucleophilic addition
- c) Radical mechanism
- d) Rearrangement of carbocations

8. Compared to conventional heating methods, microwave-induced Fries rearrangement reactions typically exhibit:

- a) Lower yields
- b) Longer reaction times
- c) Higher reaction selectivity
- d) Greater use of toxic catalysts

9. The Fries rearrangement is widely used in the synthesis of:

- a) Aromatic ketones
- b) Aliphatic alcohols
- c) Saturated hydrocarbons
- d) Carboxylic acids

10. Microwave irradiation in the Fries rearrangement improves:

- a) Solvent polarity
- b) Reaction yield and efficiency
- c) Selective product formation
- d) Toxicity of the reagents

11. The Diels-Alder reaction involves the cycloaddition of a:

- a) Diketone and an alkene
- b) Alkene and a diene
- c) Alkyne and a diene
- d) Diketone and an alkyne

12. Under microwave conditions, the Diels-Alder reaction typically:

- a) Requires lower temperatures
- b) Proceeds faster with increased yield
- c) Generates more side products
- d) Has reduced regioselectivity

13. Which catalyst is commonly used in microwave-assisted Diels-Alder reactions?

- a) Palladium
- b) Silver nitrate
- c) Platinum
- d) Lewis acids

14. The Diels-Alder reaction is highly favored for its ability to form:

- a) Cyclic ketones
- b) Aromatic rings
- c) Six-membered rings
- d) Bridged bicyclic compounds

15. Microwave irradiation in the Diels-Alder reaction enhances:

- a) Use of toxic solvents
- b) Regioselectivity
- c) Production of enantiomers
- d) Reaction reversibility

16. The product of a Diels-Alder reaction is often:

- a) More reactive than the reactants
- b) A single diastereomer
- c) Less stable than the starting materials
- d) Highly toxic

17. Compared to traditional heating methods, microwave-assisted Diels-Alder reactions typically exhibit:

- a) Longer reaction times
- b) Lower overall yield

- c) Improved selectivity and yield
d) Greater need for high pressures
18. The Diels-Alder reaction is commonly used in the synthesis of:
a) Aromatic compounds
b) Polymers
c) Carbonyl compounds
d) Complex natural products
19. Microwave-induced Diels-Alder reactions are beneficial because they:
a) Increase the number of reaction steps
b) Use excess reagents
c) Reduce solvent usage
d) Produce toxic byproducts
20. The reaction mechanism of the Diels-Alder reaction involves:
a) Electrophilic attack on a diene
b) Nucleophilic attack on an alkene
c) Radical chain reaction
d) Concerted cycloaddition process
21. Decarboxylation involves the removal of a carboxyl group from:
a) Aromatic compounds
b) Alkyl halides
c) Carboxylic acids
d) Ketones
22. Under microwave conditions, decarboxylation reactions often require:
a) Higher reaction temperatures
b) Longer reaction times
c) Toxic solvents
d) Increased catalyst loading
23. Which of the following reagents is commonly used in microwave-assisted decarboxylation?
a) Sodium hydroxide
b) Silver nitrate
c) Copper sulfate
d) Palladium on carbon
24. The product of the decarboxylation of benzoic acid is:
a) Benzene
b) Benzaldehyde
c) Benzoic anhydride
d) Benzyl alcohol
25. Microwave irradiation in decarboxylation reactions enhances:
a) Reactivity of starting materials
b) Formation of side products
c) Yield and reaction rate
d) Toxicity of the reagents
26. The decarboxylation of acetic acid under microwave conditions yields:
a) Methane
b) Ethylene
c) Acetaldehyde
d) Methanol
27. Compared to conventional methods, microwave-induced decarboxylation reactions typically exhibit:
a) Lower selectivity
b) Higher energy consumption
c) Improved efficiency and selectivity
d) Longer reaction times
28. Decarboxylation is commonly employed in the synthesis of:
a) Aliphatic alcohols
b) Aromatic amines
c) Alkanes
d) Aromatic hydrocarbons
29. Microwave-assisted decarboxylation reactions are beneficial because they:
a) Increase waste production
b) Require toxic catalysts
c) Use excess reagents
d) Reduce reaction times and energy usage
30. The mechanism of decarboxylation involves the loss of:
a) A carboxyl group
b) A hydrogen atom
c) A hydroxyl group
d) A halogen atom
31. Saponification involves the hydrolysis of esters to yield:
a) Alcohols and carboxylic acids
b) Alkanes and ketones
c) Aldehydes and alcohols
d) Amines and alcohols
32. Under microwave conditions, saponification reactions typically:
a) Require acidic conditions
b) Proceed with increased reaction time
c) Use toxic solvents
d) Proceed rapidly with high yield
33. Which catalyst is commonly used in microwave-assisted saponification reactions?
a) Platinum
b) Sodium hydroxide
c) Palladium chloride
d) Silver nitrate
34. The product of the saponification of ethyl acetate is:
a) Ethanol and acetic acid
b) Ethanol and ethyl alcohol

TOPIC – 11

1. Ultrasound-assisted organic transformations in green chemistry are advantageous primarily because they:

- a) Increase reaction selectivity
- b) Require higher reaction temperatures
- c) Use toxic solvents effectively
- d) Generate large amounts of waste

2. The use of ultrasound in organic synthesis is particularly effective for:

- a) Reactions requiring high pressure
- b) Aromatic substitution reactions
- c) Catalyzing oxidation reactions
- d) Isomerization reactions

3. Ultrasound-assisted reactions in green chemistry are known for their ability to:

- a) Decrease reaction rates
- b) Enhance reaction kinetics
- c) Produce toxic byproducts
- d) Increase solvent usage

4. Ultrasound waves primarily induce chemical reactions by:

- a) Heating the reaction mixture
- b) Ionizing the reactants
- c) Agitating the reaction medium
- d) Catalyzing the reaction pathway

5. One advantage of ultrasound-assisted synthesis in organic chemistry is its ability to:

- a) Decrease reaction selectivity
- b) Require toxic catalysts
- c) Reduce reaction times and energy usage
- d) Increase the need for excessive heating

6. Ultrasound irradiation in organic transformations enhances:

- a) The need for inert atmosphere
- b) Production of toxic intermediates
- c) Yield and reaction rate
- d) Production of halogenated compounds

7. The mechanism of ultrasound-assisted reactions often involves:

- a) Radical chain reactions
- b) Slow diffusion of reactants
- c) Highly controlled reaction conditions
- d) Non-specific reaction pathways

8. Compared to conventional methods, ultrasound-assisted organic transformations typically exhibit:

- a) Longer reaction times
- b) Lower efficiency and selectivity
- c) Improved yield and selectivity
- d) Higher energy consumption

9. Ultrasound-assisted reactions are commonly employed in the synthesis of:

- a) Aromatic compounds
- b) Inorganic salts
- c) Non-polar solvents
- d) Alkaline metals

10. The application of ultrasound in green chemistry aligns with which principle of sustainable chemistry?

- a) Maximization of waste production
- b) Reduction of environmental impact
- c) Use of non-renewable feedstocks
- d) Increase in reaction temperature

11. Ultrasound waves are effective in promoting which type of reactions in organic synthesis?

- a) Gas-phase reactions
- b) Liquid-phase reactions
- c) Solid-phase reactions
- d) Aqueous-phase reactions

12. The product of ultrasound-assisted ozonolysis of alkenes is:

- a) Aldehydes
- b) Ketones
- c) Carboxylic acids
- d) Alcohols

13. Which catalyst is commonly used in ultrasound-assisted hydrogenation reactions?

- a) Platinum
- b) Silver nitrate
- c) Palladium chloride
- d) Sodium hydroxide

14. Ultrasound-assisted reactions are known for their ability to:

- a) Increase the need for high pressures
- b) Reduce solvent usage
- c) Produce toxic emissions
- d) Generate hazardous intermediates

15. The use of ultrasound in green chemistry is beneficial because it:

- a) Requires toxic solvents
- b) Uses non-biodegradable materials
- c) Minimizes environmental impact
- d) Increases reaction temperatures

16. Ultrasound-assisted synthesis in green chemistry often leads to:

- a) Lower reaction efficiency
- b) Higher reaction temperatures
- c) Enhanced reactivity of starting materials
- d) Decreased reaction rate

17. The application of ultrasound in organic transformations is advantageous due to its ability to:

- a) Increase toxicity of the reagents
- b) Enhance reaction complexity

- a) Increase energy consumption
- b) Enhance reaction rates
- c) Produce hazardous byproducts
- d) Facilitate solvent recycling

9. Which of the following is a common application of ionic liquids in chemical reactions?

- a) Extraction of inorganic salts
- b) Crystallization of proteins
- c) Hydrolysis of esters
- d) Catalyst recovery

10. The recyclability of ionic liquids as solvents in green chemistry is supported by their:

- a) High flammability
- b) Low biodegradability
- c) Ability to undergo phase separation
- d) Incompatibility with catalysts

11. Ionic liquids are beneficial in green chemistry because they:

- a) Require high temperatures for dissolution
- b) Produce toxic emissions
- c) Can replace traditional organic solvents
- d) Increase solvent volatility

12. The environmental benefit of using ionic liquids as solvents includes:

- a) Enhanced greenhouse gas emissions
- b) Reduction in air pollution
- c) Increased water usage
- d) Generation of non-biodegradable waste

13. Which type of reactions are particularly suitable for using ionic liquids as solvents?

- a) Aqueous-phase reactions
- b) Gas-phase reactions
- c) Solid-phase reactions
- d) Liquid-phase reactions

14. Ionic liquids are known for their ability to:

- a) Increase toxicity of reactants
- b) Facilitate separation of products
- c) Require excessive heating
- d) Reduce reaction selectivity

15. The unique property of ionic liquids that enhances their utility as green solvents is their:

- a) Low boiling point
- b) High polarity
- c) High vapor pressure
- d) High toxicity

16. The synthesis of pharmaceutical compounds using ionic liquids as solvents benefits from their:

- a) Inability to dissolve polar compounds
- b) High reactivity with metals
- c) Ability to stabilize reactive intermediates
- d) Low biocompatibility

17. Ionic liquids contribute to sustainability in chemical processes by:

- a) Increasing solvent waste
- b) Reducing energy efficiency
- c) Minimizing solvent usage

d) Requiring non-renewable feedstocks

18. The use of ionic liquids in green chemistry supports:

- a) Increased use of toxic catalysts
- b) Sustainable product development
- c) Enhanced water pollution
- d) Generation of hazardous emissions

19. Ionic liquids are effective solvents for biomass processing due to their:

- a) Inability to dissolve lignocellulosic materials
- b) High cost
- c) Ability to separate carbohydrates and lignin
- d) Limited catalytic activity

20. The application of ionic liquids in green chemistry promotes:

- a) Reduced selectivity in reactions
- b) Increased energy consumption
- c) Minimization of environmental impact
- d) Use of non-biodegradable materials

Answers

- 1. d) Possess negligible vapor pressure
- 2. a) Open vessel reactions
- 3. d) Non-renewable source
- 4. a) Hydrophobic compounds
- 5. d) Potential for recycling and reuse
- 6. b) Reduction of environmental impact
- 7. a) Lower toxicity
- 8. b) Enhance reaction rates
- 9. d) Catalyst recovery
- 10. c) Ability to undergo phase separation
- 11. c) Can replace traditional organic solvents
- 12. b) Reduction in air pollution
- 13. d) Liquid-phase reactions
- 14. b) Facilitate separation of products
- 15. b) High polarity
- 16. c) Ability to stabilize reactive intermediates
- 17. c) Minimizing solvent usage
- 18. b) Sustainable product development
- 19. c) Ability to separate carbohydrates and lignin
- 20. c) Minimization of environmental impact

XX

TOPIC – 14

1. Supercritical carbon dioxide (scCO₂) is considered a green solvent primarily because it:

- a) Is derived from fossil fuels
- b) Has high toxicity
- c) Is non-flammable
- d) Produces hazardous waste

2. The critical temperature and pressure of carbon dioxide are approximately:

- a) 0°C and 1 atm
- b) 31°C and 1 atm
- c) 100°C and 1 atm
- d) 31°C and 10 atm

3. In supercritical carbon dioxide, the density and solvation power can be controlled by adjusting:

- a) Temperature and pressure
- b) pH and ionic strength
- c) Catalyst concentration
- d) Stirring rate

4. One advantage of using scCO₂ as a green solvent is its:

- a) Low cost
- b) High flammability
- c) Limited availability
- d) Incompatibility with organic compounds

5. Carbon dioxide becomes supercritical at:

- a) Low temperatures and low pressures
- b) High temperatures and high pressures
- c) Low temperatures and high pressures
- d) High temperatures and low pressures

6. Which property of scCO₂ makes it suitable for extraction processes in green chemistry?

- a) High vapor pressure
- b) High viscosity
- c) Low surface tension
- d) Low reactivity

7. Compared to traditional organic solvents, scCO₂ typically exhibits:

- a) Higher toxicity
- b) Lower solvent power
- c) Lower selectivity
- d) Higher diffusivity

8. The green chemistry principle that aligns with the use of scCO₂ is:

- a) Maximization of waste production
- b) Reduction of environmental impact
- c) Use of non-renewable feedstocks
- d) Increase in reaction temperature

9. Supercritical carbon dioxide is commonly used in which type of processes?

- a) High-temperature catalysis

- b) Low-pressure polymerization
- c) Extraction and purification
- d) Aqueous-phase reactions

10. The recyclability of scCO₂ as a solvent in green chemistry is supported by its:

- a) High reactivity with metals
- b) Low biodegradability
- c) Ability to undergo phase separation
- d) Incompatibility with catalysts

Answers

- 1. c) Is non-flammable
- 2. b) 31°C and 1 atm
- 3. a) Temperature and pressure
- 4. a) Low cost
- 5. b) High temperatures and high pressures
- 6. c) Low surface tension
- 7. b) Lower solvent power
- 8. b) Reduction of environmental impact
- 9. c) Extraction and purification
- 10. c) Ability to undergo phase separation

XX

TOPIC – 15

1. Ethyl lactate is derived from:

- a) Petroleum
- b) Natural gas
- c) Lactic acid
- d) Ethanol

2. One advantage of ethyl lactate as a green solvent is its:

- a) High toxicity
- b) Low biodegradability
- c) Renewable sourcing
- d) Non-renewable feedstock

3. Ethyl lactate is commonly used in:

- a) High-temperature reactions
- b) Extraction processes
- c) Gas-phase reactions
- d) Electrochemical applications

4. The green chemistry principle that aligns with the use of ethyl lactate is:

- a) Maximization of waste production
- b) Reduction of environmental impact
- c) Use of non-renewable solvents
- d) High energy consumption

5. Ethyl lactate is biodegradable, which means it:

- a) Accumulates in the environment
- b) Poses a long-term hazard
- c) Breaks down naturally over time
- d) Requires special disposal methods

6. Compared to traditional solvents, ethyl lactate typically exhibits:

- a) Higher cost
- b) Lower solvation power
- c) Greater toxicity
- d) Lower volatility

7. The production of ethyl lactate involves the esterification of lactic acid with:

- a) Acetic acid
- b) Ethanol
- c) Hydrochloric acid
- d) Sodium hydroxide

8. Ethyl lactate is effective in which type of chemical reactions?

- a) Non-polar reactions
- b) Aqueous-phase reactions
- c) Gas-phase reactions
- d) High-pressure reactions

9. The recyclability of ethyl lactate as a solvent in green chemistry is supported by its:

- a) Ability to form stable emulsions
- b) Low biodegradability

- c) Compatibility with non-renewable resources
- d) Ease of recovery and reuse

10. Ethyl lactate is particularly suitable for applications requiring:

- a) High temperatures
- b) Low volatility
- c) Rapid evaporation
- d) Inert atmosphere

Answers

- 1. c) Lactic acid
- 2. c) Renewable sourcing
- 3. b) Extraction processes
- 4. b) Reduction of environmental impact
- 5. c) Breaks down naturally over time
- 6. d) Lower volatility
- 7. b) Ethanol
- 8. b) Aqueous-phase reactions
- 9. d) Ease of recovery and reuse
- 10. b) Low volatility

XX

TOPIC – 16

1. 1,3-Dipolar cycloadditions typically involve which type of intermediates?

- a) Carbocations
- b) Carbanions
- c) Carbenes
- d) 1,3-Dipoles

2. Which of the following is an example of a 1,3-dipole used in cycloaddition reactions?

- a) Ethylene
- b) Azide ion
- c) Propene
- d) Benzene

3. A typical catalyst used to promote 1,3-dipolar cycloadditions in aqueous phases is:

- a) Palladium
- b) Platinum
- c) Copper
- d) Silver

4. In aqueous phase 1,3-dipolar cycloadditions, the solvent of choice is often:

- a) Acetonitrile
- b) Water
- c) Benzene
- d) Toluene

5. The regioselectivity of 1,3-dipolar cycloaddition reactions is influenced by:

- a) Temperature
- b) Catalyst concentration
- c) Nature of the dipole and dipolarophile
- d) pH of the medium

Carbon-Carbon Bond Forming Processes

6. Suzuki-Miyaura cross-coupling reactions in aqueous phases typically employ:

- a) Palladium catalysts
- b) Silver catalysts
- c) Nickel catalysts
- d) Iron catalysts

7. Green chemistry aspects of aqueous-phase carbon-carbon bond forming processes include:

- a) High solvent usage
- b) Toxic metal catalysts
- c) Non-renewable starting materials
- d) Minimal waste generation

8. In aqueous Sonogashira reactions, which of the following is a common catalyst?

- a) Copper iodide
- b) Palladium chloride
- c) Nickel sulfate
- d) Silver nitrate

9. Aqueous Heck reactions are known for their ability to form carbon-carbon bonds using:

- a) Organoboranes
- b) Organomagnesium compounds
- c) Organosilicon compounds
- d) Organohalides

10. Aqueous-phase Stille reactions involve the coupling of organic halides with:

- a) Organotin compounds
- b) Organomercury compounds
- c) Organolead compounds
- d) Organocopper compounds

11. In aqueous-phase bromination reactions, bromine is often used in the form of:

- a) Bromine water ($\text{Br}_2/\text{H}_2\text{O}$)
- b) Bromine gas (Br_2)
- c) Hydrobromic acid (HBr)
- d) Sodium bromide (NaBr)

12. The regioselectivity of aqueous-phase bromination reactions is influenced by:

- a) Temperature
- b) pH of the medium
- c) Solvent polarity
- d) Catalyst concentration

13. Aqueous-phase bromination of aromatic compounds often requires the presence of:

- a) Palladium catalysts
- b) Copper catalysts
- c) Bromide ions
- d) Nickel catalysts

14. Which type of bromination reaction is typically used for adding bromine to alkenes?

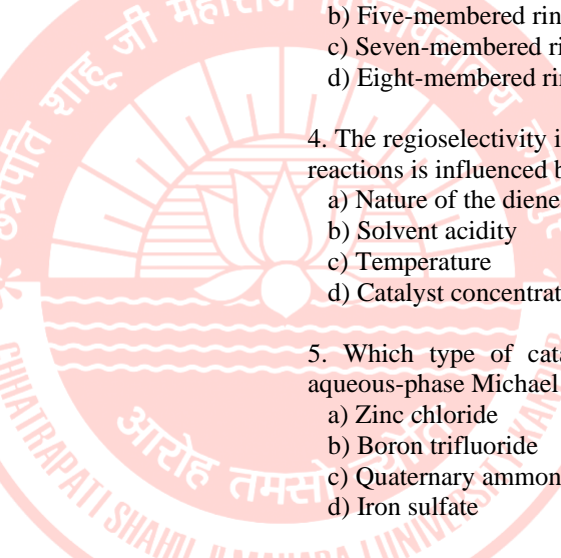
- a) Electrophilic bromination
- b) Nucleophilic bromination
- c) Free radical bromination
- d) Acid-catalyzed bromination

15. The environmental benefit of aqueous-phase bromination reactions includes:

- a) Increased toxic emissions
- b) Reduced solvent usage
- c) Higher energy consumption
- d) Enhanced waste generation

Answers

- 1. d) 1,3-Dipoles
- 2. b) Azide ion
- 3. c) Copper
- 4. b) Water
- 5. c) Nature of the dipole and dipolarophile
- 6. a) Palladium catalysts
- 7. d) Minimal waste generation
- 8. a) Copper iodide

- 
- compound?
- Six-membered rings
 - Five-membered rings
 - Seven-membered rings
 - Eight-membered rings
4. The regioselectivity in aqueous-phase Michael addition reactions is influenced by the:
- Nature of the diene and dienophile
 - Solvent acidity
 - Temperature
 - Catalyst concentration
5. Which type of catalyst is most effective for the aqueous-phase Michael addition reaction?
- Zinc chloride
 - Boron trifluoride
 - Quaternary ammonium salts
 - Iron sulfate
6. The aqueous-phase Grignard reaction is used for the synthesis of:
- Carbon-Carbon Bond Forming
 - Carbon-Nitrogen Bond Forming
 - Carbon-Oxygen Bond Forming
 - Carbon-Hydrogen Bond Forming

- a) Phosphorus ylides
- b) Organoboranes
- c) Grignard reagents

- d) Diimide reagents
9. Which of the following is a common catalyst in aqueous-phase Suzuki-Miyaura cross-coupling reactions?
- Platinum
 - Nickel
 - Palladium
 - Iron
10. Aqueous-phase Heck reactions are known for their ability to couple olefins with:
- Alkyl halides
 - Aryl halides
 - Acyl halides
 - Vinyl halides
11. The aqueous-phase Wohl-Ziegler bromination reaction typically involves the use of:
- Acetic acid
 - Hydrobromic acid
 - Bromine gas
 - Potassium bromide
12. In aqueous-phase electrophilic bromination of phenols, the electrophile attacking the aromatic ring is:
- HBr
 - Br₂
 - Br⁻
 - BrO₃⁻
13. Aqueous-phase NBS bromination reactions are selective for brominating:
- Allylic positions
 - Aromatic rings
 - Aliphatic carbons
 - Carbonyl groups
14. Bromohydrin formation in aqueous phase involves the addition of bromine to:
- Alcohols
 - Alkenes
 - Alkynes
 - Aldehydes
15. The environmental advantage of aqueous-phase bromination reactions includes:
- Increased energy consumption
 - Use of toxic catalysts
 - Reduced use of organic solvents
 - Generation of hazardous byproducts
6. b) Carbonyl compounds
7. d) Aldehydes and active methylene compounds
8. a) Phosphorus ylides
9. c) Palladium
10. b) Aryl halides
11. c) Bromine gas
12. b) Br₂
13. a) Allylic positions
14. b) Alkenes
15. c) Reduced use of organic solvents
- XX

Answers

- b) Azide ion
- a) Tetrazoles
- a) Six-membered rings
- a) Nature of the diene and dienophile
- c) Quaternary ammonium salts

TOPIC – 18

1. Green synthesis of nanomaterials aims to:

- a) Increase toxic waste
- b) Use harmful chemicals
- c) Minimize environmental impact
- d) Produce high-energy emissions

2. Which of the following is a common green precursor used in nanomaterial synthesis?

- a) Benzene
- b) Sodium borohydride
- c) Formaldehyde
- d) Dichloromethane

3. Green synthesis methods often utilize _____ as a reducing agent.

- a) Hydrogen peroxide
- b) Sodium hydroxide
- c) Chloroform
- d) Sulfuric acid

4. Plant extracts and microorganisms are examples of _____ used in green synthesis.

- a) Toxic chemicals
- b) Hazardous waste
- c) Biological agents
- d) Synthetic polymers

5. The principle behind green synthesis includes:

- a) Maximizing energy consumption
- b) Minimizing solvent usage
- c) Using non-renewable resources
- d) Increasing greenhouse gas emissions

6. Which solvent is commonly avoided in green synthesis due to its environmental impact?

- a) Water
- b) Acetone
- c) Ethanol
- d) Toluene

7. Green synthesis of metallic nanoparticles often involves which of the following techniques?

- a) Microwave irradiation
- b) Incineration
- c) Acid washing
- d) Steam distillation

8. Which of the following is a characteristic of green-synthesized nanomaterials?

- a) High toxicity
- b) Low stability
- c) Biocompatibility
- d) Inertness

9. The use of _____ in green synthesis reduces the need for high temperatures.

- a) Inorganic solvents

- b) Microwave radiation
- c) Surfactants
- d) Sunlight

10. Green synthesis methods contribute to sustainable development by:

- a) Increasing carbon footprint
- b) Generating non-biodegradable waste
- c) Decreasing environmental impact
- d) Using hazardous chemicals

11. The biogenic synthesis of nanoparticles involves:

- a) Chemical reduction
- b) Physical vapor deposition
- c) Biological entities
- d) High pressure

12. Which of the following is an advantage of green synthesis over conventional methods?

- a) Increased energy consumption
- b) Reduced reaction selectivity
- c) Enhanced toxic byproducts
- d) Mild reaction conditions

13. Green synthesis of nanomaterials is aligned with which of the following principles of green chemistry?

- a) Minimization of waste
- b) Maximize use of non-renewable resources
- c) Increase energy consumption
- d) Use of toxic solvents

14. The growth of metal nanoparticles using green methods often involves:

- a) Agitation
- b) High-speed centrifugation
- c) Ionizing radiation
- d) Magnetic fields

15. Which of the following is an example of a plant extract used in green synthesis?

- a) Benzene
- b) Ascorbic acid
- c) Sulfuric acid
- d) Ethyl acetate

16. Green synthesis methods prioritize the use of _____ as a stabilizing agent.

- a) Toxic chemicals
- b) Bio-based polymers
- c) Heavy metals
- d) Chlorinated solvents

17. The biosynthesis of nanomaterials often involves:

- a) Complex chemical reactors
- b) Precipitation from non-aqueous solvents
- c) Enzymatic activity
- d) High-energy ion bombardment

18. Green synthesis is advantageous in reducing _____ during nanomaterial production.

19. The environmental impact of green-synthesized nanomaterials is typically:
- a) Higher than conventional methods
 - b) Lower due to reduced waste and energy consumption
 - c) Unaffected by synthesis conditions
 - d) Negatively influenced by solvent choice
20. Which technique is commonly employed to characterize green-synthesized nanomaterials?
- a) Ultraviolet (UV) spectroscopy
 - b) Incineration analysis
 - c) Landfill assessment
 - d) Chemical oxidation

1. c) Minimize environmental impact
2. b) Sodium borohydride
3. a) Hydrogen peroxide
4. c) Biological agents
5. b) Minimizing solvent usage
6. d) Toluene
7. a) Microwave irradiation
8. c) Biocompatibility
9. d) Sunlight
10. c) Decreasing environmental impact
11. c) Biological entities
12. d) Mild reaction conditions
13. a) Minimization of waste
14. a) Agitation
15. b) Ascorbic acid
16. b) Bio-based polymers
17. c) Enzymatic activity
18. c) Toxicity levels
19. b) Lower due to reduced waste and energy consumption
20. a) Ultraviolet (UV) spectroscopy

- a) Proteins
- b) Lipids
- c) Sugars

9. Green synthesis methods prioritize the use of _____ to ensure biocompatibility and environmental safety.

10. Which characterization technique is commonly used to confirm the magnetic properties of green-synthesized nanoparticles?

- ## Answers

1. d) Organic solvents
2. d) Plant extract reduction
3. b) Sodium borohydride
4. c) Minimal waste generation
5. a) Ferrite nanoparticles
6. b) Biological molecules
7. b) Minimization of waste
8. d) All of the above
9. c) Renewable feedstocks
10. c) Vibrating sample magnetometry (VSM)

XX

1. Microwave-assisted nanocatalysis in water offers advantages such as:

2. The use of microwaves in nanocatalysis primarily accelerates reactions by:

3. In microwave-assisted nanocatalysis, nanoparticles act as catalysts to facilitate reactions:

- a) With lower efficiency
- b) Under anaerobic conditions
- c) At reduced reaction rates
- d) With improved kinetics

4. Green chemistry principles are supported in microwave-assisted nanocatalysis due to:

- a) Reduced energy efficiency
- b) Increased waste production
- c) Enhanced reaction control
- d) Use of hazardous solvents

5. Which type of nanoparticles are commonly used in microwave-assisted nanocatalysis?

- a) Water-insoluble nanoparticles
b) Platinum nanoparticles
c) Toxic metal nanoparticles
d) None of the above

6. The application of microwaves in nanocatalysis often leads to:

- a) Decreased reaction rates
- b) Lower reaction yields
- c) Improved reaction selectivity
- d) Increased reaction times

7. Microwave heating in nanocatalysis is advantageous because it:

- a) Requires inert atmospheres
- b) Enhances reaction temperatures uniformly
- c) Requires toxic catalysts
- d) Decreases reaction control

8. In water-based microwave-assisted nanocatalysis, which property of water contributes to the efficiency of the process?

- a) Low heat capacity
- b) High dielectric constant
- c) Low boiling point
- d) High viscosity

TOPIC – 21

1. Bacteria are commonly used in nanoparticle synthesis due to their ability to:

- a) Generate toxic byproducts
- b) Release harmful radiation
- c) Produce extracellular enzymes
- d) Decrease reaction selectivity

2. Which bacterial genus is frequently employed for silver nanoparticle synthesis?

a) Escherichia
b) Bacillus
c) Staphylococcus
d) Streptococcus

3. The biosynthesis of gold nanoparticles by bacteria typically involves:

- a) Intracellular reduction
- b) High-temperature processing
- c) Chemical precipitation
- d) Mechanical grinding

- a) High energy consumption
- b) Use of toxic solvents
- c) Environmentally benign process
- d) Low reaction efficiency

5. The green chemistry principle supported by bacterial nanoparticle synthesis is:

- a) Maximization of waste
- b) Use of non-renewable resources
- c) Minimization of toxicity
- d) High solvent usage

6. Yeast-mediated synthesis of nanoparticles often utilizes:

- a) Organic solvents
- b) Carbon dioxide
- c) Reducing sugars
- d) Toxic heavy metals

7. Which yeast species is known for its ability to synthesize selenium nanoparticles?

- Saccharomyces cerevisiae*
- Candida albicans*
- Aspergillus niger*
- Pseudomonas aeruginosa*

8. The role of yeast in nanoparticle synthesis primarily involves:

- Intracellular accumulation
- Extracellular reduction

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