Semester-I

ELECTIVE I
19CHP105-A GREEN CHEMISTRY 4H 4C

Instruction Hours/week: L:4 T:0 P:0 Marks: Internal:40 External: 60 Total:100
External Semester Exam: 3 Hrs

Course Objectives

1. To introduce the concept of Green chemistry.
2. To introduce the 12 principles of Green chemistry as well as the tools of Green chemistry.
3. To demonstrate how to evaluate a reaction or process and determine “Greener” alternatives.
4. To focus on the application of greener routes to improve industrial processes and to produce important products.

Course outcomes

The student understood the following

1. Designed of chemical products and processes that reduce or eliminate the use and generation of hazardous substances.
2. Created awareness for reducing waste, minimizing energy consumption in organic synthesis.
3. Implemented techniques of green synthesis in organic reactions
4. Used the various alternative resources for green technology in organic synthesis.
5. Applied the concept of microwaves and ionic liquids in various chemical reactions.

UNIT I- Introduction to Green Chemistry and Principles of Green Chemistry

What is Green Chemistry? Need for Green Chemistry. Goals of Green Chemistry. Limitations/ Obstacles in the pursuit of the goals of Green Chemistry. Twelve principles of Green Chemistry with their explanations.

UNIT II-Designing a Green Chemical synthesis

Designing a Green synthesis using these principles: prevention of waste/ byproducts; maximum incorporation of the materials used in the process into the final products, atom economy, and calculation of atom economy of the rearrangement, addition, substitution and elimination reactions. Green solvents–supercritical fluids, water as a solvent for organic reactions, ionic liquids, fluorous biphasic solvent, PEG, solvent less processes, immobilized solvents and how to compare greenness of solvents.

UNIT III – Alternative sources of Energy

Energy requirements for reactions – alternative sources of energy: use of microwaves and ultrasonic energy. Microwave assisted reactions in water: Hofmann elimination, methyl benzoate to benzoic acid, oxidation of toluene and alcohols; microwave assisted reactions in organic solvents. Diels-Alder reaction and decarboxylation reaction. Ultrasound assisted reactions: sono chemical Simmons-Smith Reaction (Ultrasonic alternative to iodine).

UNIT IV- Green synthesis/reaction

Green starting materials, Green reagents, Green solvents, reaction conditions, Green catalysis and Green synthesis- Real world cases (Traditional processes and green ones) Synthesis of Ibuprofen, Adipic acid , disodium iminodiacetate (alternative to Strecker synthesis).

UNIT V- Hazard assessment and mitigation in chemical industry

Future trends in Green Chemistry-oxidation-reduction reagents and catalysts; biomimetic, multifunctional reagents; Combinatorial green chemistry; Proliferation of solventless reactions; Noncovalent derivatization. Biomass conversion, emission control and biocatalysis.

SUGGESTED READINGS

1. Ahluwalia, V. K., & Kidwai, M. (2007). New Trends in Green Chemistry (II Edition). New Delhi: Anamalaya Publisher.
2. Anastas, P. T., & Warner, J. C. (1998). Green Chemistry: Theory and Practice. Oxford: Oxford University Press.
3. Matlack, A. S. (2001). Introduction to Green Chemistry. New York: Marcel Dekker.
4. Cann, M. C., & Connely, M. E. (2000). Real-World cases in Green Chemistry. Washington: American Chemical Society.
5. Ryan, M. A., & Tinnesand, M. (2002). Introduction to Green Chemistry, Washington: American Chemical Society.
6. Lancaster, M. (2010). Green Chemistry: An Introductory Text (II Edition). Cambridge: RSC Publishing.
7. Clark, J. H, & Macquarrie, D. J. (2002). Handbook of Green Chemistry & Technology. Abingdon: Blackwell Publishing.

Karpagam Academy of Higher Education
(Established Under Section 3 0f UGC Act,1956)
Coimbatore – 641021

Department of Chemistry

Lecture Plan

Incharge Staff : Dr. K. Sundaram
Class : I M.Sc. Chemistry
Title : Green Chemistry
Subject code :19CHP105-A
Total hours : 48

UNIT-I

Hour's required-7

S. No	Lecture Hour	Topics	Support Material
1	1	Green chemistry-Introduction	T1: 1
2	1	Need for green chemistry	T1:1-2
3	1	Goals of green chemistry, Limitations of green chemistry	T2:684-685
4	1	Twelve principles of green chemistry(1-4) with explanations	T1:2-5
5	1	Twelve principles of green chemistry(5-8) with explanations	T1:5-7
6	1	Twelve principles of green chemistry(9-12) with explanations	T1:8-11
7	1	Recapitulation and discussion of important questions	

SUPPORTING MATERIALS:

TEXT BOOKS

T1. V.K. Ahluwalia, 2012, Green Chemistry, Ane Books Pvt. Ltd., NewDelhi-110 002.

T2. Asim K. Das, 2015, Environmental Chemistry with Green Chemistry, Books and Allied (P) Ltd, Kolkata-700010

UNIT-II

Hours required-8

S.No	Lecture Hour	Topics	Support Material
1	1	Prevention of waste/ byproducts	T2: 667-669
2	1	Atom economy-calculation of atom economy	T1: 2-3
3	1	Atom economy of rearrangement and addition reaction	T1: 3
4	1	Atom economy of substitution and elimination reactions	T1: 3-5
5	1	Green solvents- Supercritical fluids, Water as solvent for organic reactions	T2: 669, 695-696, 699 T1: 251
6	1	Ionic liquids, Fluorous biphasic solvent	T1:15
7		PEG, solvent less processes, Immobilized solvents, comparison of greenness solvents	T1:66, 267
8	1	Recapitulation and discussion of important questions	

SUPPORTING MATERIALS:

TEXT BOOKS

T1. V.K. Ahluwalia, 2012, Green Chemistry, Ane Books Pvt. Ltd., NewDelhi-110 002.

T2. Asim K. Das, 2015, Environmental Chemistry with Green Chemistry, Books and Allied (P) Ltd, Kolkata-700010

UNIT-III

Hours required-8

S.No	Lecture Hour	Topics	Support Material
1	1	Alternative sources of energy, Use of microwave and ultrasonic energy	R2:22 T2: 692-695
2	1	Microwave assisted reactions in water	T1:227-229
3	1	Hoffmann elimination, methyl benzoate to benzoic acid	T1:171
4	1	Oxidation of toluene and alcohols,	R1:170-171
5	1	Microwave assisted reactions in organic solvents	R2:401
6		Diels-Alder reaction and decarboxylation reaction	T1:116
7	1	Ultrasound assisted reactions, Simmons-smith reaction	T1:16, 30, 296 T1:217
8	1	Recapitulation and discussion of important questions	

SUPPORTING MATERIALS:

TEXT BOOKS

T1. V.K. Ahluwalia, 2012, Green Chemistry, Ane Books Pvt. Ltd., NewDelhi-110 002.

REFERANCE BOOK

R1: Roger Arthur Sheldon, Isabel Arends, and Ulf Hanefeld, 2017, Green Chemistry and Catalysis, WILEY-VCH Verlag Gmbh & Co. KGaA.

UNIT-IV

Hour's required-8

S.No	Lecture Hour	Topics	Support Material
1.	1	Green starting materials, green reagents	R2:314
2	1	Green solvents, reaction conditions	T2:695
3	1	Green catalysis, Green synthesis-Real world cases (traditional processes and green ones)	R2:316 R2:284
4	1	Synthesis of Ibuprofen	T2:690-691
5	1	Synthesis Adipic acid	T2:693, 715
6	1	Synthesis disodium iminodiacetate (alternative to strecker synthesis)	T2: 694, 727
7	1	Recapitulation and discussion of important questions	

SUPPORTING MATERIALS:

TEXT BOOK

T2. Asim K. Das, 2015, Environmental Chemistry with Green Chemistry, Books and Allied (P) Ltd, Kolkata-700010

REFERANCE BOOK

R2. James Clark & Duncun Macquarrie, 2012, Hand Book of Green Chemistry and Technology, Blackwell Science Ltd.

UNIT-V

Heterocyclic compounds: **Hours required-10**

S.No	Lecture Hour	Topics	Support Material
1	1	Future trends in green chemistry	R1: 409
2	1	Oxidation –reduction reagents	R2: 241
3	1	Oxidation–reduction catalysts, Biomimetic, multifunctional reagents	R1: 14, 18
4	1	Proliferation of solvent less reactions, noncovalent derivatization,	T1: 267

		Combinatorial green chemistry	
5	1	Biomass conversion	T2: 661, R2: 355
6	1	Emission control	T2: 200-201
7	1	Bio catalysis	R1: 29
8	1	Recapitulation and discussion of important questions	
9	1	Previous year ESE question paper discussion	
10	1	Previous year ESE question paper discussion	

SUPPORTING MATERIALS:

TEXT BOOK

T2. Asim K. Das, 2015, Environmental Chemistry with Green Chemistry, Books and Allied (P) Ltd, Kolkata-700010

REFERANCE BOOKS

R1: Roger Arthur Sheldon, Isabel Arends, and Ulf Hanefeld, 2017, Green Chemistry and Catalysis, WILEY-VCH Verlag Gmbh & Co. KGaA.

R2. James Clark & Duncun Macquarrie, 2012, Hand Book of Green Chemistry and Technology, Blackwell Science Ltd.

UNIT-I

SYLLABUS

Introduction to Green Chemistry and Principles of Green Chemistry:
What is Green Chemistry? Need for Green Chemistry.Goals of Green Chemistry.Limitations/ Obstacles in the pursuit of the goals of Green Chemistry.Twelve principles of Green Chemistry with their explanations.

Green chemistry

1. The term *green chemistry* was coined by Paul Anastas in 1991.
2. It is also called as sustainable chemistry
3. It is a philosophy of chemical research and engineering that encourages the design of products and processes that minimize the use and generation of hazardous substances.
4. Green chemistry seeks to reduce and prevent pollution at its source.
5. Green chemistry applies to organic chemistry, inorganic chemistry, biochemistry, analytical Chemistry, and even physical chemistry.
6. It seems to focus on industrial applications. The focus is on minimizing the hazard and maximizing the efficiency of any chemical choice.

Difference between Green chemistry and Enviornmental chemistry

EnvironmentalChemistry is the chemistry of the natural environment, and of pollutant chemicals in nature, It does apply to any chemistry. It is distinct from environmental chemistry which focuses on chemical phenomena in the environment.

Recent key developments in green chemistry:

1. Use of supercritical carbon dioxide as green solvent,
2. Use of aqueous hydrogen peroxide for clean oxidations
3. Use of hydrogen in asymmetric synthesis.
4. On water reactions, and

5. Dry media reactions.

Definition of Green Chemistry

Green Chemistry is defined as the design of chemical products and processes that reduce and/or eliminate the use and/or the generation of hazardous substances.

This approach requires an open and interdisciplinary view of material and product design, applying the principle that it is better to consider waste prevention options during the design and development phase, rather than disposing or treating waste after a process or material has been developed.

Through a principle-based approach, green chemistry results in increased efficiency, reduced hazards and the elimination of waste.

The symptoms of good product design

Designing safer, economical, and efficacious processes and products.

All of these aspects can result in economic benefit for institutions that implement these practices. Green Chemistry offers a concrete path to achieve sustainable and safe laboratory practices.

What is Sustainability

Sustainability is most commonly defined as:

"Development that meets the needs of the present without compromising the ability of future generations to meet their own needs."

It's about innovative and environmentally sustainable products that compete in a global economy. It's about achieving the highest standards of safety, health and environmental stewardship. It's about being responsible to our customers, our employees, the community and our planet.

Nobel Prize for Green Chemistry

The 2005 Nobel Prize for Chemistry was awarded for "the development of the metathesis method in organic synthesis,"

The Nobel Prize Committee states that, "this represents a great step forward for 'green chemistry', reducing potentially hazardous waste through smarter production. Metathesis is an example of how important basic science has been applied for the benefit of man, society and the environment."

Tools used in the Green Chemistry

1. Avoiding hazardous materials

Polystyrene foam is a common material used in packing and food transportation.

Traditionally, CFC and other ozone-depleting chemicals were used in the production process of the foam sheets, presenting a serious environmental hazard.

Flammable, explosive, and toxic hydrocarbons have also been used as CFC replacements, but they present their own problems.

Dow Chemical discovered that **supercritical carbon dioxide** works well as a blowing agent, without the need for hazardous substances, allowing the polystyrene to be more easily recycled.

The CO_2 used in the process is reused from other industries, so the net carbon released from the process is zero.

For this in 1996, Dow Chemical won the 1996 Greener Reaction Conditions award.

2. Reneawable raw materials

a. **Polylactic acid Polymerization process**.

Lactic acid is produced by fermenting corn and converted to lactide, using tin-catalyzed cyclization.

The polymer, is used in textiles, cutlery, and food packaging.

The process substitutes renewable materials for petroleum feedstocks, doesn't require the use of hazardous organic solvents, and results in a high-quality polymer that is recyclable and compostable.

In 2002, Nature Works won the Greener Reaction Conditions Award for their improved

polylactic acid polymerization process.

b. **Production and downstream applications of bio-based succinic acid.**

Succinic acid is a platform chemical that is an important starting material in the formulations of everyday products.

Traditionally, succinic acid is produced from petroleum-based feedstocks.
BioAmber has developed a technology that produces succinic acid from the fermentation of renewable feedstocks at a lower cost and lower energy expenditure than the petroleum equivalent while sequestering CO_2 rather than emitting it.
In 2011, the Outstanding Green Chemistry Accomplishments by a Small Business Award went to BioAmber Inc.

3. Reduction of waste products

Enztyme interesterification process.

A clean, enzymatic process for the interesterification of oils and fats by interchanging saturated and unsaturated fatty acids.

The result is commercially viable products without *trans*-fats(For the human health benefits)

The process has reduced the use of toxic chemicals and water, prevents vast amounts of byproducts, and reduces the amount of fats and oils wasted.

In 2005, Novozymes was awarded the Greener Synthetic Pathways Award

5. Catalyst

Converting waste glycerin from biodiesel production to propylene glycol.

Through the use of a copper-chromite catalyst he was able to lower the required temperature of conversion while raising the efficiency of the distillation reaction.

Propylene glycol produced in this way could be cheap enough to replace the more toxic ethylene glycol that is the primary ingredient in automobile antifreeze.

In 2006, Professor Galen J. Suppes, from the University of Missouri in Columbia, was awarded the Academic Award

6. Microwave Oven

A reaction which is closer to a true solventless reaction is a Knoevenagel condensation of ketones with (malononitrile) where a 1:1 mixture of the two reactants (and ammonium acetate) is irradated in a microwave oven.

7. Selection of solvents

Ionic liquids

The choice of solvent is the main component of a reaction system by volume (approx. 90%).

Chlorinated solvents should be avoided, as many of these solvents are toxic and volatile, and are implicated in the destruction of the ozone layer.

Alternative solvents include ionic liquids, for example, which are non-volatile and can provide non-aqueous reaction media of varying polarity.

Ionic liquids have significant potential, since if systems can be developed in which the products can be removed by extraction or distillation and the catalyst remains in the ionic liquid.

The solvent and the catalyst can be reused.

Water as a solvent

The solvent of choice for green chemistry is water, which is a non-toxic liquid but with limited chemical compatibility.

The Diels-Alder Reaction are often even accelerated when run in an aqueous medium, while on the other hand, many reactants and reagents, including most organometallic compounds, are totally incompatible with water.

Supercritical CO_2 medium

Chemical reactions run under neat conditions (no solvent) and in a supercritical CO_2 medium can also be considered as green choices.

Green Chemistry

A traditional concept in process chemistry has been the optimization of the Reaction time and yield.

From our modern perspective, this limited viewpoint must be enlarged,

For example

1. toxic wastes can destroy natural resources.

2. Many feedstocks for the production of chemicals are based on petroleum, which is not a renewable resource.

In order to address the following points :

1.What alternatives can be developed and used.

2. we must ensure that future generations can also use these new alternatives.

3. "Sustainability" is a concept that is used to distinguish methods and processes that can ensure the long-term productivity of the environment, so that even subsequent generations of humans can live on this planet. Sustainability has environmental, economic, and social dimensions.

Paul Anastas of the U.S. Environmental Protection Agency formulated some simple rules of thumb for how sustainability can be achieved in the production of chemicals - the "Green chemical principles":

The principles cover such concepts as:

- the design of processes to maximize the amount of raw material that ends up in the product;
- the use of safe, environment-benign substances, including solvents, whenever possible;
- the design of energy efficient processes;
- the best form of waste disposal: not to create it in the first place.

The 12 principles are:

1. It is better to prevent waste than to treat or clean up waste after it is formed.
2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. Chemical products should be designed to preserve efficacy of function while reducing toxicity.
5. The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
6. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
7. A raw material or feedstock should be renewable rather than depleting wherever technically and economically practicable.
8. Reduce derivatives - Unnecessary derivatization (blocking group, protection/ deprotection, temporary modification) should be avoided whenever possible.
9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.
11. Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. Substances and the form of a substance used in a chemical process should be chosen to minimize potential for chemical accidents, including releases, explosions, and fires.

1. It is better to prevent waste than to treat or clean up waste after it is formed.

It is most appropriate to carry out a synthesis by following a pathway so that formation of waste is minimum or absent. One type of waste product common and often avoidable is the starting material or reagent that remains unreacted. The well known saying “Prevention is better than cure should be followed”.

2. Synthetic methods should be designed to maximize the incorporation of all the materials used in the process into the final product.

If one mole of the starting material produces one mole of the product, the yield is 100 %. However, such a synthesis may generate significant amount of waste or by product which is not visible in the above calculation. Such a synthesis, even though gives 100% yield, is not considered to be green synthesis. In order to find, if a particular reaction is green, the concept of atom economy was developed by Berry Trost of Stanford University. This considers the amount of stating materials incorporated into the desired final product. Thus by incorporation of greater amounts of the atoms contained in the starting materials (reactants) in to the formed products, fewer waste by products are obtained. In this way, using the concept of atom economy along with ideas of selectivity and yield, “greener” more efficient synthesis can be developed. The atom economy for a reaction can be calculated using the following equation:

$$\text{Percent atom economy} = \frac{\text{Molecular weight of desired product}}{\text{Molecular weights of all reactants}} \times 100\%$$

To illustrate the benefits of atom economy, consider the synthesis of ibuprofen.In the former process, developed in the 1960s, only 40% of the reactant atoms were incorporated into the desired ibuprofen product; the remaining 60% of the reactant atoms found their way into unwanted by-products or waste that required disposal .The new method requires fewer reaction steps and recovers 77% of the reactant atoms in the desired product. This 'green' process eliminates millions of pounds of waste chemical by-products every year, and it reduces by millions of pounds the amount of reactants needed to prepare this widely used analgesic.

3. Whenever practicable synthetic methodologies should be designed to use and generate a substance that poses little or no toxicity to human health and the environment.

Wherever practicable, synthetic methodologies should be designed to use and generate substances that pose little or no toxicity to human health and the environment. Redesigning existing transformations to incorporate less hazardous materials is at the heart of Green Chemistry.

4. Chemical products should be designed to preserve efficiency of function while reducing toxicity.

The designing of safer chemical is now possible since there have been great advances in the understanding of chemical toxicity. It is now fairly understood that a correlation exist between chemical structure e.g. presence of functional groups and the existence of toxic effects. The idea is to avoid the functionality related to the toxic effect. Chemical properties of a molecule, such as water solubility, polarity etc. so that they can manipulate molecules to the desired effects.

5. The use auxiliary substances (e.g. solvents, separating agents) should be made unnecessary wherever possible and innocuous when used.

An auxiliary substance is one that helps in manufacture of a substance, but does not become an integral part of the chemical. Such substances are used in the manufacture, processing at every step. Major problem with many solvents is their volatility that may damage human health and the environment. Even processes like recrystalisation require energy and substances to change the solubility. The problem of solvents has been overcome by using such solvents which do not pollute the environment. Such solvents are known as green solvents. Examples include liquidcarbon dioxide (supercritical CO2), ionic liquid water. Even reactions have been conducted in solid state. For example the condensation reaction of orthoesters with ophenylenediamines in presence of KSF clay under solvent free conditions using microwave.

Many solvents used in traditional organic synthesis are highly toxic. The Green Chemistry approach to the selection of solvents has resulted in several strategies. One method that has been developed is to use supercritical carbon dioxide as a solvent .Supercritical carbon dioxide is formed under conditions of high pressure in which the gas and the liquid phases of carbon dioxide combine to a single –phase compressible fluid that becomes an environmentally benign solvent (temperature 31oC, 7280 kPa, or 72 atmospheres). Supercritical CO2 has remarkable properties .It behaves as a material whose properties are intermediate between those of a solid and those of a liquid .The properties cab be controlled by manipulating temperature and pressure .Supercritical CO2 is environmentally benign because of its low toxicity and easy recyclability.
Carbon dioxide is not added to the atmosphere; rather, it is removed from the atmosphere for use in chemical processes. It is used as a medium to carry out a large number of reactions that would otherwise have many negative environmentalconsequences. It is even possible to perform stereoselective synthesis in supercritical CO2.

Some reactions can be carried out in ordinary water, the most green solvent possible. Recently, there has been much success in using near-critical water at higher temperatures where water behaves more like an organic solvent .Eckert and Liotta were able to run Friedel-Crafts reactions in near –critical water without the need for the acid catalyst AlCl3, which is normally used in large amounts in these reactions. In the past 5 years, many new ionic liquids have been developed with a broad range of properties. By selecting the appropriate ionic liquid, it is now possible to carry out many types of organic reactions in these solvents. In some reactions, a well –designed ionic solvent can lead to better yields under milder conditions than is possible with traditional solvents.

Another approach to making organic chemistry greener involves the way in which a reaction is carried out ,rather than in the selection of starting material, reagents, or solvents. Microwave technology can be used in some reactions to provide the heat energy required to make the transformation go to completion .With microwave technology ,reactions can take place with less toxic reagents and in ashorter time, with fewer side reactions, all goals of Green Chemistry. Microwave technology has also been used to create supercritical water that behaves more like an organic solvent and could replace more toxic solvents in carrying out organic reactions.

Another Green Chemistry approach is the use of a catalyst which facilitates transformations without the catalyst being consumed in the reaction and without being incorporated in the final product. Therefore, use of catalyst should be preferred whenever possible.

6. Energy requirements should be recognized for their environmental and economic impacts and should be minimized.

Energy generation, as we know has a major environmental effect. The requirement of energy can be kept to a base minimum in certain cases by the use of a catalyst. For example in conversion of benzyl chloride into benzyl cyanide if we use phase transfer catalyst, the conversion goes to completion in a very short time.

$$C_6H_5CH_2Cl \quad + \quad \text{aq KCN} \longrightarrow C_6H_5CH_2CN \quad + \quad KCl$$

Benzyl chloride

Benzyl cyanide

Conventionally, we have been carrying reaction by heating on wire gauze, in oil bath or heating mantels. It is now possible that the energy to a reaction can be supplied by using microwaves, by sonication or photo chemically. Simple examples are,

$$\text{(a)}\quad C_6H_5CONHC_6H_5 \xrightarrow[\text{MW,12 MINS}]{} C_6H_5COOH$$

$$\text{(b)}\quad RCOOH + ROH \xrightarrow[H_2SO_4\text{,Ultrasound}]{\text{Esterification}} RCOOR$$

7. A raw material or feedstock should be renewable rather than depleting, whenever technically and economically practicable.

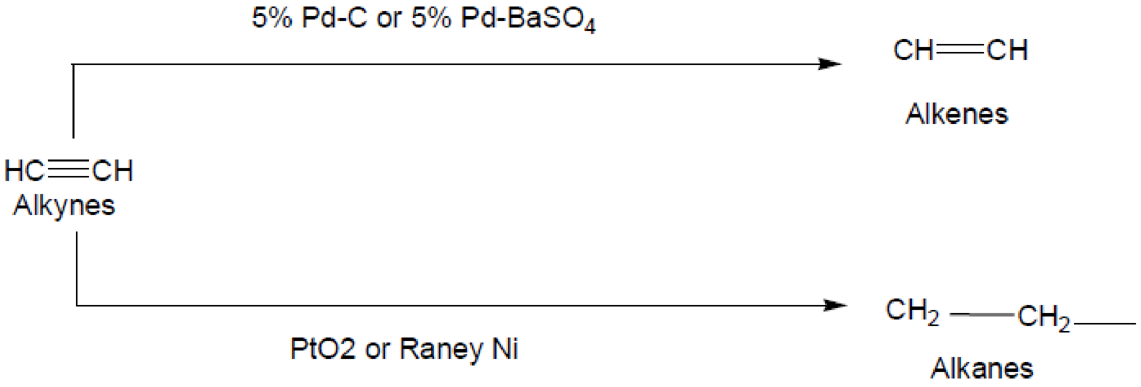
Non reversible or depleting sources can exhausted by their continual use. So these are not regarded as sustainable from environmental point of view. The starting materials which are obtained agricultural or biological processes are referred to as renewable starting materials. Substances like carbon dioxide (generated from natural sources or synthetic routes like fermentation etc) and methane gas (obtained from natural sources such as marsh gas, natural gas etc) are available in reasonable amounts and so are considered as renewable starting material. Methane, a constituent of biogasand natural gas can easily be converted into acetylene by partial combustion. Acetylene is a potential source of number of chemicals such as ethyl alcohol, acetaldehyde, vinyl acetate etc.

8. Unnecessary derivatization (blocking group, protection, deportation, temporary modification of physical/chemical processes) should be avoided whenever possible.

A commonly used technique in organic synthesis is the use of protecting or blocking group. These groups are used to protect a sensitive moiety from the conditions of the reaction, which may make the reaction to go in an unwanted way if it is left unprotected. This procedure adds to the problem of waste disposal.

9. Catalytic reagents (as selective as possible are superior to stoichiometric reagents.

The catalyst as we know facilitates transformation without being consumed or without being incorporated into the final product. Catalysts are selective in their action in that the degree of reaction that takes place is controlled, e.g. mono addition v/s multiple addition. A typical example is that reduction of triple bond to a double bond or single bond.



In addition to the benefits of yield and atom economy, the catalysts are helpful in reducing consumption of energy. Catalysts carry out thousands of transformation before being exhausted.

10. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.

It is extremely important that the products designed to be synthesized should be biodegradable. They should not be persistent chemicals or persistent bio accumulators. It is now possible to place functional groups in a molecule that will facilitate its biodegradation. Functional groups which are susceptible to hydrolysis, photolysis or other cleavage have been used to ensure that products will be biodegradable. It is also important that degradation products do not possess any toxicity and detrimental effects to the environment. Plastic, Pesticides (organic halogen based) are examples which pose to environment.

11. Analytical methodologies need to be further developed to allow for real time, in process monitoring and control prior to the formation of hazardous substances.

Methods and technologies should be developed so that the prevention or minimization of generation of hazardous waste is achieved. It is necessary to have accurate and reliable reasons, monitors and other analytical methodologies to assess the hazardous that may be present in the process stream. These can prevent any accidents which may occur in chemical plants.

12. Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions and fires.

The occurrence of accidents in chemical industry must be avoided. It is well known that the incidents in Bhopal (India) and Seveso (Italy) and many others have resulted in the loss of thousands of life. It is possible sometimes to increase accidents potential inadvertently with a view to minimize the generation of waste in order to prevent pollution. It has been found that in an attempt to recycle solvents from a process (for economic reasons) increases the potential for a chemical accident or fire.

Attempts are being made to quantify the *greenness* of a chemical process, to calculate chemical yield, , the price of reaction components, safety in handling chemicals, hardware requirements, energy and ease of product workup and purification.

To Implement these Green Chemical Principles it requires investment, since the current, very inexpensive chemical processes must be redesigned.

However, in future when certain raw materials cost and also the costs for energy increases, such an investment will pay back as the optimized processes become less expensive than the unoptimized ones. The development of greener procedures can therefore be seen as an investment for the future. It also helps to ensure that the production complies with future legal regulations.

Solventless reactions

1. In principle, any liquid can be used as a solvent. However, the number of commonly used solvents is severely restricted.

2. They include a few hydrocarbons, chlorinated hydrocarbons, a few ethers, esters, alcohols, amide derivatives, sulphoxides, etc. liquid ammonia, carbon disulfide and of course water, are also frequently used as medium to carry out synthesis.

3. Solvent is usually considered to be an inevitable component of a reaction. The suitability of a solvent for a reactiondepends on the following factors.

a. A solvent should be selected for a new reaction based on its physical and chemical properties.

b. At times the liquid reactant itself would serve as solvent.

A reaction under solvent free condition or in solid state was generally thought to be not quite feasible, or not quite efficient. However, the chemists concern for developing environment-friendly synthetic procedures has made them to focus their attention to minimize the use of solvents that are a major cause of pollution. This has led to vigorous research activity and reinvestigation of known reactions to achieve organic synthesis under solvent-free condition.

Why Are Reactions Performed Using Solvents?

1. To dissolve reactants.

2. To slow or increase the rate of reactions.

3. To act as a heat sink or heat transfer agent.

4. To prevent hot spots and run-away reactions.

5. The reactants can interact effectively if they are in a homogeneous solution, which facilitates the stirring, shaking or other ways of agitation, whereby the reactant molecules come together rapidly and continuously.

Issues with Organic Solvents

1. Organic solvents are of concern to the chemical industry because of the sheer volume used in synthesis, processing, and separation.
2. Organic solvents are expensive
3. Organic solvents are highly regulated.
4. Many organic solvents are volatile, flammable, toxic, and carcinogenic

Solvent alternatives

1. Use of solvent less reactions
2. Use of "non-organic" solvents
3. Processing technology

Advantages to Solvent less Organic Reactions

- There is no reaction medium to collect, purify, and recycle.
- Reaction times can be dramatically shortened.
- Lowered energy usage.
- Considerable reduction in batch size volume.

Less expensive

Ways to be Solvent-Free

1. **Neat** – reagents react together in the liquid phase in the absence of a solvent.

   Example: Aldol condensation reaction

2. **Solid-state synthesis** – two macroscopic solids interact directly and form a third,

solid product without the intervention of a liquid or vapor phase

Examples

- Oxidations
- Reductions
- Halogenations and Hydro halogenations
- Michael Additions and Aldol Additions
- Elimination Reactions
- [2+2], [4+2], and [6+2] Cycloaddition
Reactions
- Aldol Condensation Reaction

A **dry media reaction** or **solid-state reaction** or **solventless reaction** is a chemical reaction system in the absence of a solvent. The drive for the development of dry media reactions in chemistry is

- economics (save money on solvents)
- ease of purification (no solvent removal post-synthesis)
- high reaction rate (due to high concentration of reactants)
- environmentally friendly (solvent is not required), see green chemistry

Drawbacks to overcome:

1. Reactants should mix to a homogeneous system
2. High viscosity in reactant system
3. Unsuitable for solvent assisted chemical reactions. Not all reactions will work in the absence of solvent.
4. Function of catalysts.
5. Exothermic reactions are potentially dangerous.
6. Specialized equipment needed for some procedures.

7. If aqueous quench and organic extraction are performed, this reduces green benefit

Use of non-organic solvents

1. Liquid and supercritical CO2
2. Ionic liquids
3. Fluorous Phase Chemistry
4. Water

In some of these reactions(aldol condensation) all the starting materials are solids, they are ground together with some sodium hydroxide to form a liquid, which turns into a paste which then hardens to a solid.

In another development the two components of an aldol reaction are combined together with the asymmetric catalyst S-proline in a ball mill in a mechano synthesis. The reaction product has 97% enantiomeric excess.

Greener Reactions under solventless conditions

Due to the growing concern for the influence of the organic solvent on the environment as well as on human body, organic reactions without use of conventional organic solvents have attracted the attention of synthetic organic chemists. Although a number of modern solvents, such as fluorous media, ionic liquids and water have been extensively studied recently, not using a solvent at all is definitely the best option. Development of solvent-free organic reactions is thus gaining prominence.

Reactions in water

Most of the Natural chemistry occur in aqueous media

Why Water?

- Cost - water is the world’s cheapest solvent.
- Safety – doesn’t get any safer than water.
- Some reactions work better in water.

Limitations of Water as a Solvent

- Some reactions will never work in water.
- Poor solubility of most organic compounds.
- Solubility may be increased by use of organic co-solvents, pH control, surfactants, and hydrophilic auxiliaries.

Green Concerns of Water

- The product may need to be extracted into an organic solvent to purify it.
- This generates aqueous effluent containing solvent, which must be properly disposed.

Loss of Greenness

- Anytime water is used in an organic reaction, an additional waste stream is created.
- Solvent
- Aqueous quench / workup
- Aqueous wash

POSSIBLE QUESTIONS

POSSIBLE QUESTIONS

PART B (2 Mark Questions)

1. What is Green Chemistry?
2. Why do we need Green Chemistry?
3. Write a comparative statement on green chemistry and synthetic chemistry.
4. What are the economic benefits of Green Chemistry?
5. What is the goal of the Green Chemistry Initiative?
6. Give one example to 100% atom economy?
7. What is meant by Green Chemistry?
8. What are the educational challenges lying behind the Green Chemistry?
9. What is the difference between Environmental Science and Green Chemistry?
10. Is Green Chemistry more expensive that traditional Chemistry?
11. What is meant by Less Hazardous Chemical Synthesis
12. Explain the greener reagents with two examples.
13. How do you evaluate the chemical reactions according to their yield and atom efficiency?
14. Why are reactions performed using solvents?
15. What is meant by Non-organic solvents? Give examples.
16. What are fluorous solvents. Give two examples.
17. What are the advantages in carrying out the reactions using a micro wave oven

PART C (8 Mark Questions)

1. What is green Chemistry? What are the twelve principles of green chemistry
2. “Green Chemistry is important in alternate reaction pathways”-Explain
3. How does the Green Chemistry Initiative differ from traditional efforts to reduce pollution?
4. Explain the following reactions with special reference to green chemistry. (a) Aldol condensation (b) Diels-Alder reaction
5. Explain the advantages and limitations of solventless reactions. Give some examples for solid state reactions.
6. Write notes on organic reactions in aqueous media.
7. What are the tools used in the green chemistry
8. Comment on “designing safer chemicals” in green chemistry
9. Explain an atom efficient Process taking an Elimination reaction as an example

Questions	A	B	C	D	Answer
Which of the following are among the 12 principles of green chemistry?	Design commercially viable products	Use only new solvents	Use catalysts,not stoichiometric reagents	Re-use waste	Use catalysts, not stoichiometric reagents
Green chemistry aims to?	Design chemical products and process that maximise profits	Design safer chemical products and processes that reduce or eliminate the use and generation of hazardous substances	Design chemical products and processes that work most efficiently	Utilize non-renewable energy	Design safer chemical products and processes that reduce or eliminate the use and generation of hazardous substances
Green chemists reduce risks by?	Reducing the hazard inherent in a chemical product or process	Minimizing the use of all chemicals	Inventing technologies that will clean up toxic sites	Developing recycled products	Reducing the hazard inherent in a chemical product or process
Which of the following is challenging for chemists?	Awarness of the benefits of green chemistry	Developing chemicals that are recyclable	Training for cleaning up chemical spills	Knowing when to reduce and eliminate hazardous waste	Knowing when to reduce and eliminate hazardous waste
Buisness benefits of green chemistry include?	Reduced costs associated with waste treatment and disposal	Innovating 'greener' products to entice customers	Greater compliance with environmental legislation	All of the above	All of the above
What is the U.S. Presidental green chemistry challenge award?	An award related to recycling	An award for industry only	The only chemistry award given by the president	Challenge companies to become fuel efficient	The only chemistry award given by the president

The first listed of the 12 principles of green chemistry is?	Prevent waste	Catalysis	Atom economy	Benign solvents	Prevent waste
This word is synonymous with green chemistry and also means harmless, or gentle and not life threatening?	Sustainable	Benign	User friendly	Greenness	Benign
An example for green chemistry is ?	Recycled carpet	A product made on earth day	A sublimation reaction	Bio plastics	Bio plastics
Biodiesel is an example of which of the 12 principles of green chemistry?	1-Waste prevention	7-Use of renewable feedstocks	9-Use of catalysis	5-Safer solvents	7-Use of renewable feedstocks
Green chemistry can reduce all but which of the following?	Cost	Risk & hazard	Awarness	Waste	Awarness
Which is fulfilling the needs of the present generation without compromising the ability of future generations to meet their needs?	Sustainability	Green chemistry	Life cycle assessment	Recycling	Sustainability
When discussing sustainability and green chemistry often used moral arguments and	Environment	Technology	Politics	Ethics	Ethics
Which of the following three terms is used in the 'Sustainability triangle'?	Micro-economics	Planet	Social responsibility	economics	Social responsibility
The following legislation gave birth to today's green chemistry initiatives?	Clean water act of 1972	Montreal protocol of 1989	Pollution prevention act of 1990	Superfund act of 1980	pollution prevention of act 1990
In 1998, this state signed	Oregon	California	Newyork	Florida	California

green chemistry legislation promising to remove politics from the evaluation of disputed chemicals?					
Which of the following are among the 12 principles of green chemistry?	Design commercially viable products	Use only new solvents	Use catalysts, not stoichiometric reagents	Re-use waste	Use catalysts, not stoichiometric reagents
The first listed of the 12 Principles of Green Chemistry is?	Prevent waste	Catalysis	Atom economy	Benign solvents	Prevent waste
Green chemists reduce risk by?	Reducing the hazard inherent in a chemical product or process	Minimizing the use of all chemicals	Inventing technologies that will clean up toxic sites	Developing recycled products	Reducing the hazard inherent in a chemical product or process
Which of the following is a challenge for green chemists?	Awareness of the benefits of green chemistry	Developing chemicals that are recyclable	Training for cleaning up chemical spills	Knowing when to reduce and eliminate hazardous waste	Knowing when to reduce and eliminate hazardous waste
Heart of green chemistry is	to maximize the waste products formation	to minimize the waste products formation	to increase the toxic materials	to increase toxic materials and waste products formation	to minimize the waste products formation
During thunderstorms, water dissolves	dust particles	HCl	nitric acid	clouds	nitric acid
Out of total amount of water available for human use is	0.30%	0.2%	40%	50%	0.2%
Density of water becomes maximum at	10°C	4°C	5°C	12°C	4°C
Branch of chemistry dealing	Biochemistry	Organic chemistry	Environmental	Inorganic chemistry	Environmental chemistry

with plantation and overcoming greenhouse effect is			chemistry		
Our bodies cannot produce	minerals	proteins	vitamins	carbohydrates	vitamins
Maximum amount of ozone (O3) is present in	troposphere	stratosphere	mesosphere	thermosphere	stratosphere
Upset caused in natural balance of concentration of greenhouse gases is called	pollution	global warming	atmospheric poisoning	earth heating	global warming
Ozone gas (O3) has	unpleasant odor	pleasant odor	no odor	orange color	unpleasant odor
Amount of Nitrogen (N2) present in dry air is	20%	78%	48%	68%	78%
Gas responsible for global warming is	oxygen	carbon dioxide	carbon monoxide	nitrogen	carbon dioxide
Ozone (O?) comprises of	one oxygen atom	2 oxygen atoms	3 oxygen atoms	4 oxygen atoms	3 oxygen atoms
Percentage of nitrogen (N) in urea (CH4N2O) is	50%	46.60%	40%	20%	46.60%
Fertilizer which doesn't affect texture of soil is	urea	ammonium sulphate	ammonium phosphate	super phosphate	urea
Which of the following is not one of the twelve principles of green chemistry?	Using high temperatures to speed up reactions	Minimising toxic reagents used in a synthesis	Maximisation of atom economy	Minimising the use of solvents	Using high temperatures to speed up reactions
Which of the following is not a priority in green chemical development?	Optimising the overall yield of a drug	Optimising the activity of a drug	Developing a cheap synthetic route	Optimising the purity of a drug	Developing a cheap synthetic route
Green chemistry aims to?	Design chemical products and	Design safer chemical products and processes that reduce or eliminate	Design chemical products and	Utilize non-renewable energy	Design safer chemical products and processes that reduce or eliminate

	process that maximize profits	the use and generation of hazardous substances	processes that work most efficiently		the use and generation of hazardous substances
Which of the following are among the 12 Principles of Green Chemistry?	Design commercially viable products	Use only new solvents	Use catalysts, not stoichiometric reagents	Re-use waste	Use catalysts, not stoichiometric reagents
Green chemists reduce risk by?	Reducing the hazard inherent in a chemical product or process	Minimizing the use of all chemicals	Inventing technologies that will clean up toxic sites	Developing recycled products	Reducing the hazard inherent in a chemical product or process
Which of the following is a challenge for green chemists?	Awareness of the benefits of green chemistry	Developing chemicals that are recyclable	Training for cleaning up chemical spills	Knowing when to reduce and eliminate hazardous waste	Knowing when to reduce and eliminate hazardous waste
Business benefits of green chemistry include?	Reduced costs associated with waste treatment and disposal	Innovating 'greener' products to entice customers	Greater compliance with environmental legislation	All of the above	All of the above
What is the U.S. Presidential Green Chemistry Challenge Award?	An award related to recycling	An award for industry only	The only chemistry award given by the President	Challenges companies to become fuel efficient	The only chemistry award given by the President
The first listed of the 12 Principles of Green Chemistry is?	Prevent waste	Catalysis	Atom economy	Benign solvents	Prevent waste
Green chemistry synthesis	High	Dichloromethane	Fossil fuels	Microwave	Microwave

could also involve which of the following?	temperature				
This word is synonymous with green chemistry and also means harmless, or gentle and not life threatening?	) Sustainable	Benign	User friendly	Greenness	Benign
The term used to measure a product or person's environmental impact is?	Handprint	CO2 print	Footprint	Hazardous print	Footprint
Bio-polymers exemplify Green Chemistry Principle # 10, which is?	Catalysis	Prevent waste	Benign solvents & auxiliaries	Design for degradation	Design for degradation
The use of solar power is covered within Green Chemistry Principle #6, which is?	Atom economy	Design for energy efficiency	Design benign chemicals	Less hazardous synthesis	Design for energy efficiency
An example of green chemistry is?	Recycled carpet	A product made on Earth Day	A sublimation reaction	Bio-plastics	Bio-plastics
Biodiesel is an example of which of the 12 Principles of Green Chemistry?	Waste prevention	Use of renewable feedstocks	Use of catalysis	Safer solvents	Use of renewable feedstocks
Green chemistry can reduce all but which of the following?	Cost	Risk & Hazard	Awareness	Waste	Awareness
Which of the following gases is not a green house gas?	CO	O3	CH4	H2O vapour	CO
The consequences of global warming may be	increase in average temperature of the earth	melting of Himalayan Glaciers.	increased biochemical oxygen demand.	eutrophication.	increase in average temperature of the earth
The formation of ethene	an addition	an elimination reaction	an oxidation	a substitution	an elimination reaction

from the dehydration of ethanol can best be described as	reaction		reaction	reaction	
What is the major driver for focussing on solvents when addressing the 'greenness' of a process?	They are petroleum derived	They are serious pollutants	They are toxic	they make up the largest component (by mass) of a process	they make up the largest component (by mass) of a process
Who proposed green chemistry principles	Paul daldon	john Warner	William bent	Anastas	john Warner
For green chemistry raw material should be	non - renewable	renewable	conventional	economical	renewable
For the green reaction Bi-products must be high	TRUE	FALSE	Not applicable	None	FALSE
Heart of green chemistry is	to maximize the waste products formation	to minimize the waste products formation	to increase the toxic materials	to increase toxic materials and waste products formation	to minimize the waste products formation
Among them which is green solvent	benzene	dichloro methane	super critical water	duetrated water	super critical water

UNIT-II

SYLLABUS

Designing a Green Chemical synthesis:
Designing a Green synthesis using these principles: prevention of waste/ byproducts; maximum incorporation of the materials used in the process into the final products, atom economy, calculation of atom economy of the rearrangement, addition, substitution and elimination reactions. Green solvents– supercritical fluids, water as a solvent for organic reactions, ionic liquids, fluorous biphasic solvent, PEG, solventless processes, immobilized solvents and how to compare greenness of solvents.

Designing a Green synthesis using these principles: prevention of waste/ byproducts

- An ideal reaction is
- Is Simple.
- Is Safe.
- Has a High Yield and Selectivity.
- Is Energy Efficient.
- Uses Renewable and RecyclableReagents and Raw Materials.

There are a wide range of things that need to be considered when designing a chemical reaction, including alternative raw materials, solvents, reaction pathways and reaction conditions (which will be discussed further in this chapter). The design of a chemical reaction can become quite tedious, specially when attempting to minimize or eliminate it’s environmental impact. The given criteria (on the slide) for an ideal chemical reaction should all be considered, but it can become extremely difficult to match all points, therefore the goal is to optimize the balance of the criteria. In this chapter, we will discuss how to best tackle this task.

This is a brief qualitative description of different equations that can be used to determine alternative reaction pathways. In order to assess the equations more, a semi-quantitative approach can be taken, using atom and math efficiency. These techniques and other tools will be discussed further along in the module. Also, an example of each possible alternative reaction pathway is given below.

Addition(A + B----- AB)

No waste needs to be treated because the reaction is direct.

Addition reactions incorporate the starting materials into the final product and, therefore, do not produce waste that needs to be treated, disposed of, or otherwise dealt with.

The addition of HX to an alkene is an organic reaction in chemistry where HX, or a halogen sigma bonded to a hydrogen atom, adds to the carbon-carbon double bond of an alkene following Markovnikov's rule (Markovnikov's rule is observed).

The general chemical formula of the reaction is as follows:

C=C + HX ----------- H-C-C-X

Substitution (AB + C ----- AC + B)

Necessarily generates stoichiometric quantities of substances as byproducts and waste that are not part of the target molecule.

Substitution reactions, necessarily generate stoichiometric quantities of substances as byproducts and waste

In chemistry, Nucleophilic Substitution is a type of chemical reaction in which one nucleophile (electron donor) replaces another as a covalent substituent of some atom. In the examples given here, the nucleophilic atom is carbon.

An example of nucleophilic substitution is the hydrolysis of an alkyl bromide, R-Br, under alkaline conditions, where the "attacking" nucleophile is hydroxide ion, OH-:

R-Br + OH ---------- R-OH + Br-

The bromide ion, Br-, is said to be the leaving group.

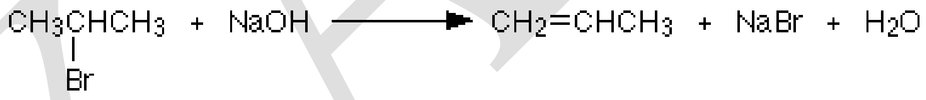
Elimination(AB----- A + B)

Does not require other substances, but does generate stoichiometric quantities of waste that are not part of the final target molecule.

Elimination reactions do not require input of materials during the course of the reaction other than initial input of a starting materials, but they do generate stoichiometric quantities of substances that are not part of the final target molecule.

Halogenoalkanes also undergo Elimination Reactions in the presence of sodium or potassium hydroxide.

The 2-bromopropane has reacted to give an alkene - propene.

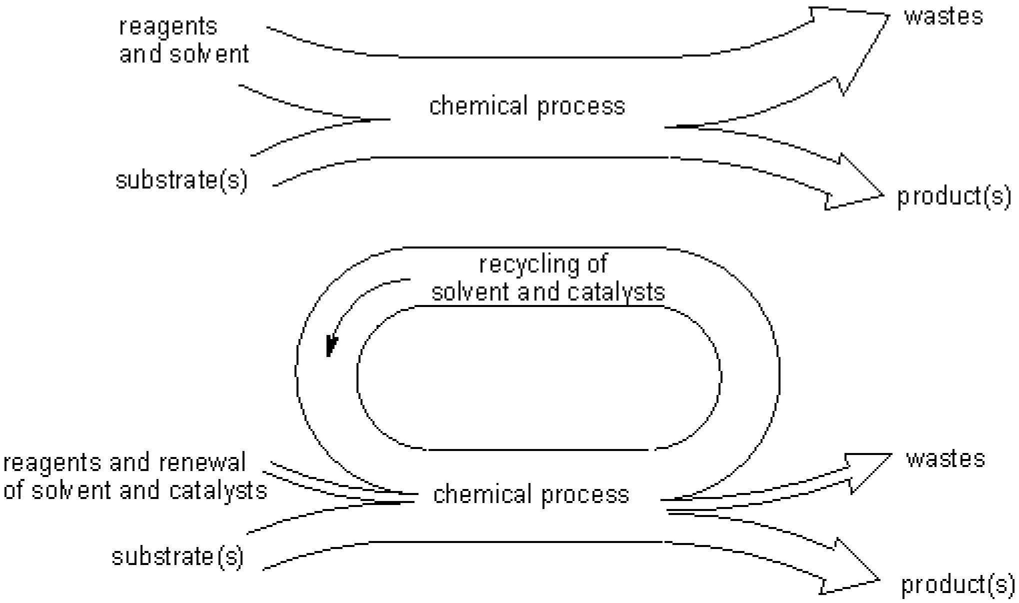


$$CH_3\underset{\substack{|\\ Br}}{CH}CH_3 + NaOH \longrightarrow CH_2{=}CHCH_3 + NaBr + H_2O$$

Notice that a hydrogen atom has been removed from one of the end carbon atoms together with the bromine from the centre one. In all simple elimination reactions the things being removed are on adjacent carbon atoms, and a double bond is set up between those carbons.

Evaluating chemical reactions according to their yield

A typical chemical process generates products and wastes from raw materials such as substrates, solvents and reagents. If most of the reagents and the solvent can be recycled, the mass flow looks quite different:



Thus, the prevention of waste can be achieved if most of the reagents and the solvent are recyclable. For example, catalysts and reagents such as acids and bases that are bound to a solid phase can be filtered off, and can be regenerated (if needed) and reused in a subsequent run. In the production of chemical products on very large scale, heterogeneous catalysts and reagents can be kept stationary while substrates are continuously added and pass through to yield a product that is continuously removed (for example by distillation).

The mass efficiency of such processes can be judged by the E factor (Environmental factor):

$$\textbf{E factor} = \frac{\textbf{Mass of wastes}}{\textbf{Mass of product}}$$

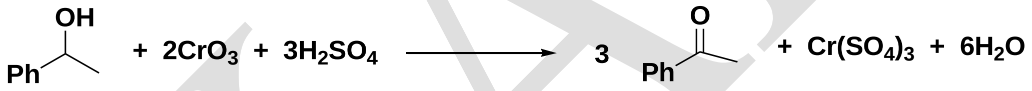
Whereas the ideal E factor of 0 is almost achieved in petroleum refining, the production of bulk and fine chemicals gives E factors of between 1 and 50. Typical E factors for the production of pharmaceuticals lie between 25 and 100. Note that water is not considered in this calculation, because this would lead to very high E factors. However, inorganic and organic wastes that are diluted in the aqueous stream must be included. Sometimes it is easier to calculate the E factor from a different viewpoint, since accounting for the losses and exact waste streams is difficult:

$$\text{E factor} = \frac{\text{Mass of raw materials - Mass of product}}{\text{Mass of product}}$$

In any event, the E factor and related factors do not account for any type of toxicity of the wastes. Such a correction factor (an “unfriendliness” quotient, Q) would be 1 if the waste has no impact on the environment, less than 1 if the waste can be recycled or used for another product, and greater than 1 if the wastes are toxic and hazardous. Such discussions are at a very preliminary stage, and E factors can be used directly for comparison purposes as this metric has already been widely adopted in the industry.

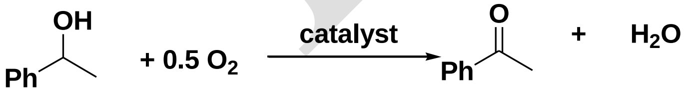
Another attempt to calculate the efficiency of chemical reactions that is also widely used is that of atom economy or efficiency. Here the value can be calculated from the chemical equation:

$$\text{atom efficiency} = \frac{\text{molecular weight of desired product}}{\text{molecular weight of all substances formed}}$$



120 g/mol. 3 392 g/mol 16g/mol.6

$$\text{atom efficiency} = \frac{3.120}{3.120 + 392 + 6.18} = 42\%$$



120 g/mol 18g/mol

$$\text{atom efficiency} = \frac{120}{120 + 18} = 87\%$$

Atom efficiency is a highly theoretical value that does not incorporate any solvent, nor the actual chemical yield.

An experimental atom efficiency can be calculated by multiplying the chemical yield with the theoretical atom efficiency.

Anyway, the discussion remains more qualitative than quantitative, and does not yet quantify the type of toxicity of the products and reagents used.

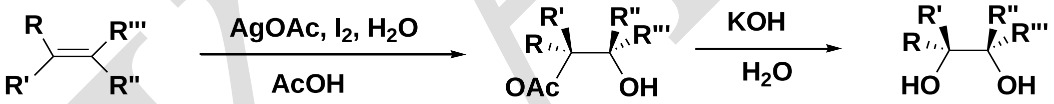
Still, atom economy as a term can readily be used for a direct qualitative description of reactions.

Considering specific reactions, the development of green methods is focused on two main aspects:

1. choice of solvent, and

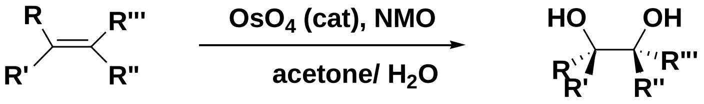
2. the development of catalyzed reactions.

Example: The development of catalyzed reactions for dihydroxylations have made possible the replacement of the Woodward Reaction in the manufacture of steroids, in which huge amounts of expensive silver salts were used and produced, and thus had become an economic factor:



Woodward Reaction

The Woodward reaction can be replaced through the use of stoichiometric quantities of OsO_4, but osmium tetroxide is both very toxic and very expensive, making its use on a commercial scale prohibitive. Only in its catalytic variant, which employs *N*-methylmorpholine-*N*-oxide as the stoichiometric oxidant and catalytic quantities of OsO_4, can this be considered a green reaction that can be used on industrial scale.



Upjohn Dihydroxylation

Some systems have already been reported in which H_2O_2 is used to reoxidize the *N*-methylmorpholine, allowing this material also to be used in catalytic amounts. Considering the atom efficiency using H_2O_2 as the terminal oxidant, H_2O as the stoichiometric byproduct is much better than *N*-methylmorpholine. Notably, catalytic systems are available in which the osmium catalyst is encapsulated in a polyurea matrix or bound to a resin, so that the catalyst can be more easily recovered and reused. An additional advantage of such polymer-bound catalysts is the avoidance of toxic transition metal impurities, for example in pharmaceutical products.

Industrial chemists evaluate synthetic routes and their associated economic and evironmental costs by calculating the relative efficiency of the chemicalreactions involved. Percentage yield provides a means of comparison of thetheoretical and actual quantity of product, and historically has been the main means of evaluating reaction efficiency. More recently, however, calculation of ‘atom economy’ has become a more important means of comparing the efficiency of chemical reactions.

The concept of ‘atom economy’ was developed by Professor Barry Trost at Stanford University and derives from the principles of ‘green chemistry’.Green chemistry is the design of chemical products/processes that reduce or eliminate the use or generation of hazardous substances. Historically, the chemical industry responded to environmental legislation by treatment, rather than prevention of waste. However, with waste treatment costs becoming increasingly economically unviable, chemical manufacturers are being forced to consider the economic benefits of applying the principles of green chemistry. Atom economy is a measure of the proportion of reactant atoms which are incorporated into the desired product of a chemical reaction. Calculation of atom economy therefore also gives an indication of the proportion of reactant atoms forming waste products. Chemists commonly calculate percentage yield (Equation 1) to ascertain the efficiency of a particular reaction.

Equation I

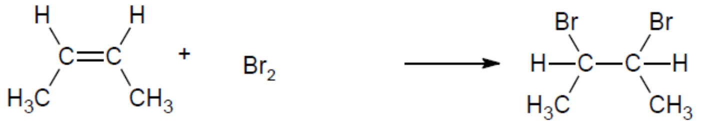
$$\text{\% Yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

Using this strategy, a reaction proceeding with 100% yield of desired productis deemed to be perfectly efficient. However, calculation of percentage yieldprovides no information about the extent to which unwanted products areformed in the reaction pathway. In the chemical industry there are manyexamples of highly ‘efficient’ reactions that generate waste far greater inmass and volume than the desired product. With the inadequacies of calculating percentage yield clearly established,Trost developed an equation for atom economy

$$\boxed{\%\ \text{atom economy} = \frac{\text{Mass of desired product(s)}}{\text{Total mass of reactants}} \times 100}$$

13,000 tonnes per annum of the painkiller Ibuprofen have been produced since its introduction in the 1980s. Initially, Boots used a six-step production process with an overall atom economy of just 40.1%. In the 1990s the Hoechst Celanese Corporation (in collaboration with Boots) developed a new, improved three-stage process to producing Ibuprofen with an atom economy of 77.4%. This improvement in atom economy resulted in a reduction in the quantity of unwanted by-products, and therefore in significant environmental and economic cost savings. The atom economy of a reaction depends on the reagents used and the type of chemical reaction involved. Most chemical reactions can be classified as rearrangement (eg migration of an alkyl group), addition (Example 1),substitution (eg chlorination of methane) or elimination (eg dehydration).Rearrangement and addition reactions are atom economical by their very nature, since they simply involve reactant atoms being repositioned within the same molecule or incorporated within a second molecule. Substitution reactions, however, involve replacement of one group with another and therefore have intrinsically poor atom economy. Elimination reactions (Example 2) are also inherently atom uneconomical since eliminated atoms are always lost as waste. In developing an atom economical reaction pathway, therefore, the industrial chemist may well prefer rearrangement and addition reactions over less environmental friendly substitution and elimination reactions.

Example 1: Addition reaction – halogenation of an alkene



(Z)-but-2-ene	Bromine	2,3-dibromobutane
C_4H_8	Br_2	$C_4H_8Br_2$
1mol	1mol	1mol
(12 x 4) + (8 x 1)	2 x 79.9	(12 x 4) + (8 x 1) + (79.9 x 2)
= 56g	= 159.8g	= 215.8g

Total mass of reactants = 56 g + 159.8 g = 215.8 g
(Note: Product mass is also 215.8 g)

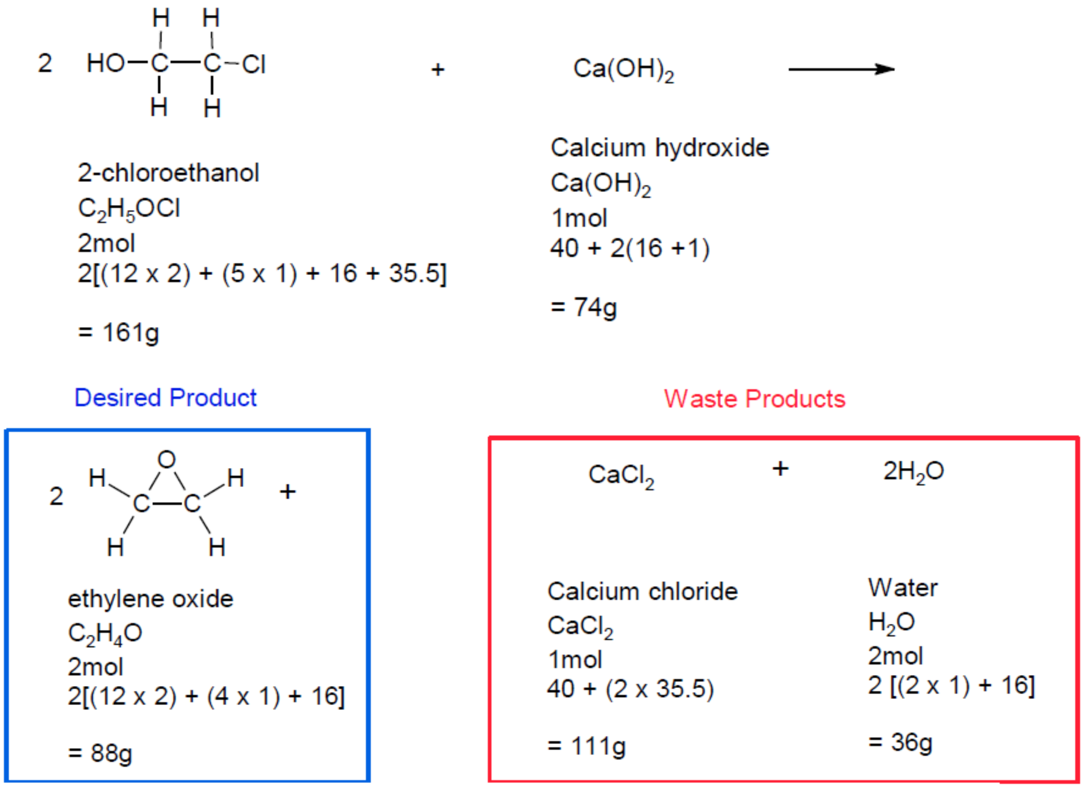
Mass of desired product (2,3-dibromobutane) = 215.8 g

$$\boxed{\% \text{ atom economy} = \frac{\text{Mass of desired product(s)}}{\text{Total mass of reactants}} \times 100}$$

$$\% \text{ atom economy} = \frac{215.8}{215.8} \times 100 = \mathbf{100\%}$$

This process is 100% atom efficient, with all the reactant atoms included within the desired product.

Example 2: Elimination reaction



2-chloroethanol
C_2H_5OCl
2mol
2[(12 x 2) + (5 x 1) + 16 + 35.5]

= 161g

Calcium hydroxide
$Ca(OH)_2$
1mol
40 + 2(16 +1)

= 74g

Desired Product

ethylene oxide
C_2H_4O
2mol
2[(12 x 2) + (4 x 1) + 16]

= 88g

Waste Products

Calcium chloride
$CaCl_2$
1mol
40 + (2 x 35.5)

= 111g

Water
H_2O
2mol
2 [(2 x 1) + 16]

= 36g

Total mass of reactants = 161 g + 74 g = 235 g
(Note: Total product mass = 235 g)

Mass of desired product ethylene oxide = 88 g

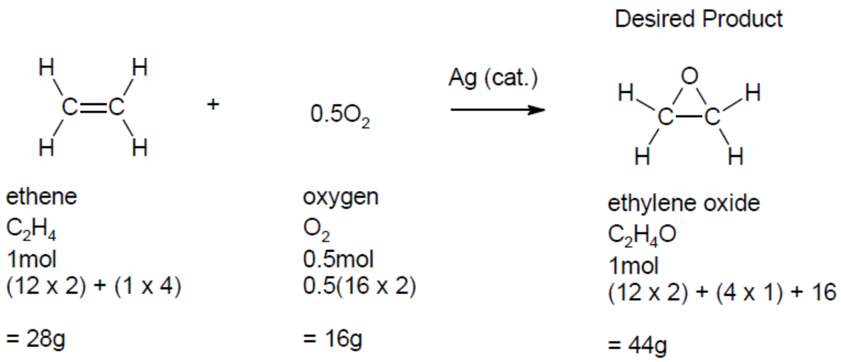
$$\% \text{ atom economy} = \frac{\text{Mass of desired product(s)}}{\text{Total mass of reactants}} \times 100$$

$$\% \text{ atom economy} = \frac{88}{235} \times 100 = \mathbf{37.4\%}$$

This elimination reaction is therefore only 37.4% atom efficient, with the remaining 62.6% in the form of unwanted waste products (calcium chloride and water).

Catalysts have a crucial role in improving the atom economy of chemical reactions. They allow the development of more effective synthetic reaction routes, which produce fewer waste products, and can be recovered and reused time and again. Catalysts also allow reactions to be run at lower temperature, reducing energy costs. The dramatic effect of a catalyst on improving atom economy is illustrated in Example 3. The introduction of a silver catalyst into the ethylene oxide production process in Example 2 improves the atom economy of the reaction from 37.4% to 100%. Although the silver catalyst is initially costly, it can be reused many times in the process.

Example 3: Use of catalyst in ethylene oxide production



Total mass of reactants = 28 g + 16 g = 44 g
(Note: Total product mass = 4 4g)

Mass of desired product ethylene oxide = 44 g

$$\boxed{\%\text{ atom economy} = \frac{\text{Mass of desired product(s)}}{\text{Total mass of reactants}} \times 100}$$

$$\%\text{ atom economy} = \frac{44}{44} \times 100 = \mathbf{100\%}$$

Atom economical approaches have become increasingly popular in the last decade due to the rising cost of raw materials (particularly petrochemicals)and increasing awareness of environmental concerns. Energy consumption, raw material costs, the nature of waste products/pollutants and the value of the final of product are also factors that will influence the selection of a particular synthetic route.

Why Are Reactions Performed Using Solvents?

• To dissolve reactants. • To slow or increase the rate of reactions. • To act as a heat sink or heat transfer agent. • To prevent hot spots and run-away reactions

Issues with Organic Solvents

• Organic solvents are of concern to the chemical industry because of the sheer volume used in synthesis, processing, and separation. • Organic solvents are expensive • Organic solvents are highly regulated. • Many organic solvents are volatile, flammable, toxic, and carcinogenic.

Solvent alternatives

A. Use of solventless reactions B. Use of “non-organic” solvents C. Processing technology

Advantages to Solventless Organic Reactions

• There is no reaction medium to collect, purify, and recycle. • Reaction times can be dramatically shortened. • Lowered energy usage. • Considerable reduction in batch size volume. • Less expensive

Ways to be Solvent-Free

• Neat – reagents react together in the liquid phase in the absence of a solvent. • Solid-state synthesis – two macroscopic solids interact directly and form a third, solid product without the intervention of a liquid or vapor phase.

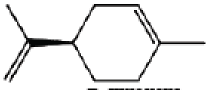
Use of non-organic solvents

• Liquid and supercritical CO 2 • Ionic liquids • Fluorous Phase Chemistry • Water

Liquid CO_2 as a green extraction solvent

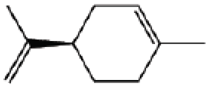
Traditional Method

Orange Peel $\xrightarrow[\text{Organic solvent}]{\text{Steam distill and/or}}$



Green Method

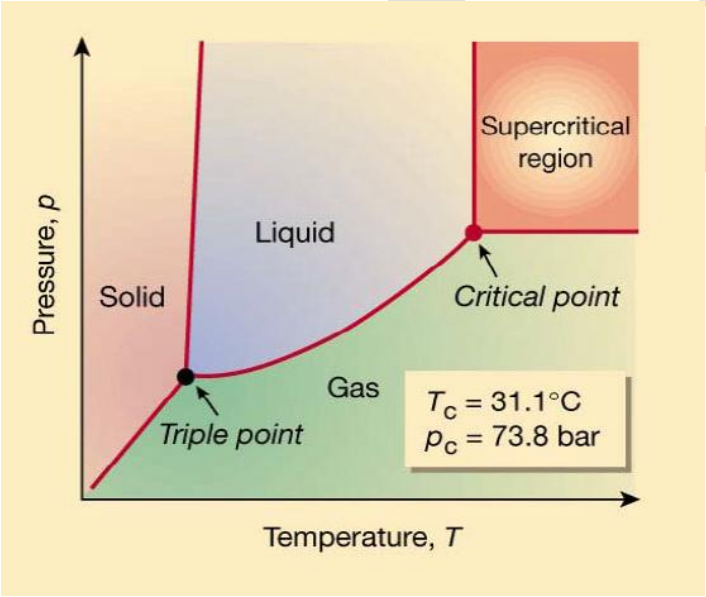
Orange Peel $\xrightarrow[\text{No organic solvent}]{CO_2\text{(liquid)}}$



Chemical Concepts:	**Green Lessons:**
Solid/liquid extraction	Use of safer solvents
Natural products (terpenes)	Prevention of waste
Spectroscopy	Green materials processing
Phase transitions	

Supercritical CO2

- What does it mean to be supercritical



Properties of scCO2

- Combination of properties from both theliquid and gas state.
- At liquid-like densities, scCO2 exhibits lowviscosity and high diffusion rates.
- High compressibility of the supercritical phase allows for solvent properties to be varied by small changes in temperature and pressure.

Properties of scCO2

- Can be handled in standard high-pressure equipment on lab or industrial scale.
- Non-toxic, non-flammable, and inexpensive.
- Non-protic and generally unreactive.
- Product isolation to total dryness is achieved by simple decompression.
- CO2 can be recovered and reused.

Commercial Applicationsof scCO2

- Natural product extraction (decaffeination)
- Polymer synthesis
- Dry cleaning

Examples of scCO2 as Solvent inSynthetic Organic Chemistry

- Hydrogenation
- Hydroformylation
- Photochemical and radical reactions
- Dies-Alder cycloadditions
- Oxidations
- Palladium mediated couplings
- Biotransformations

Limitations of scCO2

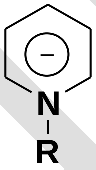
- Poor solubility of many substrates in scCO2.
- Modifiers (organic solvents) can be added to regulate solubility, but this move the process away from being green.
- CO2-philic surfactants are being developed.

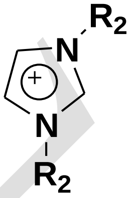
– Are expensive and have to be separated fromproducts.

Ionic Liquids

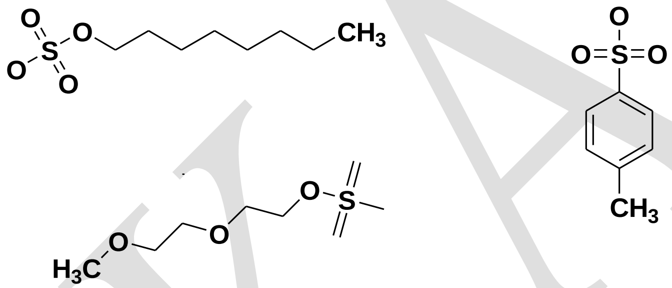
- Organic salts with melting points below100°C, often below room temperature.

$[NR_xH_{4-x}]^+$ $[PR_xH_{4-x}]^+$





Alkylammonium, alklyphosphonium, N-alkykpyridinium, and N,N’-dialkylimidazolium cations



Octyl sulphate, 2-(2-methoxyethoxy)ethyl sulphate, and tosylate anions

BF_4^- PF_6^- SbF_6^- $CH_3CO_2^-$ HSO_4^- NO_3^- NO_2^- $AlCl_4^-$

Properties of IonicLiquids

- Good solvents for a wide range of both organic and inorganic materials.
- Have potential to be highly polar yet noncoordinating.
- By varying cations and anions, ionic liquids can be tailored for specific applications.
- Possibility for reaction rate enhancement, higher selectivity and higher yields.

Properties of IonicLiquids

- High thermal stability
- Often immiscible with organic solventsand/or water
- No measurable vapor pressure
- Non-flammable
- Can be recycled
- Are they safer than solvents?

Ionic liquids have been used as solvents in a variety of reactions

- Heck Reaction
- Friedel-Crafts reactions
- Diels-Alder reactions
- Hydrogenation reactions

Other Applications of Ionic Liquids

- As biphasic systems in combination withorganic solvent or water in extraction and separation technologies.

- For catalyst immobilization and recycling.

- As electrolytes in electrochemistry

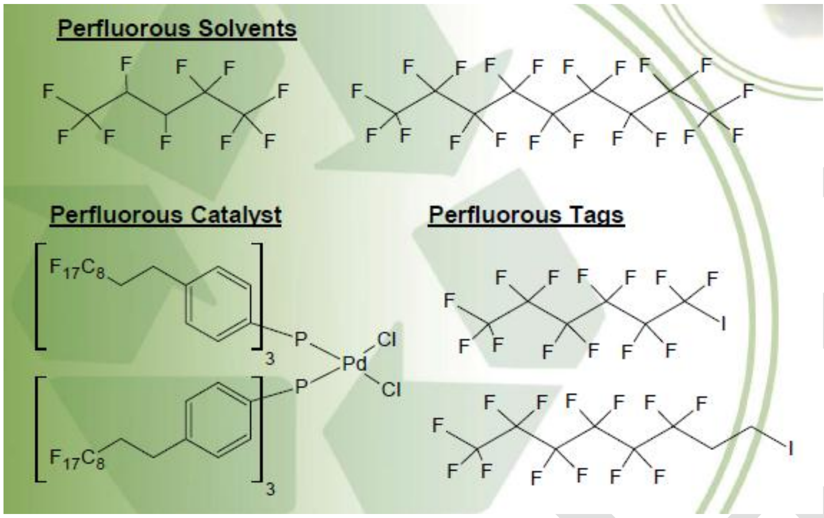
Limitations of Ionicl iquids

- Very expensive compared to organic solvents (100 to 1000 x).
- Have to be made, often using solvent.
- Products have to be extracted from ionic liquid using solvent.
- May have to wash with water prior to reuse.

Fluorous PhaseChemistry

- What does it mean to be "fluorous"?

- What does it mean to be "perfluorinated"?



Physical Properties of PerfluorinatedOrganic Compounds

- High affinity for other fluorinated compounds.
- High solubility in scCO2.
- Immiscible in water and most common organicsolvents at room temperature.
- Forms homogenous solutions at elevatedtemperatures with many of these solvents.
- Chemically inert.

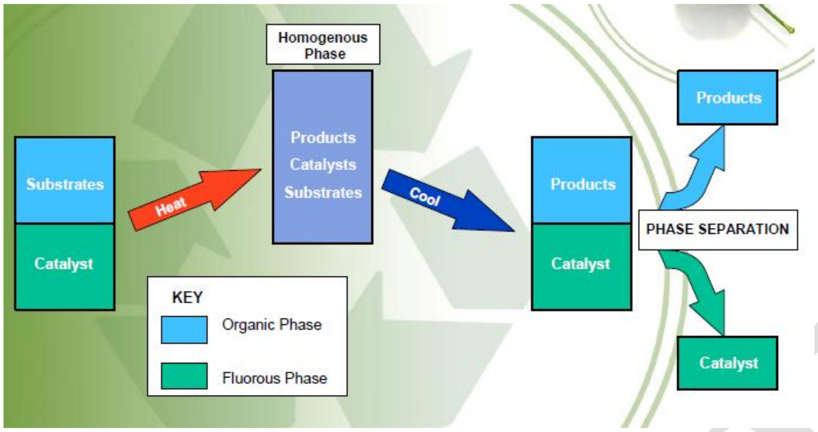
– Is this good or bad?

Uses for Fluorous Chemistry

- For the recovery and recycling of fluorouscatalysts and fluorous reagents.

- Fluorous biphasic organic synthesis.

Principle of fluorous biphasic catalysis



Advantages

- Facile recovery of expensive catalysts.
- Complementary to other biphase chemistries.
- More facile separation.
- Design of novel catalysts and reagents.
- Alternative to the solid phase in combinatorial chemistry.
- Non-toxic?

Limitations

- Fluorous solvents and reagents are very expensive.
- 60% fluorine is usually considered the lower cut off point for efficient fluorous extraction.
- Still requires use of a second solvent for biphase.

Water as a solvent

The solvent of choice for green chemistry is water, which is a non-toxic liquid but with limited chemical compatibility.

The Diels-Alder Reaction are often even accelerated when run in an aqueous medium, while on the other hand, many reactants and reagents, including most organometallic compounds, are totally incompatible with water.

Water as a solvent is not only inexpensive & environmentally benign but also shows completely different reactivity to Organic solvents. Organic reactions in water are varied and have many applications such as, in the synthesis of biologically active compounds from carbohydrates & the chemical modification of biomolecules.

Aqueous reactions could be the answer to the future of organic chemistry. The types of organic reactions in water are broad including pericyclic reactions, reaction of carbanion& carbocation equivalents, reactions of radicals &carbenes, transition-metal catalyses and oxidations-reductions.

The upside of Water as a green solvent are a) Non toxic (liquid + vapour), b) Non flammable, c) Abundantly available (better availability than organic solvent in less developed countries), d) Inexpensive.

The downside are a) Corrosion, b) Heat sink, c) High boiling point {Water-based reactions are energy intensive}, d) Solubility of organic matter is generally poor, e) Reaction range is narrower than organic solvents, f) A vital resource to be conserved & protected {100 litres of water is needed to dye 1 Kg of fibre} and g) Expands when freezes.

Most of the world's chemistry occur in aqueous media

Diels-Alder reactions
Claisen-rearrangement
Aldol reactions
Allylation reactions
Oxidations
Hydrogenations

• Cost - water is the world's cheapest solvent. • Safety – doesn't get any safer than water. • Some reactions work better in water.

Limitations of Water as a Solvent

• Some reactions will never work in water.

• Poor solubility of most organic compounds.

• Solubility may be increased by use of organic co-solvents, pH control, surfactants, and hydrophilic auxiliaries.

The product may need to be extracted into an organic solvent to purify it. • This generates aqueous effluent containing solvent, which must be properly disposed.

Processing Principles

Greenness through technology

- Goal is to minimize the number of effluent streams generated and the quantity of each stream.

- Organic solvents are not necessarily bad.

Loss of Greenness

Anytime water is used in an organic reaction, an additional waste stream is created. • Solvent • Aqueous quench / workup • Aqueous wash

Green Process

A purely organic solvent-based process (with solvent-based workup), with solvent recovery, would generate little waste. • The use of technology and good environmental practices to reduce VOCs.

Benefits of Organic Solvents

- Cheap relative to ionic liquids and fluorous solvents.

- Volatile – it takes less energy to remove solvents by evaporation.

- Solvents can be recycled by distillation, creating little waste.

- Regulated – Most countries already have industrial requirements limiting the release of VOCs.
- Chemistry is known.

Chemical reactions used to manufacture important compounds such as medicinals are essentially always carried out in solution, and this is also true of the research work that is used to invent the new compounds and to develop appropriate ways to manufacture them. In the past, continuing into the present, the solvents used are normally volatile organic compounds (VOCs), and these pose an environmental problem. Their vapors can contribute to the greenhouse effect that causes global warming, and in some cases the solvent vapors can catalyze the destruction of the ozone layer that protects the Earth and its living inhabitants from short-wavelength ultraviolet solar radiation. The vapors may also be toxic to humans, plants, or animals, or they may cause diseases. The liquids themselves can be a problem. If they are released into the earth, rivers or the ocean, they can cause direct environmental damage, while also slowly releasing their vapors. In principle, the solvents can be completely captured and purified for reuse during manufacturing, but it is difficult to prevent some loss to the environment. Hence there is interest in using environmentally benign liquids as the solvents in chemical reactions. One possibility is supercritical carbon dioxide, which is a liquid under pressure and which has attractive solvent properties. However, unless it is completely contained and reused, it will release gaseous carbon dioxide, a greenhouse gas. Thus interest has increasingly turned to water as the solvent for chemical reactions. Water is the solvent in which biochemical reactions are performed in Nature, and it is environmentally benign. However, it is a good solvent only for organic chemicals that have polar groups, such as alcohols and carboxylic acids. This may not be an insuperable problem. Over 20 years ago we reported that the special selectivities seen in water solution (see below) were also seen in some water suspensions, where one soluble component reacted with one that was poorly soluble. We pointed out that such suspensions in water could well be generally more practical ways to use water in manufacturing. Recently, Sharpless and co-workers described a remarkable acceleration of a reaction in such a suspension, which they called reactions ON water. The large reported rate effect was seen in only one particular case, but even without a large acceleration the selectivities that we describe below could perhaps make suspensions in water a practical way for the environmentally benign properties of water to be generally useful even with insoluble reaction components. One industry that has switched from VOCs to water is the paint industry. We are all familiar with the water-based paints that no longer emit strong solvent odors, and these have been widely adopted for painting automobiles, for instance. It is essentially impossible to capture all the solvent vapors that are released when a vehicle is spray painted, but when the solvent is water there is no problem. Water is not simply an environmentally benign solvent; it has special properties that are essentially unique, related to what is called the hydrophobic effect. This is the tendency for hydrocarbons or molecules with hydrocarbon components to avoid contact with water, and to associate instead with other hydrocarbon species in water. This is what makes aqueous soap solutions dissolve grease, and it is the driving force in biology for the associations that produce cell membranes, and that cause nucleic acids to form the famous double helix. It drives the folding of proteins into their shapes in enzymes and antibodies, and it also promotes the binding of biological substrates into enzymes and antibodies. As described below, the hydrophobic effect has now been used to mimic biological chemistry and to provide remarkable selectivities in the field called biomimetic chemistry. It has even been used to permit the discovery of the geometries of the transition states for some interesting reactions, information that is otherwise inaccessible.

Supercritical CO_2 medium

Chemical reactions run under neat conditions (no solvent) and in a supercritical CO_2 medium can also be considered as green choices.

Major problem with many solvents is their volatility that may damage human health and the environment. Even processes like recrystalisation require energy and substances to change the solubility. The problem of solvents has been overcome by using such solvents which do not pollute the environment. Such solvents are known as green solvents. Examples include liquid carbon dioxide (supercritical CO2), ionic liquid water. Even reactions have been conducted in solid state. For example the condensation reaction of orthoesters with phenylenediamines in presence of KSF clay under solvent free conditions using microwave. Many solvents used in traditional organic synthesis are highly toxic. The Green Chemistry approach to the selection of solvents has resulted in several strategies. One method that has been developed is to use supercritical carbon dioxide as a solvent .Supercritical carbon dioxide is formed under conditions of high pressure in which the gas and the liquid phases of carbon dioxide combine to a single –phase compressible fluid that becomes an environmentally benign solvent (temperature 31oC, 7280 kPa, or 72 atmospheres). Supercritical CO2 has remarkable properties .It behaves as a materialwhose properties are intermediate between those of a solid and those of a liquid .Theproperties cab be controlled by manipulating temperature and pressure .SupercriticalCO2 is environmentally benign because of its low toxicity and easy recyclability.

Carbon dioxide is not added to the atmosphere; rather, it is removed from the atmosphere for use in chemical processes. It is used as a medium to carry out a large number of reactions that would otherwise have many negative environmental consequences. It is even possible to perform stereoselective synthesis in supercritical CO2.

Some reactions can be carried out in ordinary water, the most green solvent possible. Recently, there has been much success in using near-critical water at higher temperatures where water behaves more like an organic solvent .Eckert and Liotta were able to run Friedel-Crafts reactions in near –critical water without the need for the acid catalyst AlCl3, which is normally used in large amounts in these reactions. In the past 5 years, many new ionic liquids have been developed with a broad range of properties. By selecting the appropriate ionic liquid, it is now possible to carry out many types of organic reactions in these solvents. In some reactions, a well –designed ionic solvent can lead to better yields under milder conditions than is possible with traditional solvents.

Fluorous solvents:

Fluorous chemistry involves the use of per fluorinated compounds or perfluorinated substituents to facilitate recovery of a catalyst or reaction product. Per fluorinated groups impart unique physical properties including high solubility in perfluorinated solvents. This property can be useful in organic synthesis and separation methods such as solid phase extraction. In practice, a perfluorinated alkyl group is incorporated into an organic reagent as an affinity tag. These reagents can then be separated from organic solvents by extraction with fluorinated solvents such as perfluorohexane.

Fluorouschemistry molecules consists of both nonfluorous and fluorous parts. The fluorouspart is a substituent contributing solubility in the fluorocarbon medium. Such perfluorosubstituents are called ponytails. Typical fluorous ponytails have the formula $CF_3(CF_2)_n(CH_2)_m$- where n is about 10 and m is about 3

Through the use of fluorous tags (ponytails) for fluorous phases or fluorous-derivatized solid phases allows for complete recovery of the tagged reagent making the use of fluorous chemistry techniques a popular topic in green chemistry.

Two main classes of fluorous solvents

1. Perfluorocarbons (PFCs)
2. Hydrofluoroethers (HFEs).

Both PFCs and HFEs are fluorous phases into which fluorous molecules may partition. They have found extensive use in fluorous liquid-liquid extraction separations.

Perfluorocarbons (PFCs)

Traditionally, fluorous solvents have been perfluorocarbons (PFCs) such as perfluorohexane, perfluoromethylcyclohexane, or perfluorodecalin. Used extensively in the electronics industry, PFCs are generally very non-polar and posess boiling points similar to their non-fluorous analogs.

These solvents are generally not miscible with either organic or aqueous solvents at ambient temperature or pressure.

Hydrofluoroethers

Hydrofluoroethers (HFEs) are an emerging class of fluorous solvents that are finding increased use in fluorous separations. They are represented by molecules such as nonafluorobutyl methyl ether, sold under the trade name HFE-7100. These solvents retain many of the fluorous characteristics of perfluorocarbons, but possess higher overall solvating power due to increased polarity relative to PFCs.

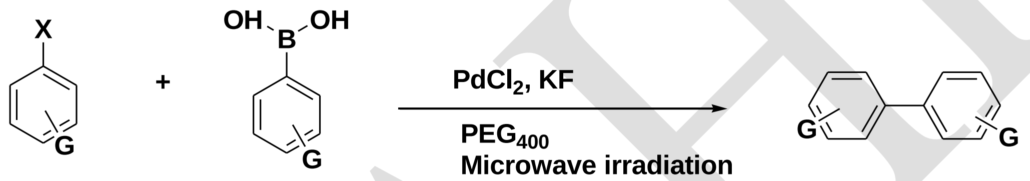
It's possible to select a perfluorinated hydrocarbon that is immiscible in another organic solvent, forming a distinct phase boundary. Such systems may become miscible at elevated temperature which is exploited in the design of some catalytic processes. Adding gaseous CO2 to the biphasic system also makes the phases miscible in many cases due to the high solubility of CO2 in both fluorous and organic solvents.

Fluorous solvents have the odd property of being both hydrophobic and lipophobic and thus are not miscible with either aqueous or many organic solvents. Fluorine, as the most electronegative element, does odd things to a molecule (and is often used in pharmaceutical compounds just because of some of these odd properties). In the perfluorinated hydrocarbons, the carbon-fluorine bonds are quite polar with the electron density higher toward the fluorine. The solvents themselves, however, are not polar due to free rotation about the C-C bonds, so they are not miscible with polar solvents and are hydrophobic.

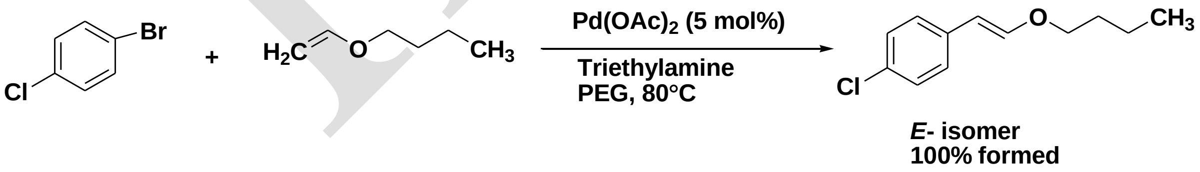
Because the F is so electronegative, the electrons are quite tightly held and the molecules have a low polarizability and unusually weak London dispersion forces, so they aren't miscible with non-polar solvents either. These weak London forces are explaied by the fact that the perfluorinated hydrocarbons have nearly the same boiling point as their corresponding normal hydrocarbon, inspite having more mass.

Polyethylene glycols (PEG) are known as compounds with wide spread industrial and medical applications. PEGs are readily soluble in polar and non-polar solvents and insoluble in aliphatic hydro carbons and supercritical CO2. A very interesting aspect of these compounds is behind their applications as solvent in organic reactions. They are inexpensive and significantly less hazardous than other organic solvents. Additionally, PEGs are stable under ambient condition because they have negligible vapor pressure and do not release VOCs. They have good stability in both acidic and basic media and are suitable reaction media for oxidation/reduction reactions. PEGs have compatibility as reaction media for various organic transformations such as N-arylation O-arylation S-arylation , allylation reactions, multicomponent reactions, oxidation , cycloaddition , polymerizations , N-alkynylation , asymmetric hydrogenation and asymmetric sharplessdihydroxylation. The important achievements related to the application of PEGs in various "well-known reactions" for carbon–carbon bond formation. In most cases, PEGs are used as alternative reaction media. Other important roles of PEGs in reactions such as phase transfer catalyst (PTC) and their stabilization properties are highlighted and 82 discussed in the proper situations.

Suzuki reaction (also known as Suzuki–Miyaura reaction) is a palladium catalyzed carbon–carbon bond formation between organoboron compounds with aromatic halides. An interesting example for Suzuki reaction in PEG . It was shown that the reaction was preceded in high yield in PEG400 (note: subscripts in all cases are average molecular weight of the applied PEG) as an inexpensive and non-toxic reaction medium.



Heck or Mizoroki–Heck reaction is a palladium-catalyzed coupling for preparation of substituted alkenes from aryl halides (or triflates) and alkenes. The first example of the Heck reaction in PEGwas reported in 2002 by Chandrasekhar et al. . They used PEG2000 as a solvent and carried out stereo- and regioselectivities Heck reaction without using additional ligands or PTC. Good to excellent E/Z diastero-isomer selec-tivitieswere obtained regardless on the electronic nature of the starting olefin. For example, a quantitative yield of E-isomer was isolated when4-chlorobromobenzene was reacted with butyl vinyl ether.



1. SOLVENTLESS REACTIONS ⎫ A dry media reaction or solid-state reaction or solventless reaction is a chemical reaction system in the absence of a solvent. ⎫ The drive for the development of dry media reactions in chemistry is:
   - Economics (save money on solvent)

- Not required to remove a solvent after reaction completion ultimetly purification step not required
- Reaction rate is high due more availability of reactants.
- Environmentaly friendly because solvent is not required.

2. Solid state reaction follows the fifth principle of green chemistry which avoid using toxic solvents in the chemical reaction.

3. ADVANTAGES
   - More efficient with more selectivity compared to reactions carried out in solvents.
   - Reactions are simple to handle, reduce pollution, comparatively. Cheaper to operate and are especially important in industry.

- Halogenation
- Michael Addition • Aldol Condensation
- Grignard Reaction Reformatsky Reaction
- Pinacol-Pinacolone Rearrangement
- Benzil-benzilic acid rearrangement
- Beckmann Rearrangement
- Armoatic Substitution Reactions Oxidative coupling of phenols

4. HALOGENATION
   Bromination of powdered (E)-o-stillbene carboxylic acid
   - Bromination with bromine in solution gives 1,2,4-bromo-3-phenyl- 3,4-dihydroisocoumarin as the major product.
   - HBr.Br2 complex in solid state at room temperature gave 12 selectively erythro-l ,2-dibromo-l ,2-dihydro stilbene carboxylic acid.

5. MICHAEL ADDITION
   - The Michael addition of chalcone to 2-phenyl cyclohexanone give 2,6-disubstituted cyclohexanone derivative in high distereoselectivity.

6. ALDOL CONDENSATION
   - The aldol condensation of the lithium enolateofmethyl 3,3-dimethyl butanoate with aromatic aldehydes gives mixture of the syn and anti products in 70% yield

Advantages

A solvent-free or solid state reaction may be carried out using the reactants alone or incorporating them in clays, zeolites, silica, alumina or other matrices. Thermal process or irradiation with UV, microwave or ultrasound can be employed to bring about the reaction.

- Solvent-free reactions obviously reduce pollution and bring down handling costs due to simplification of experimental procedure, work up technique and saving in labour. These would be especially important during industrial production

- Often, the products of solid state reactions turn out to be different from those obtained in solution phase reactions. This is because of specific spatial orientation or packing of the reacting molecules in the crystalline state. The orientational requirements of the substrate molecules in the crystalline state have provided excellent opportunities to achieve high degree of stereoselectivity in the products. This has made it possible to synthesize chiral molecules from prochiral ones either by complexation with chiral hosts or formation of intermediates with chiral partners.

- If two or more substrates are involved in the reaction, they are thoroughly ground together in a glass mortar or cocrystallized and allowed to stay at room temperature or transferred to a suitable apparatus and heated carefully in an oil bath or exposed to appropriate radiation until the reaction is complete. More sophisticated reaction procedures are also adopted, if necessary. The progress of the reaction can be monitored by TLC. In some cases, a small quantity of water or a catalyst may be added. If it is a single-compound reaction, it is subjected to heat or radiation directly. Care is to be taken to collect the volatile products, if they are produced.

Designing a Green Chemical synthesis:

Designing a Green synthesis using these principles:prevention of waste/ byproducts;maximum incorporation of the materials used in the process into the final products, atom economy, calculation of atom economy of the rearrangement, addition, substitution and elimination reactions. Green solvents– supercritical fluids, water as a solvent for organic reactions, ionic liquids, fluorous biphasic solvent, PEG, solventless processes, immobilized solvents and how to compare greenness of solvents.

POSSIBLE QUESTIONS

PART B

1. Explain the principle of prevention of waste in Green chemistry
2. What is meant by atom economy
3. Explain atom economy with a suitable example
4. Compare the atom economy of an addition and elimination reactions
5. What is meant by super critical carbon di oxide
6. What are the advantages of taking water as a solvent in organic synthesis
7. What is meant by a green solvent
8. What is meant by an ionic liquid. Give an example
9. What is meant by a fluorous solvent.
10. Give an example for substitution reaction

PART C

1. Explain atom economy with suitable examples
2. Explain atom economy of addition, elimination, substitution and rearrangement reactions
3. Compare and contrast conventional and green solvents
4. What are the advantages in using supercritical carbon di oxide as a solvent.
5. What are the advantages of taking water as a green solvent
6. Illustrate with examples to show that water is a green solvent
7. What is meant a Ionic liquid. What are the properties of ionic liquid. Classify them with suitable examples
8. Explain how to carryout a reaction in fluorous solvent

Question	A	B	C	D	Answer
Green chemistry synthesis could also involve which of the following?	High temperature	Dichloromethane	Fossil fuels	Microwave	Microwave
Which is fulfilling the needs of the present generation without compromising the ability of future generations to meet their needs?	Sustainability	Green chemistry	Life cycle assessment	Recycling	Sustainability
When discussing sustainability and green chemistry often used moral arguments and	Environment	Technology	Politics	Ethics	Ethics
Which of the following three terms is used in the 'Sustainability triangle'?	Micro-economics	Planet	Social responsibility	economics	Social responsibility
Solvent doesn't used in the reaction is called	Elimination reaction	Substitution reactions	Addition reaction	Solvent less reaction	solventless reaction
The following is often referred to as the universal solvent and is a preferred green solvent?	Water	Methanol	Ethyl acetate	Benzene	Water
A chemical process with an E-Factor of 1 creates less waste than an E-Factor of	21	25	22	23	25
Which can provide green technology solutions for a sustainable future?	Inorganic chemistry	Textile chemistry	Physical chemistry	Green chemistry	Green chemistry
Microwave radiation is selectively absorbed by the	Non polar molecules	Polar Molecules	Asymmetric molecules	Crystalline substances	Polar Molecules
The safer reagent for	Methyl iodide	Dimethyl sulfate	Dimethyl	Methyl bromide	Dimethyl

methylation is			carbonate		carbonate
Green chemistry synthesis could also involve which of the following?	High temperature	dicholoromethane	microwave oven	fossil fuels	microwave oven
The Neat reaction takes place	In the absence of solvent	In the absence of a solid support	In the absence of a catalyst	In presence of a solvent	In the absence of solvent
Liquids with a wide temperature range and no vapour pressure	Solid supports	organic catalysts	organic solvents	Ionic liquids	Ionic liquids
When movement of water molecules in liquid becomes equal to molecules in vapor form, a state is called	equilibrium	constant	ideal	non-ideal	equilibrium
Ionic bonding is very strong hence it needs a	high temperatures	low temperatures	constant temperature	high pressure	high temperatures
When gas liquefies, molecules lose kinetic energy and experience increase	forces of attraction	volume	density	pressure	forces of attraction
When liquids are heated, they	expand more than gases but less than solids	expand more than solids but less than gases	expand the least	expand the most	expand more than solids but less than gases
Least intermolecular forces are found in	solids only	liquids only	gases only	fluids	gases only
When gases are heated, they	expand more than solids but less than liquids	expand more than liquids but less than solids	expand the least	expand the most	expand the most
The property responsible for the "beading up" of water is	surface tension	vapor pressure	density	hydrogen bonding	surface tension
The direct conversion of a solid to a gas is called	fusion	sublimation	condensation	boiling	sublimation
What gives ionic liquids their	Low molecular	No ionic	High lattice	Large ions and shape	Large ions and

low melting point?	weight	bonding	energy	mismatch between them	shape mismatch between them
What is the role of the CO(g) in this reaction?	A catalyst	An oxidant	A reductant	A solvent	A reductant
What is the name of the phase transition that occurs when a solid is converted directly into a gas (without going through the liquid phase)	Melting	Boiling	Condensing	Sublimation	Sublimation
The specific enthalpy of atmospheric air most likely varies with	its pressure	its volume	its density	its temperature	its temperature
Measuring zeta potential is useful in determining which property of a liquid formulation	Viscosity	Stability	Solubility	Particle size	Stability
Fog is a solution of	water vapors in air	air in water vapor	air in air	vapors in vapors	water vapors in air
Number of moles of solute dissolved per dm3 of solution is	molality	percentage	concentration	molarity	molarity
Over 70% of earth's crust is covered with	water	land	coal	trees	water
Upset caused in natural balance of concentration of greenhouse gases is called	pollution	global warming	atmospheric poisoning	earth heating	global warming
Solvents used for cleaning electronic circuit boards are	chlorofluorocarbons	carbons	fluorides	grease	chlorofluorocarbons
Compounds which are added in soil to provide essential elements to plants are called	fertilizers	carbonates	salts	metals	fertilizers

Which of the following is the greenest solvent?	Formaldehyde	benzene	Ethanol	water	Water
The figure above shows a process that is often used as part of which 'green' product design system?	Market Flow Analysis	Customer Market Flow Analysis	Life Cycle Assessment	Product Life Analysis	Life Cycle Assessment
which is fulfilling the needs of the present generation without compromising the ability of future generations to meet their needs?	Sustainability	Green chemistry	Life Cycle Assessment	Recycling	Sustainability
Benzene, a _______ substance, is an important industrial solvent used in the production of pharmaceuticals, plastics, and dyes?	Odorless	Non-flammable	Biodegradable	Carcinogenic	Carcinogenic
which one is an excellent 'green' solvent as well as a greenhouse gas?	Methanol	CFCs	Carbon monoxide	Carbon dioxide	Carbon dioxide
Lignin, switch grass, and cellulose are all types of	Enzymes	Catalysts	Bio-based feedstock's	Anti-cancer compounds	Bio-based feedstock's
The following is often referred to as the universal solvent and is a preferred green solvent?	Water	Methanol	Ethyl Acetate	Benzene	Water
Soybean is used to replace traditional inks in printer cartridges, highlighting which of the Green chemistry principles?	Atom economy	Use of Renewable Feedstock's	Reduce derivatives	Prevent waste	Use of Renewable Feedstock's

This 'green' chemical is used in household cleaners to remove stains and is also a favorite dressing on salads!?	Vinegar (acetic acid)	Citric acid	Hydrochloric acid (HCl)	water	Vinegar (acetic acid)
An example of chemical toxics prevention is?	Removing water from industrial reactions	Eliminating the formation of chlorinated organics in paper	Utilizing ammonia instead of vinegar	Monitoring BPA (Bisphenol A) in plastic bottles	Eliminating the formation of chlorinated organics in paper
Green chemistry synthesis could also involve which of the following?	High temperature	Dichloromethane	Fossil fuels	Microwave	Microwave
Which of the following is not one of the twelve principles of green chemistry?	Using high temperatures to speed up reactions	Minimising toxic reagents used in a synthesis	Maximisation of atom economy	Minimising the use of solvents	Using high temperatures to speed up reactions
What term is used to describe the process by which a synthetic procedure is developed such that it is suitable for a production plant?	Plant development	Product development	Process development	Production development	Process development
Which of the following solvents is unacceptable on large scale?	Heptane	Diethyl ether	Xylene	Dimethoxyethane	Diethyl ether
Which of the following reagents is acceptable on large scale	Palladium chloride	Sodium dithionite	Pyridinium chlorochromate	Tin chloride	Tin chloride
What is the percentage atom economy for elimination reaction?	46.10%	36.30%	56.30%	23.50%	36.30%

Which of the following solvents can not be bio-derived?	Heptane	DCM	Toluene	Ethanol	Heptane
Synthetic methods should be designed to minimize incorporation of all materials used in the process in to final called	atom economy	prevention	a & b	none of above	atom economy
Among them which is green solvent	benzene	dichloro methane	super critical water	duetrated water	super critical water
The constituent in Deals – alder reaction	dienes	allyl halides	vinyl halide	all the above	all the above
Which of the following reaction gives 100% atom economy	clemmenson reduction	elimination reaction	diels alder reaction	aldol condensation	diels alder reaction
The usage of Phosgene and methyl chloride in the synthesis of Poly carbonates has been replaced by	di-phenyl carbonate	phenol – formaldehyde	phenyl carbonate	carbon dioxide	di-phenyl carbonate
The audible frequency range of ultrasounds	less than 16KHZ	greater then	equal to 16 KHZ	none of above	greater then
Microwave reaction are faster than thermal reaction	TRUE	FALSE	not applicable	none of above	TRUE
Addition reactions give	90% atom economy	75% atom economy	50% atom economy	100% atom economy	75% atom economy
What is the percentage atom economy for addition reaction?	25.00%	50.00%	60.00%	75.00%	75.00%
Which of the following is the greenest solvent?	Formaldehyde	benzene	Ethanol	water	Water
Greener synthetic methods	Ambient	High	Low	High pressure.	Ambient

should be carried out under the conditions	temperature and Pressure	temperature	Temperature		temperature and Pressure
Diels alder reaction is a	[3+1] cycloaddition	[4+2] cycloaddition	[2+2] cycloaddition	[2+2] cycloaddition	[4+2] cycloaddition
Diels alder reaction is a	4π-electron system	2π-electron system	6π-electron system	3π-electron system	4π-electron system

UNIT-III

SYLLABUS

Energy requirements for reactions – alternative sources of energy: use of microwaves and ultrasonic energy. Microwave assisted reactions in water: Hofmann elimination, methyl benzoate to benzoic acid, oxidation of toluene and alcohols; microwave assisted reactions in organic solvents. Diels-Alder reaction and decarboxylation reaction. Ultrasound assisted reactions: sonochemical Simmons-Smith Reaction (Ultrasonicalternative to iodine).

Microwave reactions

A related development that had a great impact on heterogeneous reaction is the use of microwave (MW) irradiation techniques for the acceleration of organic reactions. It is a useful technique for a variety of applications inorganic synthesis and functional group transformations. The focus has shifted to less cumbersome solvent-free methods wherein the neat reactants, often in the presence of mineral oxides or supported catalysts, undergo facile reactions to provide high yields of pure products thus eliminating or minimizing the use of organic solvents.

Microwave reactions involve selective absorption of MW energy by polar molecules. The non-polar molecules are inert to MW dielectric loss. The initial experiments with microwave techniques concentrate on the use of solvents with high dielectric strength such as dimethyl sulfoxide (DMSO) and dimethylformamide (DMF). The rate increase in these reactions are due to rapid superheating of the polar solvents. However, in these solution-phase reactions, the development of high pressures and the use of specialized Teflon vessels and sealed containers are some of the limitations. During recent years, the microwave heating methods has been added by accomplishing reactions on solid supports under solvent-free conditions. In these reactions, the organic compounds adsorbed on the surface of inorganic oxides, such as alumina, silica and clay, or 'doped' supports absorb microwaves whereas the solid support does not absorb or restrict their transmission. The bulk temperature is relatively low in such solvent free reactions although higher localized temperatures may be reached during microwave irradiation. These solvent-free MW assisted reactions provide an opportunity to work with open vessels thus avoiding the risk of high pressure development and for scaling up process.

The practical feasibility of microwave assisted solvent-free methods has been followed in useful transformations involving protection/ deprotection, condensation, oxidation, reduction, rearrangement reactions and in the synthesis of various heterocyclic systems on inorganic solid supports. The problems associated with waste disposal of solvents (used many-fold in chemical reactions) and excess chemicals are avoided or minimized.

Microwave heating: Here, microwaves couple directly with the molecules of the entire reaction mixture, leading to a rapid rise in the temperature. Since the process is not limited by the thermal conductivity of the vessel, the result is an instantaneous localized superheating of any substance that will respond to either dipole rotation or ionic conductivity. Only the reaction vessel contents are heated and not the vessel itself; better homogeneity and selective heating of polar molecules might be achieved.

The acceleration of chemical reactions by microwave exposure results from the interactions between the material and electromagnetic field leading to the thermal and specific (non-thermal) effects.

For microwave heating, the substance must possess a dipole moment. A dipole is
sensitive to external electric field and tries to align itself with the field by rotation. If submitted to an alternating current, the electric field is inversed at each alter and therefore dipoles tend to move together to follow the inversed electric field. Such a characteristic induces rotation and friction of the molecules, which dissipates as internal homogeneous heating. The electric field of commonly used irradiation frequency (2450 MHz) oscillates 4.9 × 109 times per second. Thus,

microwave heating is directly dependent on dielectric properties of a substance, dielectric constant (ε') and dielectric loss (ε"). The ability of a material to convert electromagnetic energy into heat energy at a given frequency and temperature, is calculated using

$$\varepsilon'' / \varepsilon' = \tan \delta$$

where δ is the dissipation factor of the sample, ε" is the dielectric loss, which measures the efficiency with which heat is generated from the electromagnetic radiation and ε' is the dielectric constant which gives the ability of a molecule to be polarized by an electric field. The high value of dissipation factor δ indicates large susceptibility to microwave energy.

The conduction mechanism leads, due to the much stronger interaction of ions with electric field, to the generation of heat. The ions will move under the influence of an electric field, resulting in expenditure of energy due to an increased collision rate, converting kinetic energy into heat. The heat generated by both mechanisms adds up resulting in a higher final temperature. Since the ability of a molecule to couple with the microwave radiation is a function of its molecular polarisability (i.e. a function of its dipole moment), only polar molecules interact with microwave energy. As a guide, compounds with high dielectric constants such as water, ethanol, acetonitrile, *N*,*N*-dimethylformamide (DMF), acetic acid, chloroform. dichloromethane, acetone, ethylene glycol etc., tend to heat rapidly under microwave irradiation, while less polar substances, such as aromatic and aliphatic hydrocarbons or compounds with no net dipole moment, such as carbon dioxide, carbon tetrachloride, diethyl ether etc. as well as highly ordered crystalline substances, are poorly absorbing. Thus, polar molecules in a non-polar solvent would absorb energy, but not the solvent or the reaction vessel, if it is made of teflon ($\mu = 2.1$ at 22 °C) or ceramic or even pyrex ($\mu = 4.5–6.0$).

Two types of microwave reactors can be used in the Laboratory.

1. Multimode Microwave Reactors

2. Monomode Microwave reactors.

Working of the Microwave Oven

In a microwave oven, microwaves are generated by a magnetron. A magnetron is a thermo-ionic diode having an anode and a directly heated cathode. As the cathode is heated, electrons are released and are attracted towards the anode. The anode is made up of an even number of small cavities, each of which acts as a tuned circuit. The anode is, therefore, a series of circuits, which are tuned to oscillate at a specific frequency or at its overtones.

A very strong magnetic field is induced axially through the anode assembly and has the effect of bending the path of electrons as they travel from the cathode to the anode. As the deflected electrons pass through the cavity gaps, they induce a small charge into the tuned circuit, resulting in the oscillation of the cavity. Alternate cavities are linked by two small wire straps, which ensure the correct phase relationship. This process of oscillation continues until the oscillation has achieved a sufficiently high amplitude. It is then taken off by the anode via an antenna. The variable power available in domestic ovens is produced by switching the magnetron on and off according to the duty cycle.

Microwave dielectric heating is effective when the matrix has a sufficiently large dielectric loss tangent (i.e. contains molecules possessing a dipole moment). The use of a solvent is not always mandatory for the transport of heat. Therefore, reactions performed under solvent-free conditions present an alternative in the microwave chemistry and constitute an environmentally benign technique, which avoids the generation of toxic residues, like organic solvents and mineral acids, and thus allows the attainment of high yields of products at reduced environmental costs. This emerging environmentally benign technique belongs to the upcoming area of green chemistry.

Interaction of microwaves with different materials

Most common domestic microwave ovens utilize the frequency of 2.45 GHz, and this may be a reason that all commercially available microwave reactors for chemical use operate at the same frequency. Heating in microwave cavities is based upon the ability of some liquid and solids to absorb and transform electromagnetic energy into heat. In general, during the interaction of microwaves with materials three different behaviors of a material can be observed depending whether the material is counted among.

(1) electrical conductors (e.g. metals, graphite)
(2) Insulators, which are considered as materials with good dielectric properties ex-tremly poor conductors) (e.g. quartz glass, porcelain, ceramics, Teflon)
(3) Lossy dielectrics, which are materials that exhibit so called dielectric losses, which in turn results in heat generation in an oscillating electromagnetic field (e.g. water).

When a strongly conducting material (e.g. a metal) is exposed to microwave irradiation, Microwaves are largely reflected from its surface. However, the material is not effectively heated by microwaves, in response to the electric field of microwave radiation, electrons move freely on the surface of the material, and the flow of electrons can heat the material through a resistive heating mechanism. In opposite, in the case of insulators (e.g. porcelain), microwaves can penetrate through the material without any absorption, losses or heat generation. They are transparent to microwave. Passage of microwave radiation which is electromagnetic in nature can give rise to absorption of microwave energy and heat generation due to the so called dielectric heating mechanism.

Various Types of Microwave assisted Organic Reactions

The microwave-assisted organic reactions have been broadly classified into two categories: microwave-assisted reactions using solvents; microwave-assisted reactions using solvent-free conditions.

Microwave Assisted Reactions using Solvents

In the case of the microwave-assisted reactions using (organic) solvents, the reactants are usually dissolved in the solvent, which often couples effectively with microwaves and thus acts as the energy transfer medium.

An alternative method for performing microwave assisted organic reactions, termed enhanced microwave synthesis (EMS), has also been examined. By externally cooling the reaction vessel with compressed air, while simultaneously administering microwave irradiation, more energy can be directly applied to the reaction mixture. In the conventional microwave synthesis (CMS), the initial microwave power is high, increasing the bulk temperature (TB) to the desired value very quickly. However, upon reaching this temperature, microwave power decreases or shuts off completely in order to maintain the desired bulk temperature without exceeding it. When microwave irradiation is off, classical thermal chemistry takes over, losing the full advantage of microwave irradiation, which is used to reach TB faster. Microwave enhancement of chemical reactions will only take place during the application of the microwave energy. This source of energy will directly activate the molecules in a chemical reaction, and therefore it is not desirable to suppress its application. EMS ensures that a high, constant level of microwave energy is applied, resulting in the significantly greater yields and cleaner chemistries. Recently, the combination of two prominent green chemistry principles, namely microwaves and water has become very popular and received substantial interest.

Approaches to Microwave-assisted synthesis

Organic Chemistry

Because, for the majority of applications, the rates ofmicrowave-heated reactions will be comparable withthose from conventional heating, what advantagesdo microwaves offer for clean processing? Briefly,there are general advantages, others that are morespecific and some that are relevant to particularmethods.

The main general advantages include:

(1) Microwave energy can be introduced remotely,without contact between the source and thechemicals.

(2) Energy input to the sample starts and stopsimmediately when the power is turned on or off.

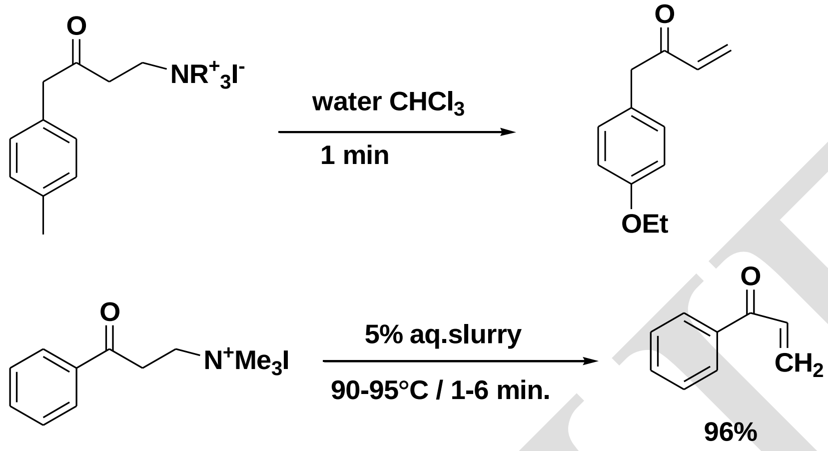
(3) Heating rates are higher than can be achievedconventionally if at least one of the components can couple strongly with microwaves.

Microwave Assisted Reactions in Water

Hofmann elimination

An example is the exploitation of the different dielectric properties of water and chloroform in the Hofmann elimination reaction reported by Strauss and Trainor. The aim of their study was to produce aryl vinyl ketones from the corresponding quaternary ammonium salts (see Figure 1.5) using a Hofmann elimination mechanism. Problems are encountered if this reaction is performed using conventional heating since the conjugated ketones produced are heat-sensitive and polymerization is difficult to avoid at high temperatures. These researchers performed the reaction successfully by stirring a mixture of N-[2-(4'-ethoxybenzoyl)ethy]-N, N, N-trimetylammonium iodide, water and chloroform under microwave heating. They reported a product yield of 96%. Typically, 40 seconds after commencement of the reaction, the temperatures of the aqueous and the organic phases were 105 and 48 °C respectively, due to differences in the dielectric properties of the solvents. As the reaction proceeded the product, 4'-ethoxyphenyl vinyl ketone, was extracted and diluted into the poorly microwave-absorbing, cooler, organic phase hence avoiding the secondary polymerization reaction. Figure 1.5 A scheme showing the production of aryl vinyl ketones from a corresponding quaternary ammonium salt.

In this method, normally quaternary ammonium salts are heated at high temperature and the yield of the product is low. Use of microwave irradiation has led to high-yielding synthesis of a thermally unstable Hofmann elimination product (Scheme 1). In this water-chloroform system is used.



A scheme showing the production of aryl vinyl ketones from a corresponding quaternary ammonium salt

Hydrolysis of Methylbenzoate to Benzoic Acid (Saponification)

Saponification of methylbenzoate in aqueous sodium hydroxide under microwave conditions (2.5 min) gives 5 84% yield of the benzoic acid.

$$\underset{\text{Methylbenzoate}}{C_6H_5COOCH_3} \xrightarrow[\text{mw 25 min}]{\text{aq. NaOH}} \underset{\substack{\text{Benzoic acid} \\ \text{(84\%)}}}{C_6H_5COOH}$$

Hydrolysis

Microwave reactions have been extensively used for hydrolysis.

Hydrolysis of Benzyl Chloride

Hydrolysis of benzyl chloride with water in microwave oven gives 97% yield6 of benzyl alcohol in 3 min (Scheme 2). The usual hydrolysis in normal way takes about 35 min.

$$\underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} + H_2O \xrightarrow[\text{3 min}]{\text{mw}} \underset{\substack{\text{Benzyl alcohol}\\(97\%)}}{C_6H_5CH_2OH}$$

Hydrolysis of benzamide

The usual hydrolysis of benzamide takes 1 hr. However, under microwave conditions, the hydrolysis is completed in 7 min giving5 99% yield of benzoic acid.

$$\underset{\text{Benzamide}}{C_6H_5CONH_2} \xrightarrow[\text{mw 7 min}]{20\%\ H_2SO_4} \underset{\substack{\text{Benzoic acid}\\(99\%)}}{C_6H_5COOH}$$

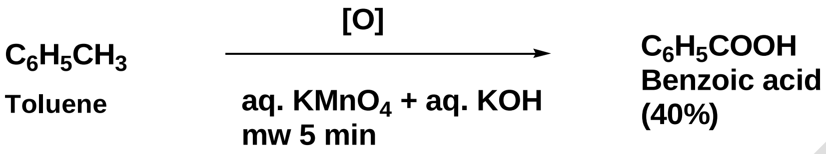
Hydrolysis ofN-phenyl Benzamide

The acid hydrolysis ofN-phenylbenzamide usually takes 18-20 hr. However, under microwave conditions the reaction is completed in 12 min giving6 74% of benzoic acid

$$\underset{\text{N-phenylbenzamide}}{C_6H_5CONHC_6H_5} \xrightarrow[\text{mw 12 min}]{20\%\ H_2SO_4} \underset{\substack{\text{Benzoic acid}\\(74\%)}}{C_6H_5COOH}$$

Oxidation o/Toluene

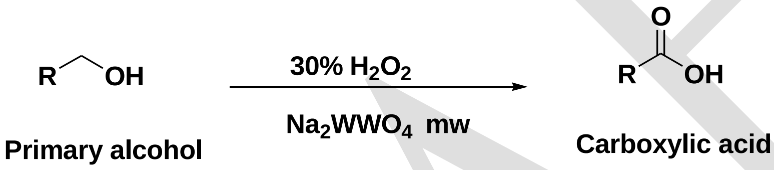
Oxidation of toluene with KMn04 under normal conditions ofrefluxing takes 10-12 hr compared to reaction in microwave conditions5, which takes only 5 min and the yield is 40%



$$\underset{\text{Toluene}}{C_6H_5CH_3} \xrightarrow[\text{aq. KMnO}_4\text{ + aq. KOH, mw 5 min}]{[O]} \underset{\text{Benzoic acid (40\%)}}{C_6H_5COOH}$$

Oxidation of Alcohols

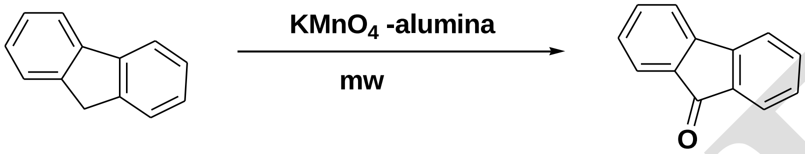
A number of primary alcohols can be oxidised to the corresponding carboxylic acid using sodium tungstate as catalyst in 30% aqueous hydrogen peroxide.



Similarly, secondary alcohols have been oxidised5a under microwave irradiation by using doped supports like clayfen (montmorillonite KIO + iron (III) nitrate), silica manganese dioxide, claycop (montmorillonite KIO + copper(II) nitrate)-H20 2, Cr03-wet alumina, iodobenzenediacetate-alumina,
CuS04-alumina, oxone-wet alumina

R,R_1 = various aromatic, aliphatic and heterocyclic groups

Also oxidation oflinear and cyclic secondary alcohols and benzylic alcohols to the corresponding carbonyl compounds under microwave irradiation conditions can be achieved. Arenes on oxidation with KMn04 impregnated on alumina under microwave irradiation in dry media (instead of several days under classical conditions) gave5b ketones (CH2 group is oxidised to keto)



Thiols have been oxidised5b to disulphides on mineral supports like silica, celite, florisel, alumina

$$C_6H_5COOH + nC_3H_7OH \xrightarrow[\text{mw 6 min}]{\text{conc. } H_2SO_4} C_6H_5COOC_3H_7$$

Benzoic acid **Propylbenzoate 70%**

Microwave-Assisted Reactions in Organic Solvents

This section includes those microwave induced reactions in which one or both the reactants (ifliquid) act as a solvent and also those reactions in which organic solvent is used to assist the reaction.

Esterification: Reaction of Carboxylic Acid and Alcohol

A mixture of benzoic acid and n-propanol on heating in a microwave oven for 6 min in presence of catalytic amount of cone. sulphuric acid gives propylbenzoate

$$ArCH_2OR + R^1COOH \xrightarrow[\text{Ln= Ld, Nd Sm, Dy, Br} \atop \text{mw 2 min}]{LnBr_3} ArCH_2OCOR^1 + ROH$$

Esterification*:*

Reaction of Carboxylic Acids and Benzyl Ethers Using LnBr3 (Ln = La, Nd, Sm, Dy, Er)

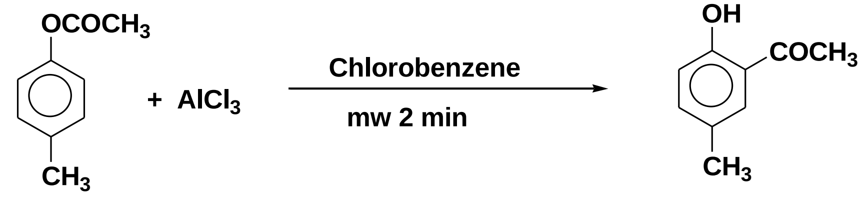
A mixture of carboxylic acid and benzyl ether on heating in a microwave oven in the presence of LnBr3 afforded8 the esters in 2 min

$$ArCH_2OR + R^1COOH \xrightarrow[\text{Ln = Ld, Nd Sm, Dy, Er} \atop \text{mw 2 min}]{Ln\ Br_3} ArCH_2OCOR^1 + ROH$$

Fries Rearrangement

Fries rearrangement is a useful method for the preparation of phenolic ketones and is usually carried out by heating a mixture of substrate and aluminium chloride.

There is considerable rate enhancement of Fries rearrangement by conunercial microwave ovens over conventional methods. Thus, a mixture of p-cresyl acetate and anhydrous aluminium chloride are heated in dry chlorobenzene in a sealed tube in a microwave oven for 2 min to give9 85% yield of the product

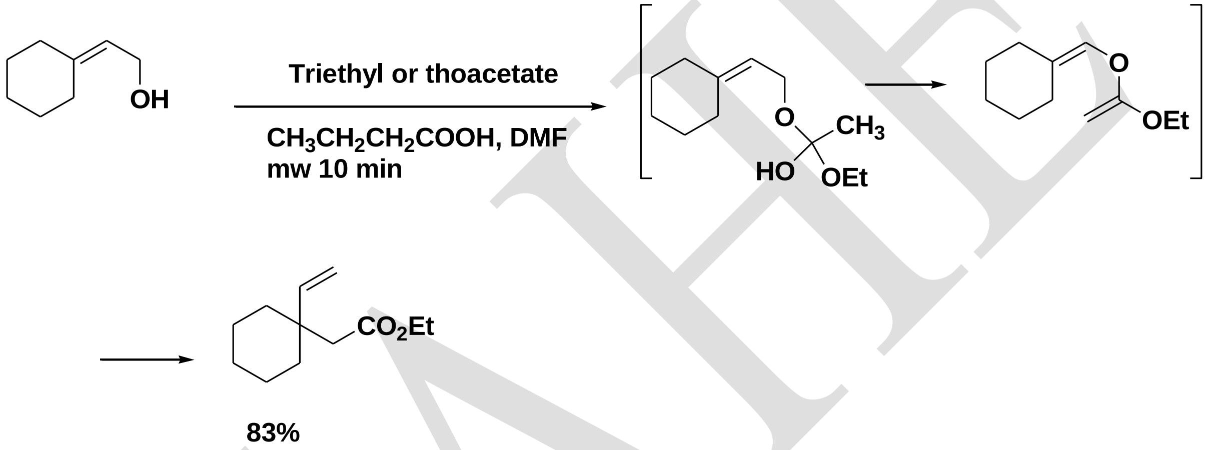


p-Cresyl acetate

2-Hydroxy-4-methyl acetophenone
85%

Orthoester Claisen Rearrangement

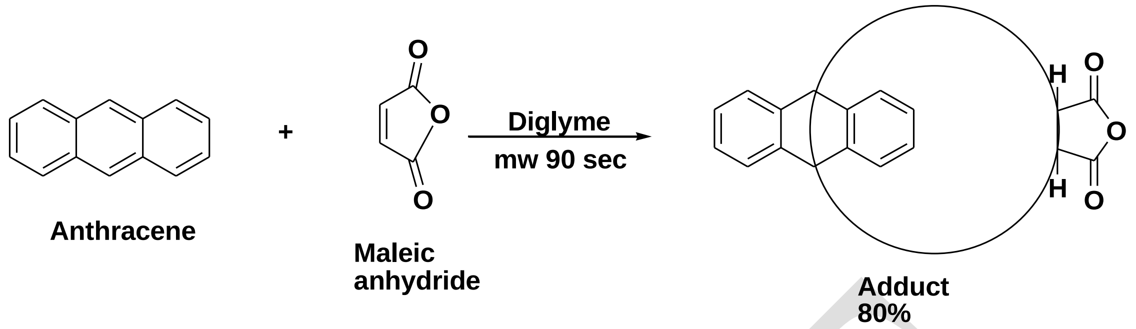
In the usual conventional procedure, a mixture of allyl alcohol, triethyl orthoacetate and propanoic acid is heated in a sealed tube for 48 hr. However, under microwave conditionslO a mixture of allyl alcohol, triethyl orthoacetate and propanoic acid in dry dimethylformamide is heated in microwave oven for 10 min. The product (Scheme 11) is obtained in 83% yield.



Diels Alder Reaction

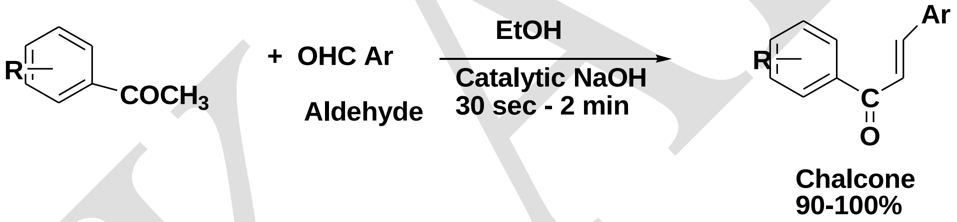
The reaction involves 1,4-addition of an alkene (e.g., maleic anhydride) to a conjugated diene (e.g. anthracene) to form an adduct of six membered ring. Under usual conditions '1 the reaction requires a reflux period of 90 min However, under microwave conditions3,12 diglyme is used as a solvent and

80% yield of the adduct is obtained in 90 sec



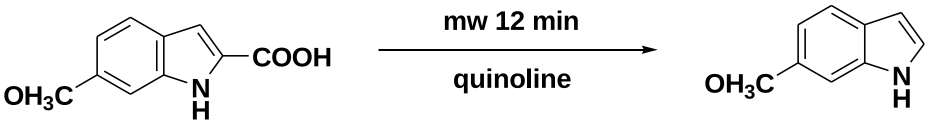
Synthesis o/Chalcones

Microwaves have been used for the synthesis 13 of chalcones and related enones. Considerable rate enhancement is observed, bringing down the reaction time from hours to minutes in improved yield



Decarboxylation

Conventional decarboxylation of carboxylic acids involve refluxing in quinoline in presence of copper chromite and the yields are low. However, in the presence of microwaves 14, decarboxylation takes place in much shorter time as illustrated



6-Methoxy indole-2-carboxylic acid

6-Methoxyindole
99%

Ultrasound assisted reactions:

sonochemical Simmons-Smith Reaction (Ultrasonicalternative to iodine).

Introduction

The word 'ultrasound' has become common knowledge due to the widespread use of ultrasound scanning equipments in medical applications. Ultrasound refers to sound waves having frequencies higher than those to which the human ear can respond (*fl,* > 16 KHz) (Hz = Hertz = cycles per second). High frequency ultrasound waves are used in medical equipments. The ultrasound frequencies ofintetest for chemical reactions (about 20-100 KHz) are much
lower than those used for medical applications, but the power used is higher. The ultrasound is generated with the help of an instrument having an ultrasonic transducer, a device by which electrical or mechanical energy can be converted into sound energy. The most commonly used are the electromechanical transducers which convert energy into sound - they are mostly made of quartz and are commonly based on the piezoelectric effect. When equal and opposite electrical charges are applied to opposite faces of a crystal of quartz, expansion or contraction occurs. Application of rapidly reversing charges sets up a vibration that emits ultrasonic waves called the *piezoelectric effect.* In modern ultrasonic equipments, the piezoelectric transducers are made from ceramic impregnated barium titanate. Such devices convert over 95% of the electrical energy into ultrasound. In practice, the devices only have an optimum operating frequency.

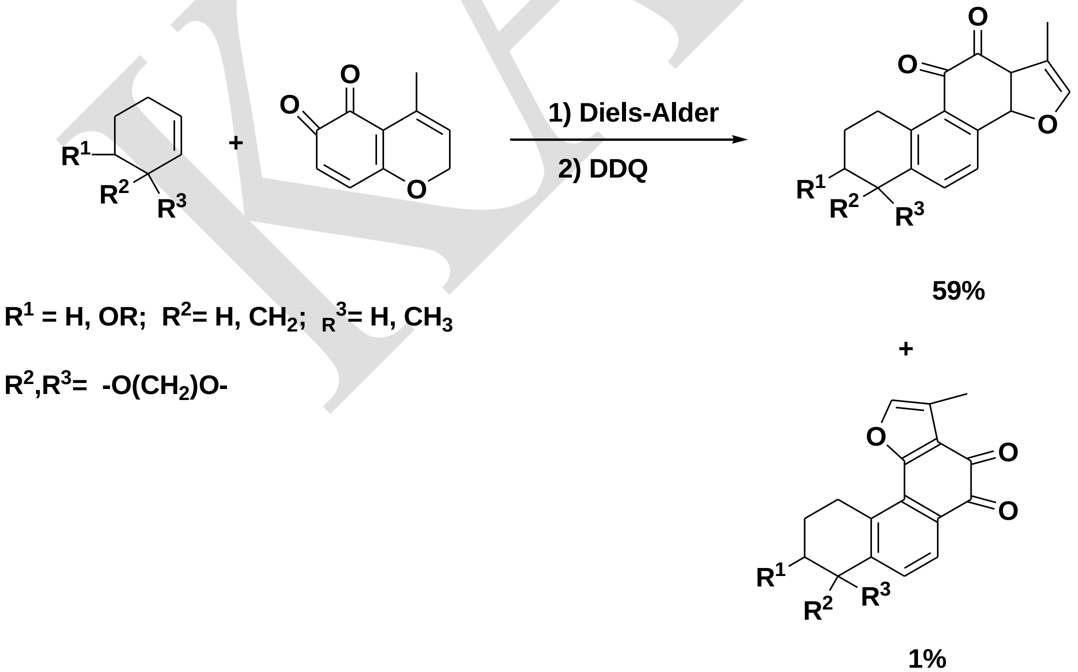
When a sound wave, propagated by a series of compression and refraction cycles, pass through a liquid medium, it causes the molecules to oscillate around their mean position. During the compression cycle, the average distance between the molecules is reduced and during refraction, the average distance between the molecules is increased. In the refraction cycle, under appropriate conditions, the attractive forces of the molecules of the liquid may be overcome, causing formation of bubbles. In case the internal forces are great enough to

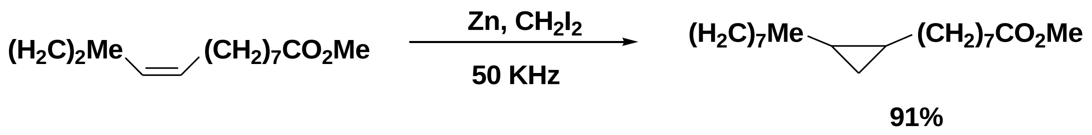
ensure collapse of these bubbles, very high local temperature (around 5000°C) and pressure (over 1000 bar) may be created. It is this very high temperature' and pressure that initiate chemical reactions. The term 'sonochemistry' is used to describe the effect of ultrasound

waves on chemical reactivity. A number of reviews on the chemical applications of ultrasound have been published.

Simmons-Smith Reaction

In this reaction, sonochemically activated zinc and methylene iodide are used. The generated carbene adds on to an olefinic bond to give 91 % yield of the cyclopropane derivative compared to 51 % yield by the normal route.





The' above method can be scaled Up41 and has several advantages. The reagent used, ZnlCH2I2 is known as Simmons-Smith reagent. Ketones on reaction with Simmons-Smith reagent results in methylenation of carbonyl group. Normally such methylenation of carbonyl group requires complex reagents. It can now be accomplished by sonication.

Alternative energy sources for reactions

Running reactions can be energy intensive. When chemists boil a reaction, they simultaneouslycool the solvent vapours. The resulting droplets fall into the reaction so that the reaction neverruns dry. But this standard process requires energy to both heat and cool the reaction, inaddition to the water being constantly run through a condenser. Therefore, some green chemists look to new energy sources to drive reactions. Microwaveassisted reactions can be run in water at a small scale, often with accelerated rates due totemperature and pressure effects. Reactions to build oxygen-, nitrogen- or sulfur-containingrings common in medicinal chemistry can also be driven using microwaves. Alternatively, the energy from grindingreagents together using a mortar and pestle or a ball grinder can be enough to trigger areaction.

Ultrasound sonication is another energy source with useful applications such as deprotecting an amine, protecting hydroxyls on sugars, or reducing an α,β-unsaturated ketone in a steroid The sound waves create areas of high and low pressure, much like ripples in a pond, as they travel through liquid. Bubbles form in the low-pressure areas, collapse when they reach high-pressure regions, and send shockwaves through the reaction. Surprisingly, ultrasound sonication can influence the products of a reaction. When chemists stirred a suspension of benzyl bromide and alumina-supported potassium cyanide, they retrieved diphenylmethane, which contains two connected benzene rings, as the product of a Friedel-Crafts reaction. But when they sonicated the reaction, the cyanide ion replaced the bromine atom, giving benzyl cyanide as the product. The researchers suspect that the bubbles generated during sonication masked the metallic catalytic sites on the solid support.

In 1830, scientists discovered *photo-voltaic* compounds, which release energy when exposed to light. This discovery eventually led to the development of *solar cells and solar power*.

In 1839, William Robert Grove invented the first *hydrogen fuel cell*, which harnessed electricity from the reaction between hydrogen and oxygen.

In the late 1880, *hydroelectric power* first became commercially available in the United States, and solar power was discovered in Europe. Governments established the first energy departments shortly before the turn of the century.

In 1947, The first nuclear reactor project aimed at energy production was initiated in Brookhaven, New York.

In 1970, the US Environmental Protection Agency (EPA) was established. Damage to natural areas as a result of *energy harvesting* was one of the first issues addressed by the agency.

In 1976, Congress authorized a committee to examine the potential for the development of electric vehicles, with the goal of reducing dependence on fossil fuels.

Solar power is the conversion of sunlight into electricity, either directly using *photovoltaics (PV)*, or indirectly using*concentrated solar power (CSP)*. Concentrated solar power systems use lenses or mirrors and tracking systems to focus a large area of sunlight into a small beam. Photovoltaics convert light into an electric current using the photovoltaic effect.

How can an organization use it? Public and private entities can take advantage of the benefits of solar power for business in a wide variety of ways:

- Install a commercial solar power system (rooftop equipment, field array or carport) and become an owner/operator, lessee or participant in a solar power purchase agreement (PPA).
- Purchase solar energy that's been generated by an offsite commercial solar installation.
- Construct or retrofit a building to incorporate a solar hot water, cooling or ventilation system.

Wind power is the use of air flow through wind turbines to mechanically power generators for electricity. Wind power, as an alternative to burning fossil fuels, is plentiful, renewable, widely distributed, clean, produces no greenhouse gas emissions during operation, and uses little land.

Bioenergy

The term "biomass" refers to organic matter that has stored *energy* through the process of *photosynthesis*. It exists in one form as plants and may be transferred through the food chain to animals' bodies and their wastes, all of which can be converted for everyday human use through processes such as *combustion*, which releases the *carbon dioxide* stored in the plant material.

Many of the *biomass fuels* used today come in the form of wood products, dried vegetation, crop residues, and aquatic plants. Biomass has become one of the most commonly used renewable sources of energy in the last two decades, second only to*hydropower* in the generation of electricity.

It is such a widely utilized source of energy, probably due to its low cost and indigenous nature, that it accounts for almost 15% of the world's total energy supply and as much as 35% in developing countries, mostly for cooking and heating.

Advantages of Biomass Energy includes:

1) Biomass used as a fuel reduces need for fossil fuels for the production of heat, steam, and electricity for residential, industrial and agricultural use.
2)Biomass is always available and can be produced as a renewable resource.
3)Biomass fuel from agriculture wastes maybe a secondary product that adds value to agricultural crop.
4)Growing Biomass crops produce oxygen and use up carbon dioxide.
5)The use of waste materials reduce landfill disposal and makes more space for everything else.
6)Carbon Dioxide which is released when Biomass fuel is burned, is taken in by plants.
7)Less money spent on foreign oil.

Disadvantages of Biomass Energy includes:

1)Agricultural wastes will not be available if the basic crop is no longer grown.
2)Additional work is needed in areas such as harvesting methods.
3)Land used for energy crops maybe in demand for other purposes, such as faming, conservation, housing, resort or agricultural use.

This is a type of renewable energy derived from biomass to create heat and electricity (or to produce liquid fuels used for transportation, like ethanol and biodiesel). Biomass refers to any organic matter coming from recently living plants or animals. Even though bioenergy generates about the same amount of carbon dioxide as fossil fuels, the replacement plants grown as biomass remove an equal amount of CO_2 from the atmosphere, keeping the environmental impact relatively neutral. There are a variety of systems used to generate this type of electricity, ranging from directly burning biomass to capturing and using methane gas produced by the natural decomposition of organic material.

How can an organization use it? Depending on your operation, there are many ways to incorporate bioenergy into your sustainable energy plans:

- Organizations can convert to fleet vehicles that use biofuels such as ethanol or biodiesel.
- Manufacturing facilities can be equipped to burn biomass directly, producing steam captured by a turbine to generate electricity. In some cases, this process can power the facility as well as heating it. For example, paper mills can use wood waste to produce electricity and steam for heating.
- Farm operations can convert waste from livestock into electricity using small, modular systems.
- Towns can tap the methane gas created by the anaerobic digestion of organic waste in landfills and use it as fuel for generating electricity.

Geothermal Power

Energy from the Earth What could be more natural or plentiful? The source of geothermal power is the heat contained inside the Earth; heat so intense that it creates molten magma. There are a few different types of geothermal energy that can be tapped. “Some geothermal systems are formed when hot magma near the surface (1,500 to 10,000 meters deep) directly heats groundwater.” The heat generated from these hot spots flows outward toward the surface, manifesting as volcanoes, geysers, and hot springs.

Naturally-occurring hot water and steam can be tapped by energy conversion technology to generate electricity or to produce hot water for direct use. “Other geothermal systems are formed even when no magma is nearby as magma heats rocks which in turn heat deeply-circulating groundwater.” In order to maximize the energy gleaned from these so-called “hot dry rocks,” geothermal facilities will often fracture the hot rocks and pump water into and from them in order to use the heated water to generate electricity.

Advantages of Geothermal Energy:

- **Reduce Reliance on Fossil Fuels** : Dependence on fossil fuels decreases with the increase in the use of geothermal energy. With the sky-rocketing prices of oil, many countries are pushing companies to adopt these clean sources of energy. Burning of fossil fuels releases greenhouse gases which are responsible for global warming.
- **No Pollution** : This is one of the main advantage of using geothermal energy since it does not create any pollution and help in creating clean environment. Being the renewable source of energy, geothermal energy has helped in reducing global warming and pollution. Moreover, Geothermal systems does not create any pollution as it releases some gases from deep within the earth which are not very harmful to the environment.
- **Direct Use** : Since ancient times, people having been using this source of energy for taking bath, heating homes, preparing food and today this is also used for direct heating of homes and offices. This makes geothermal energy cheaper and affordable. Although the initial investment is quite steep but in the long run with huge cost saving it proves quite useful.

How can an organization use it? Geothermal energy can be part of a commercial utility energy solution on a large scale, or be part of a sustainable business practice on a local level. Direct use of geothermal energy may include:

- Heating office buildings or manufacturing plants
- Helping to grow greenhouse plants
- Heating water at fish farms
- Aiding with various industrial processes (e.g. pasteurizing milk)

Hydroelectric

Remaining waterwheels previously used to operate the gristmills and sawmills of early America are now largely functioning as historic sites and museums. Today, the kinetic energy of flowing rivers is captured in a much different way and converted into hydroelectricity. Probably the most familiar type of hydroelectric power is generated by a system in which dams are constructed to store water in a reservoir. When released, the water flows through turbines to produce electricity. This is known as “pumped-storage hydropower”—water is cycled between lower and upper reservoirs to control electricity generation between times of low and peak demand. Another type, called “run-of-river hydropower,” funnels a portion of river flow through a channel and does not require a dam. Hydropower plants can range in size from massive projects like the Hoover Dam to micro-hydroelectric power systems.

How can an organization use it? Direct use of hydroelectric power is naturally dependent on geographic location. Assuming a dependable waterway source is accessible and available, it could be used in the following ways:

- Micro-hydroelectric plants can be constructed to supply electricity to farm and ranch operations or small municipalities.
- Small towns can harness the energy of local waterways by building moderately-sized hydroelectric power systems.

Hydrogen

Hydrogen is the simplest (comprised of one proton and one electron) and most abundant element in the universe, yet it does not occur naturally as a gas on earth. Instead, it is found in organic compounds (hydrocarbons such as gasoline, natural gas, methanol and propane) and water (H_2O). Hydrogen can also be produced under certain conditions by some algae and bacteria using sunlight as an energy source. Hydrogen is high in energy, yet produces little or no pollution when burned. Hydrogen fuel cells convert the potential chemical energy of hydrogen into electricity, with pure water and heat as the only byproducts. However, practical and widespread commercialization of these fuel cells will likely be limited until costs come down and durability improves.

How can an organization use it? Almost all the hydrogen used in the United States is used in industry to refine petroleum, treat metals, produce fertilizer and process foods. In addition, hydrogen fuel cells are used as an energy source where hydrogen and oxygen atoms are combined to generate electricity. There are also currently a few hundred hydrogen-powered vehicles operating in the United States, a number that could increase as the cost of fuel cell production drops and the number of refueling stations increases. Other practical applications for this type of renewable energy include:

- Large fuel cells providing emergency electricity for buildings and remote locations
- Marine vessels powered by hydrogen fuel cells

POSSIBLE QUESTIONS

PART B

1. What are microwaves
2. How does a microwave oven work
3. What are ultrasonic waves
4. Write notes on Hoffmann elimination reaction
5. What are the advantages of performing a reaction in a microwave oven
6. Explain a reaction taking place with water as a solvent in a microwave oven
7. Give an example for a reaction taking place without a solvent in a microwave synthesizer.
8. How chalcones are prepared.

PART C

1. Microwave heating is more efficient than ordinary heating-explain.

2. Explain the principles of sonochemistry. Write any three of the important ultrasonic promoted synthesis.
3. Write Diels alder reaction on the basis of microwave ultra sound assisted synthesis.

4. Illustrate the Hoffmann elimination reaction.
5. What are the advantages of ultrasound synthesis?
6. What is polyethylene glycol? Give the Suzuki coupling reaction in polyethylene glycol.

7. Explain the Diels-Alder reactions under microwave irradiation.

8. Describe the oxidation reactions of toluene and alcohol.

9. How will you carried out Simmons-Smith reaction under sonification. Give the important applications.

10. Explain the microwave reactions in organic solvents.

Question	A	B	C	D	Answers
Which of the following process where a quaternary amine is reacted to create a Tertiary amine and an alkene by treatment with excess methyl iodide followed by treatment with silver oxide, water, and heat	diels alder reaction	retro-Diels–Alder reaction	Simmons-Smith Reaction	Hofmann elimination	Hofmann elimination
The Diels–Alder reaction is an	organic chemical reaction	medicinal chemistry	green chemistry	environmental chemistry	organic chemical reaction
The Diels–Alder reaction is specifically a	[4+2] cycloaddition	[2+2] cycloaddition	[3+5] cycloaddition	[4+4] cycloaddition	[4+2] cycloaddition
Which of the following is formed between a conjugated diene and a substituted alkene, commonly termed the dienophile, to form a substituted cyclohexene system	Diels–Alder reaction	Hofmann elimination	retro-Diels–Alder reaction	Simmons-Smith Reaction	Diels–Alder reaction
Diels–Alder reactions can be reversible under certain conditions; the reverse reaction is known as the	hetero diels alder reaction	Hofmann elimination	retro-Diels–Alder reaction	Simmons-Smith Reaction	retro-Diels–Alder reaction
The Diels-Alder reaction is a conjugate addition reaction of a conjugated diene to an alkene (the dienophile) to produce a	cyclobutane	cycloheptane	cyclopentane	Cyclohexene	Cyclohexene
Which is a chemical reaction that removes a carboxyl group and releases carbon dioxide?	Decarboxylation	demethylation	dehydration	dehydrogenation	Decarboxylation
Enzymes that catalyze decarboxylations are called	dehydraxylase	dehydrogenase	decarboxylases	demethylase	decarboxylases
Which reaction affords the cyclopropanation of olefins?	Simmons-Smith Reaction	retro-Diels–Alder reaction	hetero diels alder reaction	Hofmann elimination	Simmons-Smith Reaction
Which is an organic cheletropic reaction?	Hofmann elimination	hetero diels alder reaction	retro-Diels–Alder reaction	Simmons–Smith reaction	Simmons–Smith reaction
The Simmons–Smith reaction is generally	Cyclopropanation	cyclopentation	cycloheptane	cyclobutane	Cyclopropanation

preferred over other methods of					
Which of the following science is applying microwave radiation to chemical reactions	Microwave chemistry	environmental chemistry	green chemistry	synthetic chemistry	Microwave chemistry
Ultrasound energy is a type of	electrical energy	chemical energy	mechanical energy	kinetic energy	mechanical energy
Ultrasound is distinguished by vibrations with a frequency greater than	20,000 Hz	40,000Hz	30,000Hz	10,000Hz	20,000 Hz
Primary alcohols can be oxidized to form	aldehydes and hydrocarbons	carboxylic acid and hydrocarbons	aldehyde and carboxylic acids	ketones and carboxylic acids	aldehyde and carboxylic acids
secondary alcohols normally terminates at the	aldehyde	alcohol	ester	ketone	ketone
Tertiary alcohols are resistant to	reduction	Oxidation	methylation	carboxylation	Oxidation
The oxidation of a primary alcohol at the aldehyde level is possible by performing the reaction in	absence of water	presence of water	absence of alcohol	presence of alcohol	absence of water
The indirect oxidation of primary alcohols to carboxylic acids normally proceeds via the corresponding aldehyde, which is transformed via an aldehyde hydrate by	reaction with alcohol	reaction with ester	reaction with water	reaction with ether	reaction with water
In which reactions one atom is replaced by another atom	Substitution reactions	Addition reactions	Rearrangement reactions	Elimination reactions	substitution reaction
The reaction involve rearrangement of atoms that make up a molecule is	Rearrangement reactions	Substitution reactions	Elimination reactions	Addition reactions	rearrangement reaction
In which reaction two atoms or groups of atoms are lost from the reactant to form a pi bond?	Elimination reaction	Substitution reactions	Addition reaction	Rearrangement reactions	elimination reaction
Reversible reactions in which a compound with two pi electrons are used to form a sigma bond is	Cycloaddition reactions	Electrocyclic reactions	Sigmatropic rearrangements	Addition reactions	electrocyclic reaction

The selective absorption of microwaves	10^9-10^{11} HZ	10^8-10^{10} HZ	10^7-10^9 HZ	10^9-10^{12} HZ	10^9-10^{11} HZ
Ultra sound covers the range	20 kHz to 100 kHz	30 kHz to 100 kHz	20 kHz to 200 kHz	10 kHz to 100 kHz	20 kHz to 100 kHz
Sonification in homogeneous solution produces	accoustic cavitation	cavitation	aquatic cavitation	none of the above	accoustic cavitation
Hoffmann elimination leads to formation of	olefin	alkanes	alcohols	acids	olefin
The formation of olefins by heating quaternary ammoniummhydroxides, this reaction known as	knoevenagel condensation	claisen condensation	perkin condensation	Hofmann elimination	Hofmann elimination
In Hoffmann elimination, the resulting yield of olefins are prepared from	sodium hydroxide	potassium hydroxide	ammonium hydroxide	quaternary ammonium hydroxide	quaternary ammonium hydroxide
The solvent used in Hoffmann elimination under microwave irradiation is	H_2O-$CHCl_3$	H_2O-CCl_4	CH_3OH-$CHCl_3$	CH_3OH-CCl_4	H_2O-$CHCl_3$
The Hoffmann elimination under microwave irradiation yield is	85%	90%	97%	80%	97%
The compound having a double bond or triple bond called	dienophile	free radical	carbanion	carbocation	dienophile
Dienophiles are	2π-electron system	4π-electron system	3π-electron system	6π-electron system	2π-electron system
2π-electron system present in	nucleophile	electrophile	dienophile	free radical	dienophile
In Diels Alder reaction how many sigma bonds are formed	2	1	4	5	2
How many π-bonds are expenses in Diels Alder reaction	4	1	2	3	2
Diels alder reactions are highly	stereospecific	regiospecific	both stereospecific and regiospecific	none of the above	regiospecific
Which one of the following is not true	water	opolyethylene	supercritical	dimethyl	dimethyl

		glycol	water	sulphaoxide	sulphaoxide
Disodium iminodiacetate is an essential reactant in manufacturing of	pesticides	fertilizers	insecticides	herbicides	herbicides
The green synthesis of disodium iminodiacetate is prepared from	ethylamine	diethylamine	diethanol amine	dimethanol amine	diethanol amine
The catalyst used in the green synthesis of disodium iminodiacetate is	Cu	Zn	Fe	Sn	Cu
The conventional synthesis of disodium iminodiacetate also known as	Williamson syntheisi	Perkin syntheis	Strecker synthesis	Claisen synthesis	Strecker synthesis
A typical reaction which has been carried out in aqueous phase is the	Diels-Alder reaction	Mannich reaction	Knoevengal condensation	Friedel-crafts reaction	Diels-Alder reaction
The reactants are stirred in a suitable solvent with a suitable adsorbent or solid support is	Solid phase organic synthesis without any solvent	Solid supported organic synthesis	Aqueous phase reaction	Electrocyclic synthesis	solid supported organic synthesis
The atom economy of all addition reactions are	100%	10%	phlouroglucinol	10%	100%
The atom economy of all rearrangement reactions are	100%	10%	Reductive process	10%	100%
The atom economy for the conventional synthesis of ibuprofen	100%	10%	Very high temperature and low pressure	40%	40%
The atom economy for the greener synthesis of ibuprofen	100%	10%	Catalyst percentage	77%	77%
% atom economy is used to	Measure the unwanted product produced in a reaction	Identify the Solvent percentage	Plant protein	Feasibility of a reaction	Measure the unwanted product produced in a reaction
% atom economy is high for the following reaction	Addition reaction	Elimination reaction	Substitution reaction	Fusion reactions	Addition reaction

% atom economy is high for the following reaction	Rearrangement reaction	Elimination reaction	Substitution reaction	Fusion reactions	Rearrangement reaction
% atom economy is low for the following reaction	Rearrangement reaction	Elimination reaction	Addition reaction	Fusion reactions	Elimination reaction
% atom economy is low for the following reaction	Rearrangement reaction	Substitution reaction	Addition reaction	Fusion reactions	Substitution reaction
Separation of the reaction components from the starting material is much simpler than with	Chemically unstable	Low cost	flammable	Not readily available	Low cost
Supercritical carbon dioxide is used to remove	Traditional solvents	water	The CO	Toxic substances	Traditional solvents
Green chemistry, also called	sustainable chemistry	medicinal chemistry	environmental chemistry	synthetic chemistry	sustainable chemistry
Which is an area of chemistry and chemical engineering focused on the designing of products and processes that minimize the use and generation of hazardous substances	medicinal chemistry	environmental chemistry	synthetic chemistry	Green chemistry	Green chemistry
How many routes to synthesis ibuprofen	2	3	4	1	2

UNIT-IV

SYLLABUS

Green synthesis/reaction: Green starting materials, Green reagents, Green solvents, reaction conditions, Green catalysis and Green synthesis- Real world cases (Traditional processes and green ones) Synthesis of Ibuprofen, Adipic acid , disodium iminodiacetate (alternative to Strecker synthesis).

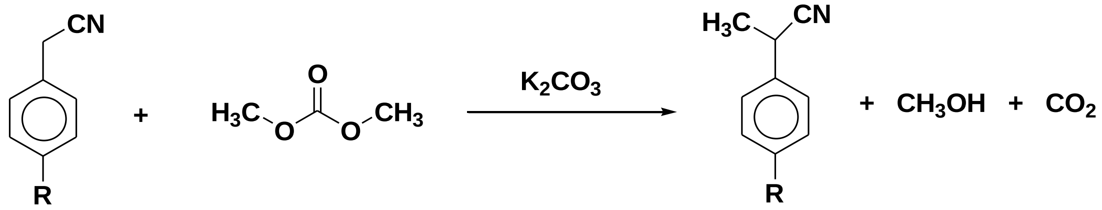
Choice of Reagents

Selection of the right reagent for a reaction is made on the basis of efficiency, availability and its effect on environment. The selection of a particular reagent versus another reagent for the same transformation can effect the nature of by-products, percentage yield etc.

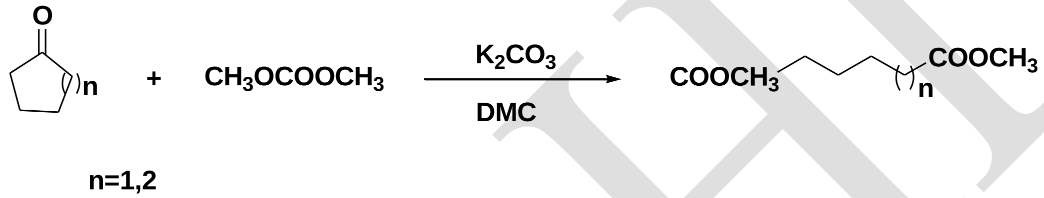
In order to carry out the transfonnation of selected feedstock into the target molecule the criteria of efficiency, availability and effect of the reagent used must be kept in mind. Some of the green reagents are as follows.

Dimethylcarbonate

Conventional methylation reactions employ methyl halides or methyl sulfate. The toxicity ofthese compounds and their environmental consequences render these syntheses somewhat undesirable. Tundo1•2 developed a method to methylate active methylene compounds selectively using dimethy1carbonate (DMC) (Scheme I) in which no inorganic salts are produced.



Dimethy1carbonate (DMC) can also act as an organic oxidant. Cyclopentanone and cyclohexanone react with DMC and a base to yield adipic and pimelic methyl (or ethyl) esters, respectivelylY



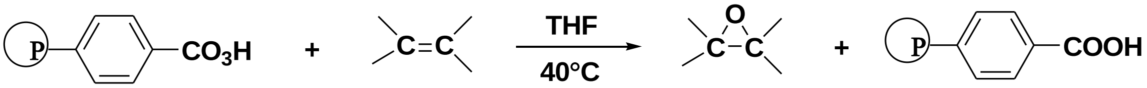
Many oxidative processes have negative environmental consequences. By creating long-lived catalytic and recyclable oxidants, metal ion contamination in the environment can be minimized by using molecular oxygen as the primary oxidant. Several ligand systems that are stable towards oxidative decomposition in oxidizing environments are being developed.

Polymer Supported Reagents

Besides DMC, there are a group of reagents which though are ordinary reagents, are bound to polymer support. The main advantage of using these reagents is that any excess of the reagent can be recovered by filtration and used again. Also, the isolation of the product is very easy. Some of such reagents are given as follows:

Polymer Supported Peracids

These are used for epoxidations of alkenes in good yields

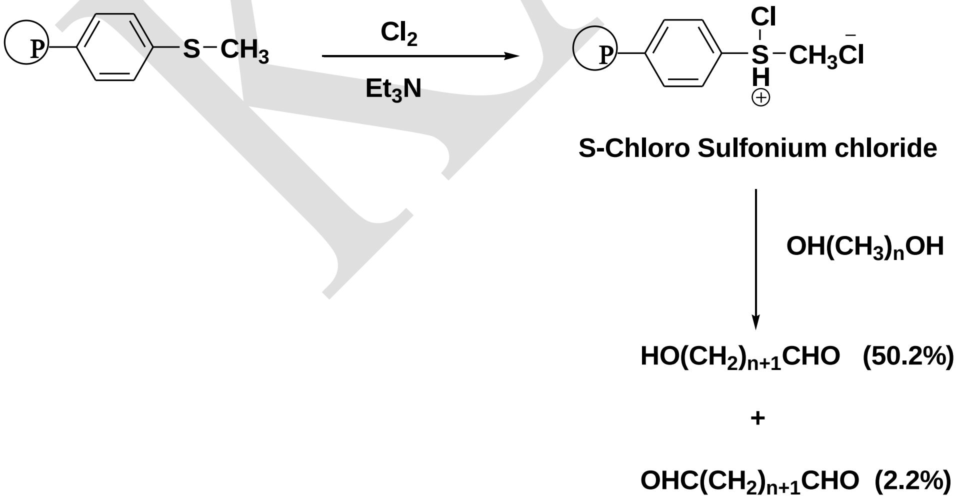


Polymer Supported Chromic Acid

The polymer supported chromic acid (Amberlyst A-26, HCrO~ form is commercially available) and has been used to oxidise primary and secondary alcohol to carbonyl compounds6 and also oxidizes allylic and benzylic halides to aldehydes and ketones

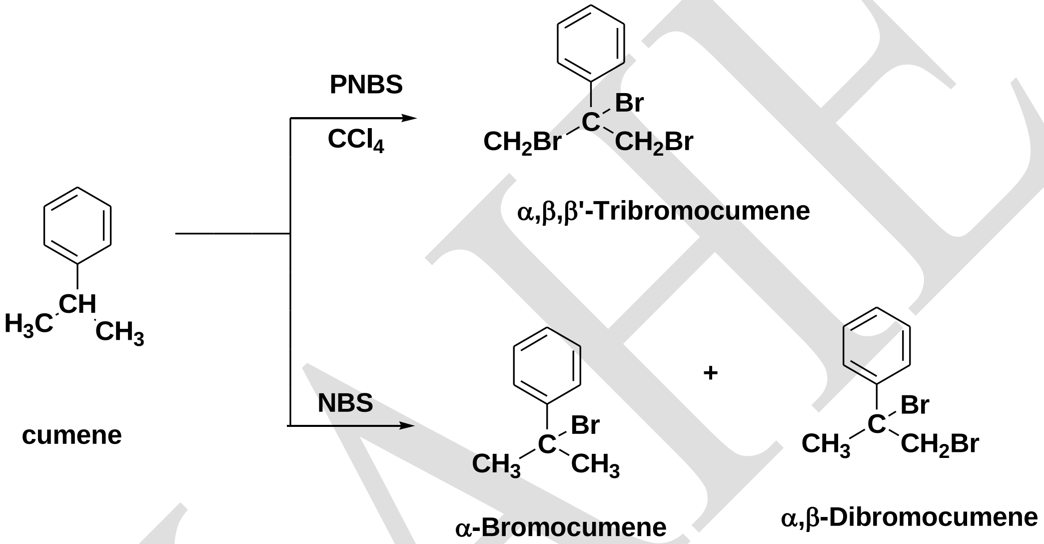
Polymeric Thioanisolyl Resin

Polystyrene methyl sulphide on reaction with chlorine in the presence of triethylamine forms s-chloro sulfonium chloride resin, which acts as a selective oxidant for the alcohols.

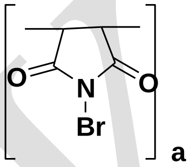


Poly-N-Bromosuccinimide (PNBS)

It is an efficient polymer based brominating agent and is used as benzylic and allylic brominating agent. Thus, cumene on bromination9 yield a,~,~'tribromocumene (Scheme 5). However, bromination with NBS gives a,~-dibromocumene and a-bromocumene.



PNBS =



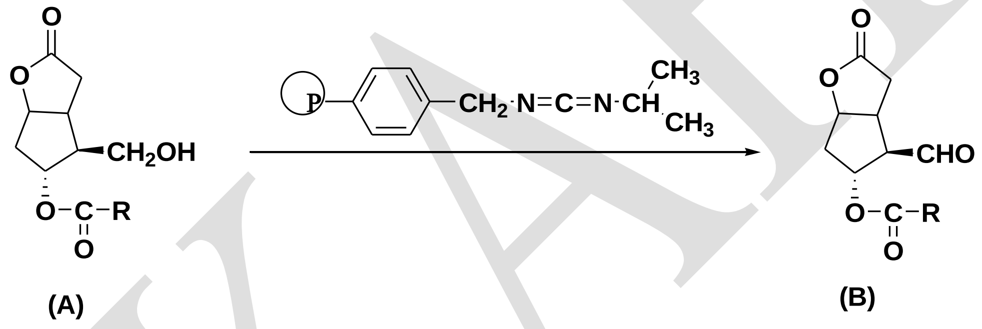
Polymeric Organotin Dihydride Reagent as a Reducing Agent

The versatility and selectivity of organotin hydride. is well documented. The use of polymeric organotin dihydride reagent involves ease of operation and reaction workup and avoids toxic vapours, characteristic of tin hydride. The polymer supported organotin dihydride reagent has been usedlO for

the conversion of aldehydes and ketones to alcohols in 80-90% yields and the reduction of halides to hydrocarbons. The use of organotin hydride for the reduction of alkyl and aryl halides in presence of other functional groups is generally superior to lithium aluminium hydride. This can also be used for the selective reduction of only one functional group of a symmetrical difunctional aldehyde (terephthaldehyde).

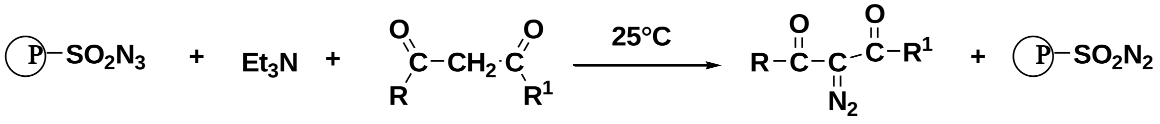
Polystyrene Carbodiimide

Polystyrene carbodiimide is useful for the synthesis of anhydrides I. It can also be used for the Moffatt oxidation of alcohols to aldehydes and ketones.
Even the labile prostaglandin intermediate (A) is readily converted to the desired
aldehyde (B)



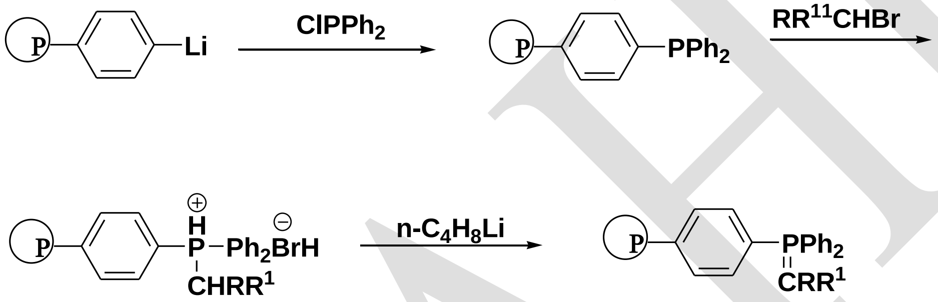
Polystyrene Anhydride
Acetylation of aniline with polystyrene anhydride gives 12 benzanilide in 90% yield. Similarly, ethyl benzoate is obtained in 90% yield by acylation of ethanol.

Sulfonazide Polymer
It provides a route by which diazo group can be transferred13 to 1,3-dicarbonyl compounds very conveniently



Polystyrene Wittig Reagent

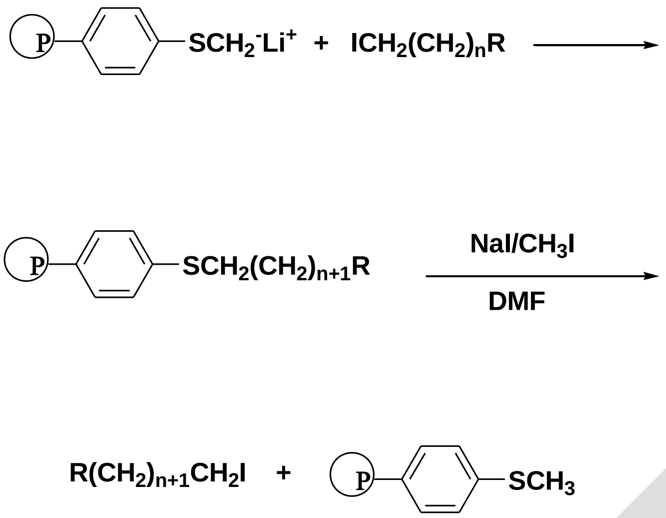
The polymeric Wittig reagent14 (prepared as given in Scheme 8) reacts witil carbonyl compounds (e.g. C6HsCOCH3, p-CIC6H4CHO, C6HsCHO etc.) to give the usual products



Polystyrene
witting reagent

Polymeric Phenylthiomethyl Lithium Reagent

The polymeric phenylthiomethyllithium reagent1S is useful for lengthening of side chain of alkyl iodide in good yield



Designing a Green Synthesis

In any synthesis of a target molecule, the starting materials that are made to react with a reagent under appropriate conditions. Before coming to a final decision, consider all the possible methods that can give the desired product. The same product can also be obtained by modifying the conditions. The method of choice should not use toxic starting materials and should eliminate by-products and wastes. Following are some of the important considerations.

Designing Safer Chemicals

It is of paramount importance that the chemicals synthesised or developed (e.g. dyes, paints, adhesives, cosmetics, pharmaceuticals etc.) should be safe to use. A typical example of an unsafe drug is thalidomide (introduced in 1961) for lessening the effects of nausea and vomiting during pregnancy (morning sickness). The children born to women taking the drug suffered birth defects (including missing or deformed limbs). Subsequent~y, the use of thalidomide was banned, the drug withdrawn and strict regulations passed for testing of new drugs, particularly for malformation-inducing hazards. With the advancement of technology, the designing and production of safer chemicals has become possible. Chemists can now manipulate the molecular structure to achieve this goal.

Choice of Starting **Materials**

It is very important to choose the appropriate starting materials. The synthetic pathway will depend on this. Also consider the hazards that may be faced by the workers (chemists carrying out the reaction and also the shippers who transport these) handling the starting materials. Till now, most syntheses make use of petrochemicals (made from petroleum), which are non-renewable. Petroleum refining also requires considerable amounts of energy. It is therefore important to reduce the use of

petrochemicals by using alternative starting materials, which may be of agriculturallbiological origin. For example, some of the agricultural products such as corn, potatoes, soya and molasses are transformed through a variety of processes into products like textiles, nylon etc. Some of the materials that have biological origin (obtained from biomass) are: butadiene, pentane, pentene, benzene, toluene, xylene, phenolics, aldehydes, resorcinol, acetic acid, peracetic acid, acrylic acid, methyl aryl ethers, sorbitol, mannitol, glucose, gluconic acid, 5-hydroxymethyl furfural, furfural, levulinic acid, furan, tetrahydrofuran, furfuryl alcohol etc.

Selection of Starting Materials

Starting materials are those obtained from renewable or non-renewable material. Petrochemicals are mostly obtained from petroleum, which is a non-renewable source in the sense that its formation take millions of years from vegetable and animal remains. The starting materials which can be obtained from agricultural or biological products are referred to as renewable starting materials (sec. 2.1). The main concern about biological or agricultural products however, is that these cannot be obtained in continuous supply due to factors like crop failure etc. Substances like carbon dioxide (generated from natural sources or synthetic routes) and methane gas (obtained from natural sources such as marsh gas) are available in abundance. These are considered as renewable starting materials.

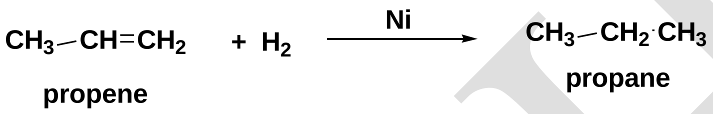
Choice of Catalysts

Certain reactions proceed much faster and at a lower temperature with the use of catalysts. Heavy metal catalysts should be avoided as they cause environmental problems and are toxic in nature. Use of visible light to carry out the required chemical transformation should be explored. Certain biocatalysts (enzymes) can also be used for various steps.

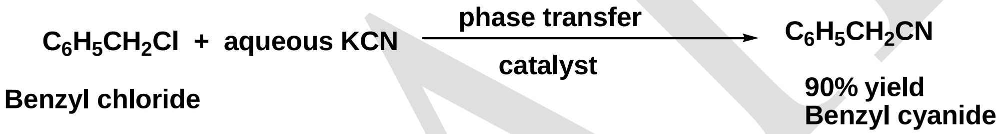
Use of Catalyst

It is well known that use of a catalyst facilitates transformation without the catalyst being consumed in the reaction and without being incorporated in the final product. Therefore, use of catalyst should be preferred whenever possible. Some of the advantages are:

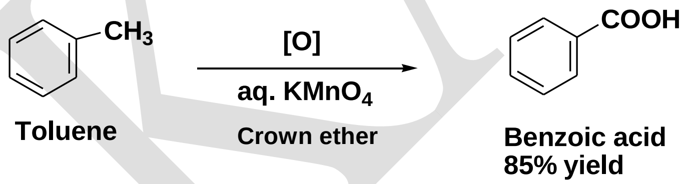
(i) Better yields. Hydrogenation or reduction of ole fins in presence of nickel catalyst



$$\underset{\text{propene}}{CH_3-CH=CH_2} + H_2 \xrightarrow{Ni} \underset{\text{propane}}{CH_3-CH_2\cdot CH_3}$$

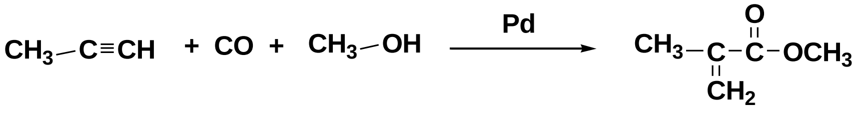


$$\underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} + \text{aqueous KCN} \xrightarrow[\text{catalyst}]{\text{phase transfer}} \underset{\text{90\% yield, Benzyl cyanide}}{C_6H_5CH_2CN}$$



(ii) The reaction becomes feasible in those cases where no reaction is normally possible

$$CH\equiv CH + H_2O \xrightarrow[H_2SO_4]{HgSO_4} CH_3-CHO$$



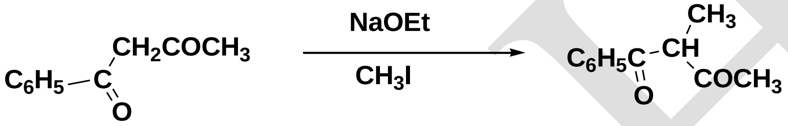
$$CH_3-C\equiv CH + CO + CH_3-OH \xrightarrow{Pd} CH_3-C(=CH_2)-C(=O)-OCH_3$$

Methyl methacrylate
(Shell corporation)

Selectivity enhancement

$$\underset{\text{Propyne}}{CH_3-C\equiv CH} + H_2 \xrightarrow[\text{mono addition}]{Pd\text{-}BaSO_4} \underset{\text{propene}}{CH_3-CH=CH_2}$$

Selectivity in C-Methylation versus O-methylation



$$C_6H_5-C(=O)-CH_2COCH_3 \xrightarrow[CH_3I]{NaOEt} C_6H_5C(=O)-CH(CH_3)-COCH_3$$

In addition to the above mentioned beneficial use of catalysts, there is significant advantage in the energy requirement. With advances in the selectivity of catalysts, certain reactions in green synthesis have become very convenient. A special advantage of the use of catalysts is better utilisation of starting materials and minimum waste product formation.

‘

Choice of Solvents

Most of the common solvents generally used cause severe hazards. One of the commonly used solvents, benzene is now known to cause or promote cancer in humans and other animals. Some ofthe other aromatic hydrocarbons, for example toluene could cause brain damage, have adverse effect on speech, vision and balance, or cause liver and kidney problems. All these solvents are widely used because of their excellent solvency properties. These benefits nevertheless, are coupled with health risks.

Commonly used halogenated solvents, like methylene chloride, chloroform, perchloroethylene and carbon tetrachloride have long been identified as suspected human carcinogens. The chlorofluorocarbons (CFCs) were used up to 20th century as cleaning solvents, blowing agents for molded plastics and for refrigeration. Despite the fact that CFCs have very low direct toxicity to humans and wild life (being non-inflammable and non-explosive, they have low accident potential), the single effect of CFCs in causing depletion of the ozone layer is a sufficient reason for not using them.

A versatile solvent, carbon dioxide l is used as liquid CO2 or supercritical CO2 fluid (the states of CO2 most commonly used for solvent use). A gas is normally converted to a liquid state by increasing the pressure exerted upon it.

However, if the substance is placed at a temperature above its critical temperature T_c (31°C for CO2) and critical pressure P_c (72.8 atm for CO2), a supercritical fluid is obtained. The T_c of a substance is the temperature above which a distinct liquid phase of the substance cannot exist, regardless of the pressure applied. P_c is the pressure at which a substance can no longer exist in gaseous state. In a supercriticalliquid, the individual molecules are pressed so close together (due to high pressure) that they are almost in liquid state. Supercritical liquids have density close to that of the liquid state and viscosity close to that of gaseous state.

Another way to carry out the reaction is without the use of solvent (solvent less reactions). One such reaction comprises those reactions in which the starting materials and the reagents serve as solvents. Alternatively, the reactions can be performed in the molten state to ensure proper mixing. There is still another reaction that can be carried out on solid surfaces such as specialized clays.

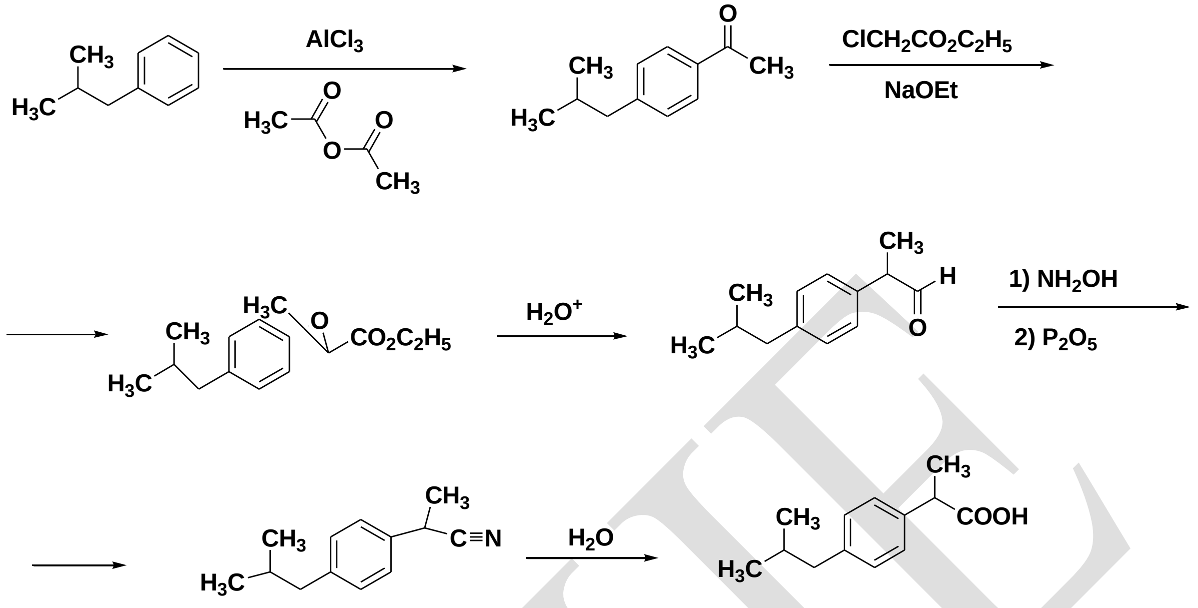
Selection of Appropriate Solvent

The solvent selected for a particular reaction should not cause any environmental pollution and health hazard. The use ofliquid or supercriticalliquid CO2 should be explored. Ifpossible, the

reaction should be carried out in aqueous phase or without the use a of solvent (solventless reactions). A better method is to carry out reactions in the solid phase (for details see Chapter 13). One major problem with many solvents is their volatility that may damage human health and the environment. To avoid this, a lot of work has been carried out on the use of immobilised solvents. The immobilised solvent
maintains the solvency of the material, but it is non-volatile and does not expose humans or the environment to the hazards of that substance. This can be done by tethering the solid molecule to a solid support or by binding the solvent molecule directly on to the backbone of a polymer. Some new polymer substances having solvent properties that are non-hazardous are also being discovered.

Synthesis oflbuprofen

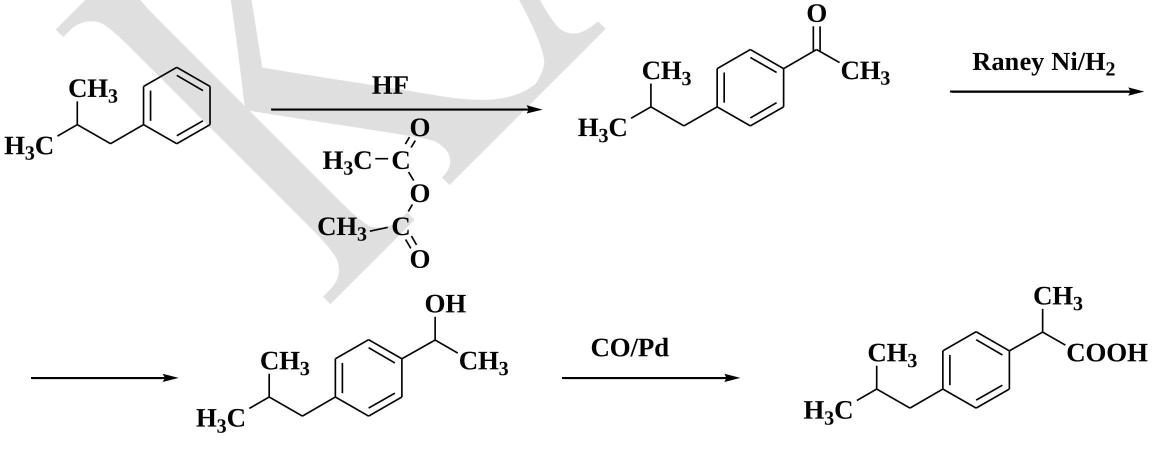
Ibuprofen is one of the products used in large quantities for making pharmaceutical drugs, in particular various kinds of analgesics (pain killers). The traditional commercial synthesis of ibuprofen was developed by the Boots Company of England in 1960s (U.S. Patent 3,385,886). This synthesis
is given



Ibuprofen

The given synthesis is a six step process and results in large quantities of unwanted waste chemical byproducts that must be disposed of. There is 40% atom economy in this synthesis.

The BHC company developed a new greener commercial synthesis of ibuprofen that consists of only three steps14

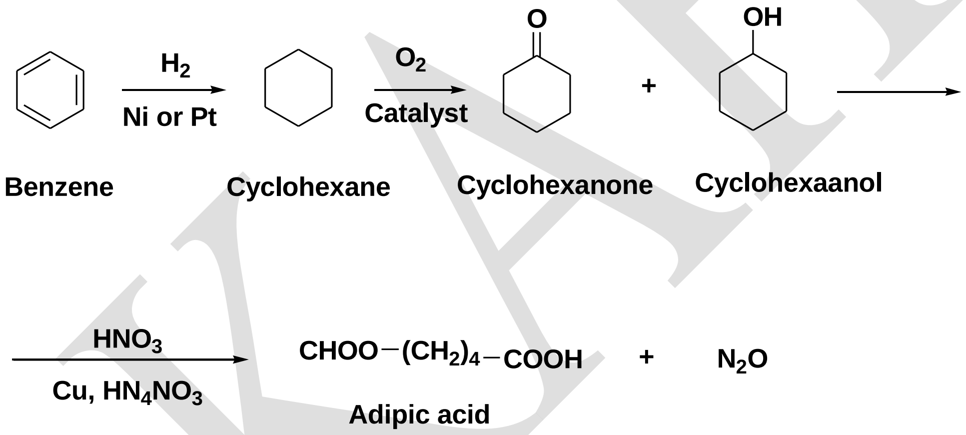


Ibuprofen

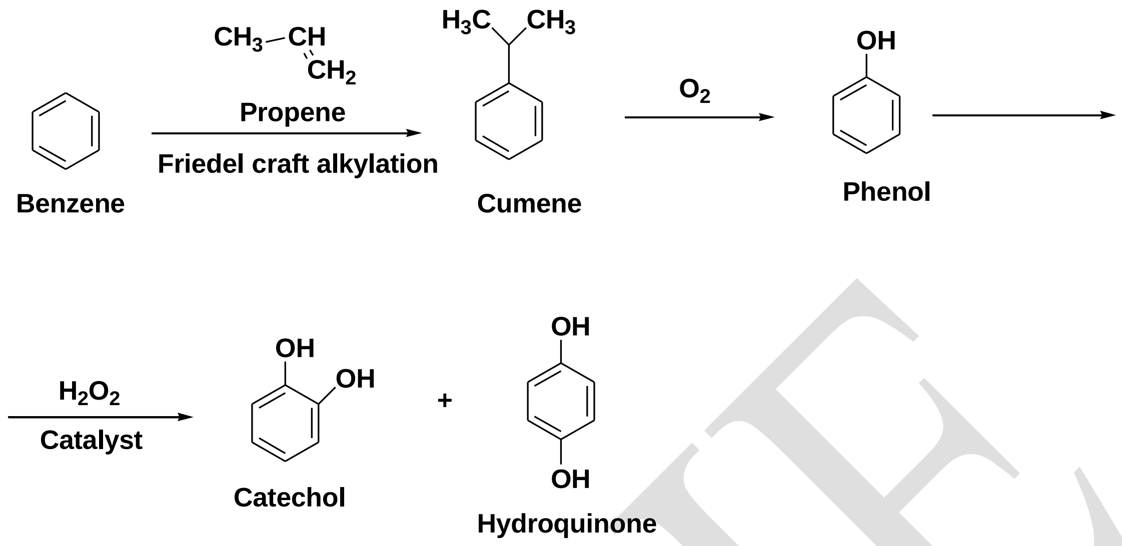
The above synthesis results in only small amount of unwanted products and has very good atom economy

Synthesis of Adipic Acid, Catechol and 3-Dehydroshikimic Acid (a Potential Replacement for BHT)

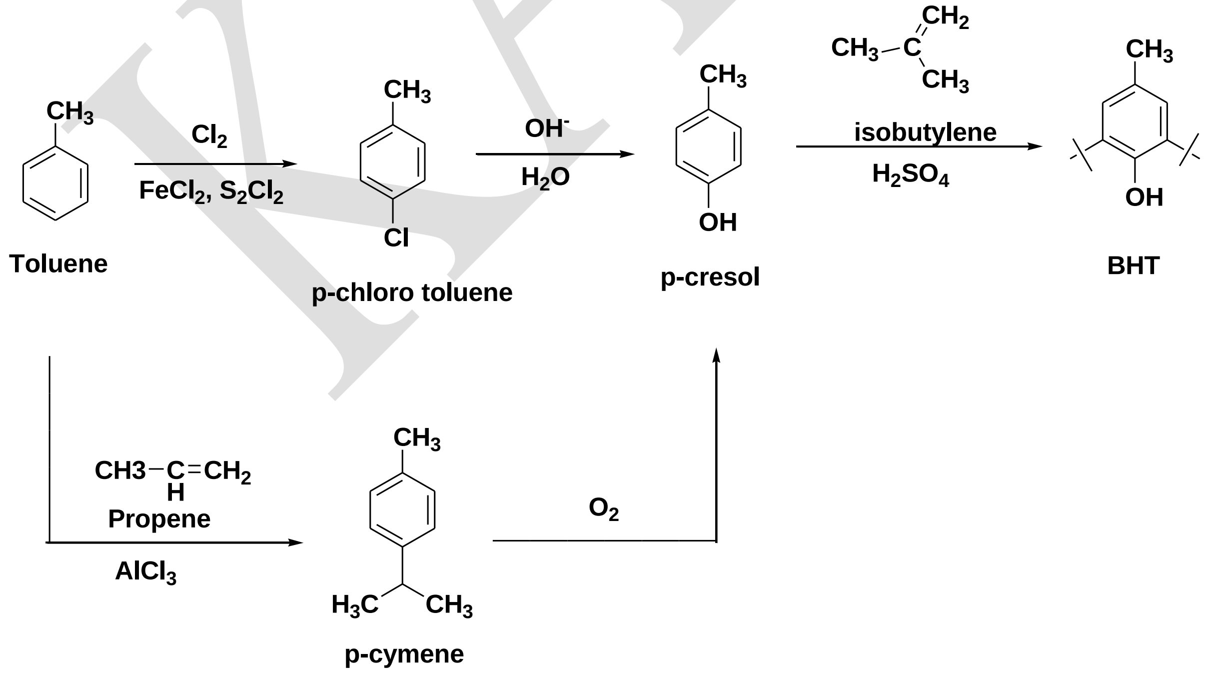
Adipic acid is required in large quantities (about 1 billion kg a year) for the synthesis of nylon, plasticizers and lubricants. Conventionally, adipic acid is made from benzene.



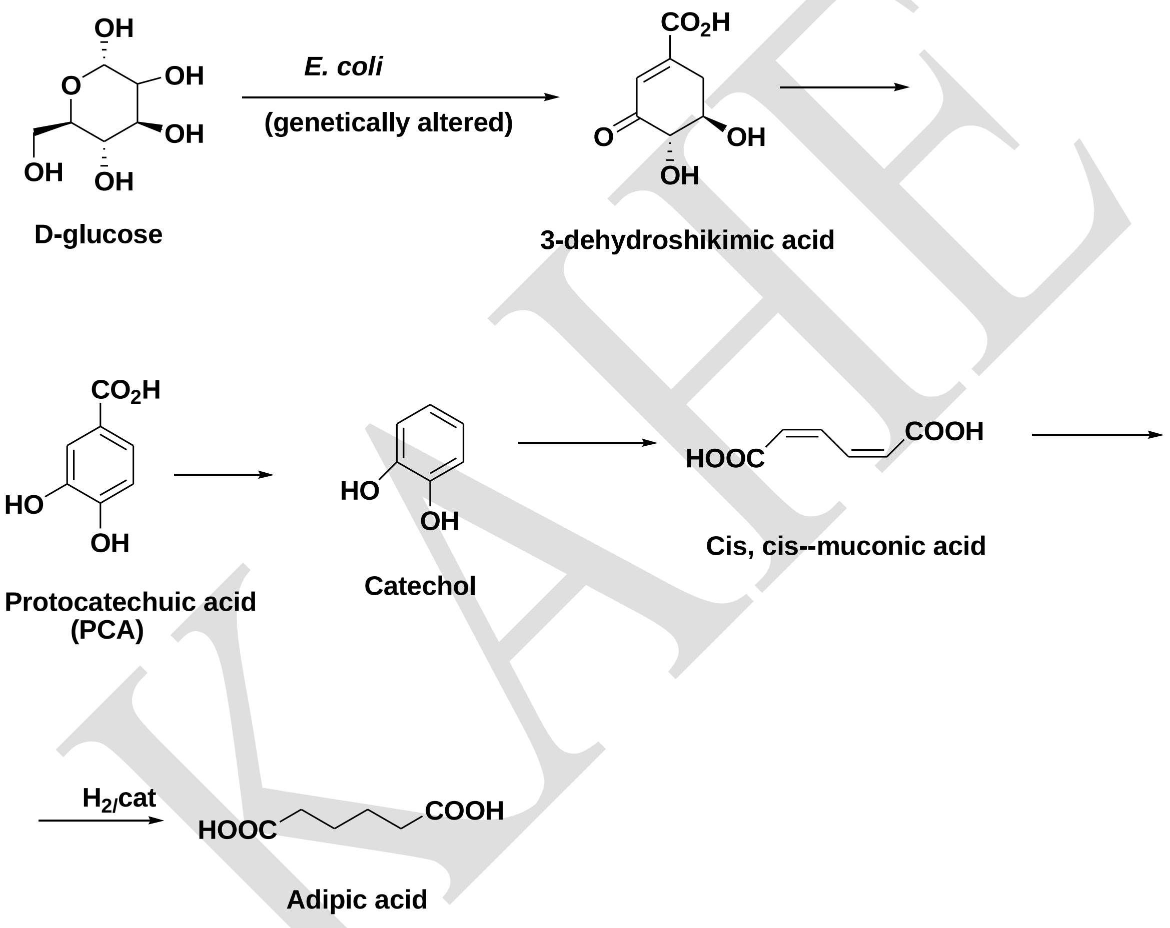
Like adipic acid, catechol is also manufactured using benzene as the starting material. The procedure is given. As seen, both adipic acid and catechol are obtained from benzene, which causes environmental and health problem. Also, benzene is produced from non-renewable source. In addition, in the synthesis of adipic acid, nitrous oxide is generated as a byproduct, which contributes to the greenhouse effect as well as destruction of the ozone layer.



BHT is obtained from toluene (which unlike benzene is not carcinogenic but is toxic in nature) as shown.



An environmentally benign (or green) synthesis of adipic acid, catechol and BHT (a potential replacement for BHT) has been developed by John W. Frost and Karen M. Draths starting with glucose and using a biocatalyst (genetically altered *E. coli* bacteria)



The above environmentally benign synthesis of catechol and adipic acid uses D-glucose (a non-toxic and a renuable resource) as the starting material. Also the synthesis is conducted in water instead of organic solvents. The reaction can also be used to stop at either catechol stage or at the adipic acid stage by using another genetically altered *E. coli.* It may be appropriate to say that in the above synthesis, use of unmodified *E. coli* gives the amino acids, L-phenylalanine, L-tyrosine and L-tryptophan via the formation of shikimic acid from dehydroshikimic acid.

POSSIBLE QUESTIONS

PART B (2 Mark Questions)

1. What are the starting materials for the synthesis of Ibuprofen in conventional synthesis
2. What are the starting materials for the synthesis of Ibuprofen in greener synthesis
3. What are green solvents. Give examples
4. Give some examples for greener reagents.
5. What are Volatile Organic Compounds and Halogenated Organic Compounds. Give examples
6. What are the Uses of Volatile Organic Compounds and Halogenated Organic Compounds
7. Write notes on chlorofluoro hydrocarbons (CFC's)
8. What are hydrochlorofluorocarbons. What are its advantages and disadvantages.
9. Comment on the statement, Carbon Dioxide: An Alternative Solvent
10. What are surfactants. Give suitable examples.

PART C (8 Mark Questions)

1. Compare and contrast the synthesis of Ibuprofen by conventional method and by green synthesis.
2. Compare and contrast the synthesis of Adpic acid by conventional method and by green synthesis.
3. Compare and contrast the synthesis of Disodium iminoacetate by conventional method and by green synthesis.
4. Illustrate with suitable examples about green catalysis
5. Explain with examples the reaction condition for greener synthesis.
6. Explain the classification of surfactants with suitable examples.
7. Explain the Micelle Structure of a Surfactant
8. Describe about the Surfactant for Liquid or Supercritical Fluid CO_2
9. What are the advantages and disadvantages in using supercritical carbon dioxide (sc-CO2) as an alternative solvent.
10. What is meant by Supercritical CO_2 . Comment on its advantages and disadvantages.

Questions	A	B	C	D	Answers
Which medication is used in the nonsteroidal anti-inflammatory drug (NSAID) class that is used for treating pain, fever, and inflammation	Ibuprofen	paracetamol	aspirin	penicillin morphine	Ibuprofen
Adipic acid is otherwise called as	hexanedioic acid	pentadioic acid	propadioic acid	butadioic acid	hexanedioic acid
Which is a key technology to achieve the objectives of sustainable (green) chemistry?	reagents	Catalysis	solvents	none of these	Catalysis
How many Principles of Green Chemistry	15	12	10	5	12
This ‘green’ chemical is used in household cleaners to remove stains and is also a favorite dressing on salads?	Vinegar	Citric acid	Hydrochloric acid	Water	Vinegar
An example of green chemistry is?	Recycled carpet	A product made on Earth Day	A sublimation reaction	Bio-plastics	Bio-plastics
Green chemistry aims to?	Design chemical products and process that maximize profits	Design safer chemical products and processes that reduce or eliminate the use and	Design chemical products and processes that work most efficiently	Utilize non-renewable energy	Design safer chemical products and processes that reduce or eliminate the use and

		generation of hazardous substances			generation of hazardous substances
Which of the following are among the 12 Principles of Green Chemistry?	Design commercially viable products	Use only new solvents	Use catalysts, not stoichiometric reagents	Re-use waste	Use catalysts, not stoichiometric reagents
Green chemists reduce risk by?	Reducing the hazard inherent in a chemical product or process	Minimizing the use of all chemicals	Inventing technologies that will clean up toxic sites	Developing recycled products	Reducing the hazard inherent in a chemical product or process
Which of the following could involve Green chemistry synthesis?	High temperature	Dichloromethane	Fossil fuels	Microwave	Microwave
Which of the following is the greenest solvent?	Formaldehyde	Benzene	Ethanol	Water	Water
Which of the following is not one of the twelve principles of green chemistry?	a) Using high temperatures to speed up reactions	Minimising toxic reagents used in a synthesis	Maximisation of atom economy	Minimising the use of solvents	Using high temperatures to speed up reactions
Which are an excellent ‘green’ solvent as well as a greenhouse gas?	Methanol	CFCs	Carbon monoxide	Carbon Dioxide	Carbon Dioxide
_______________ is fulfilling the needs of the present generation without compromising the ability of future generations to meet their needs?	Sustainability	Green chemistry	Life Cycle Assessment	Recycling	Sustainability

In a reaction the auxiliary substance is	Reactants	Products	catalyst	solvent	solvent
Which among the following is a green solvent?	Chloroform	Dichloromethane	water	carbon tetrachloride	water
Greener synthetic methods should be carried out under the conditions	Ambient temperature and Pressure	High temperature	Low Temperature	High pressure.	Ambient temperature and Pressure
Ibuprofen is a	Analgesic	polymer	Antipyretic	Plastic material	Analgesic
In the greener synthesis of ibuprofen which is not used as a catalyst	HF	Raney Ni	Pd	Aluminium chloride	HF
Which is not a tool of green chemistry	Auxillary substances	renewable feed stock	High atom economy	Energy save	Energy save
One of the raw materials used in the preparation of Nylon-6,6 is	Adipic acid	succinic acid	tartaric acid	lactic acid	Adipic acid
In conventional method for the preparation of Adipic acid, the raw material used is	ethanol	Non renewable source	propanol	Plant feedstock	Non renewable source
Which is used in the Strecker synthesis	Formaldehyde	Diethanol amine	DMC	Potassium carbonate	Formaldehyde
The raw material used in the greener synthesis of Disodium iminoacetate	Formaldehyde	HCN	Ammonia	Diethanolamine	Diethanolamine
In the conventional method for the preparation of ibuprofen,	10%	77%	50%	40%	40%

the atom economy is					
Example for a anti-inflammatory drug is	Ibuprofen	MMA	DMC	DMS	Ibuprofen
Which is an excellent 'green' solvent as well as a greenhouse gas?	Methanol	CFCs	Carbonmonoxide	Carbondioxide	Carbondioxide
Disodium iminodiacetate is an essential reactant in manufacturing of	pesticides	fertilizers	insecticides	herbicides	herbicides
The green synthesis of disodium iminodiacetate is prepared from	ethylamine	diethylamine	diethanol amine	dimethanol amine	diethanol amine
The catalyst used in the green synthesis of disodium iminodiacetate is	Cu	Zn	Fe	Sn	Cu
The conventional synthesis of disodium iminodiacetate also known as	Williamson syntheisi	Perkin syntheis	Strecker synthesis	Claisen synthesis	Strecker synthesis
The solvent selected for a particular reaction should not have any environmental pollution and health hazard is?	Selection of appropriate solvent	Selection of starting materials	Use of renewable feedstocks	Use of protecting group	selection of appropriate solvent
Which facilitate transformation and the conversions can be affected in short duration of time and consume less	Catalysts	Selection of starting materials	Percentage atom utilization	Evaluating the type of reaction	Catalysts

energy?					
Ionic liquids are good solvents for a wide range of	Inorganic materials	organic materials	Inorganic and organic materials	Physio-organic materials	inorganic and organic materials
Which of the following statements is false concerning cyclopropanation reactions?	The Simmons-Smith reagent generates a diiodo carbenoid which adds to alkenes.	Diazomethane can be used to generate methylene, but is not very useful in synthesis	Dichlorocarbene reacts with alkenes to give good yields of dichlorocyclopropane derivatives.		The Simmons-Smith reagent generates a diiodo carbenoid which adds to alkenes.
Toluene can be oxidized to produce what?	Benzaldehyde	Benzoic acid	O-xylene	All of the mentioned	All of the mentioned
Under which temperature, with a mild catalyst does toluene oxidize to benzaldehyde?	High	Moderate	Low	None of the mentioned	High
The oxidation of toluene depends on which condition?	Catalyst	Temperature	Oxygen ratio	All of the mentioned	All of the mentioned
The oxidation of toluene do not depends on which condition?	Catalyst	Temperature	Oxygen ratio	pressure	pressure
What is produced by dehydrogenating ethylbenzene over a zinc oxide catalyst?	Benzaldehyde	Styrene	Nylon-6	Benzoic acid	Styrene
Conversion of an aldehyde to an alcohol is generally known as	Reduction	Oxidation	Esterification	Polymerisation	Reduction
Which of the following	Tertiary alcohols	Alcohols undergo	Tertiary alcohols	Tertiary alcohols	Tertiary alcohols are

statements about alcohols is incorrect?	have lower boiling points than primary alcohols with an equivalent molecular weight	nucleophilic substitution.	undergo dehydration more readily than primary alcohols	are metabolised in the body to ketone	metabolised in the body to ketones
Which of the following alcohols would be oxidised to propan-2-one?	ethanol	propan-2-ol	2-methylpropan-2-ol	butan-1-ol	propan-2-ol
Propan-2-one will get oxidized to give	aldehyde	ketone	alcohol	carbonyl	alcohol
For methylation reaction the greener alternative is	Methyl halides	Dimethyl sulfate	Dimethyl carbonate	Methyl oxalate	Dimethyl carbonate
Methylation of active methylene group can be carried out by a greener reagent	Methyl halides	Dimethyl sulfate	Dimethyl carbonate	Methyl oxalate	Dimethyl carbonate
Dimethyl carbonate can be used as a greener reagent for the methylation of	Active methylene group	Methyl groups	Benzene ring	Double bonds	Active methylene group
Example for green oxidants	oxygen	chromates	permangnates	iodides	oxygen
Example for green oxidants	Hydrogen peroxides	chromates	permangnates	iodides	Hydrogen peroxides
The critical temperature of Super critical carbon dioxide	304.25 K	309.25 K	92.9 atm	404.25 K	304.25 K
The critical Pressure of	72.9 atm	82.9 atm	Compressed	102.9 atm	72.9 atm

Super critical carbon dioxide			liquid		
A substance expanding to fill its container like a gas but with a density like that of a liquid.	Super critical carbon di oxide	Buffer solution	For respiration of plants	Liquid aerosol	Super critical carbon di oxide
Super critical carbon dioxide is used in the	Chemical extraction	Green house gas	With denaturation	As an animal feed	Chemical extraction
The relatively low temperature of the process and the stability of CO	Without damage	With damage	With volume	With decomposition	Without damage
Heart of green chemistry is	to maximize the waste products formation	to minimize the waste products formation	to increase the toxic materials	to increase toxic materials and waste products formation	to minimize the waste products formation
Lignin,switch grass,and cellulose are all types of?	Enzymes	Catalysts	Bio-based feedstock's	Anti-cancer compounds	bio based feedstocks
An example for a renewable resource	Petroleum	Crude oil	Diesel	Biomass	Biomass
Example for a biocatalyst	Enzymes	Raney Nickel	Zeolites	metallic salts	Enzymes
D-glucose is used to prepare	Ethanoic acid	adipic acid	citric acid	crotonic acid	adipic acid
Soybean is used to replace traditional inks in printer cartridges,highlighting which of the green chemistry principles?	Atom economy	Use of renewable feedstock's	Reduce derivatives	Prevent waste	Use of renewable feedstock's

UNIT-V

SYLLABUS

Hazard assessment and mitigation in chemical industry: Future trends in Green Chemistry-oxidation-reduction reagents and catalysts; biomimetic, multifunctional reagents; Combinatorial green chemistry; Proliferation of solventless reactions; Noncovalent derivatization. Biomass conversion, emission control and biocatalysis.

In the last decade Green Chemistry and Green Engineering have advanced for a great variety of research and technology fields providing cutting-edge research and practical applications for a wide spectrum of chemical products and technological innovations. The most important research and technological fields of GC and GE include solutions. Among other things, reduction of global warming and use of CO2 as a raw material for chemical synthesis, microwave, electrochemical and ultrasound synthetic methods, solvent free reactions (or water as a solvent), phytoremediation, waste management and wastewater, eco-friendly dyes and pigments, innovative food products, catalysis and biocatalysis, biopolymer technology, renewable materials, renewable energy sources, etc.

Although there are many fields of innovation for GC and GE products we list below
some of the areas.

a. Biocatalysis and biotransformations processes for practical synthetic reactions

b. Directed evolution. New enzymes for organic synthesis

c. Green chemistry and synthetic processes in the pharmaceutical industry

d. Hydrogen production via catalytic splitting of water

e. Green and renewable energy sources

f. Green chemistry and agricultural technologies benign to environment

g. Green chemistry. Multicomponent reactions

h. Green flow chemistry and continuous processes in chemical industry

i. Green chemistry and biodegradable polymers
j. Green chemistry and organic solar cells
k. Solvent and solvent selection in industrial synthesis

Except for the above, there are also numerous other technological; fields of Green Chemistry and Green Engineering that have been advanced in the last years. Already, some these innovative inventions have been applied and improved sustainability, reduced environmental pollution and released less hazardous chemical products.

Oxidation Reagents and Catalysts: Though there is notable advancement in oxidation chemistry, but it is still one of the most polluting chemical technology. Oxidative transformations, as we know are the basis of necessary functionalization of fundamental molecules. It is the oxidation procedures that allows petroleum based feed stocks to become chemical products, which are the starting materials of numerous chemical industries.

Over the years, in the past many of the oxidation reagents and catalysts comprise of toxic substances like heavy metals (e.g. chromium). These substances have been used in large amounts for the manufacture of billions of kilograms of petrochemicals. All these processes have lead to the release of huge quantities of these metals into the environment. Further these toxic substances affects the human health.

During the past 2-3 decades, considerable attention has been directed towards the development of green chemistry techniques that will be environmentally benign and will also bring economic benefits to the industries. The oxidation techniques to be developed will need catalysts so that there is high turnover rates. Even if some heavy metals / transition metals have to be used, attempt should be made to use some of the most innocuous metals e.g. iron etc. The objective of green oxidation chemistry will, of course be to use and generation of non-hazardous substances, with maximum efficiency of atom incorporation.

Biomimetic, Multifunctional Reagents: In the human system, there is thousands of reactions going on due to which the body survives. The scientists are trying to understand the mechanism that the biological systems used to carry out their functions. The chemists approach is to biomimic such reactions in the laboratory. In case of synthetic chemists, most of the transformations are carried with the help of catalysts e.g. oxidation, reduction and methylation. However, biological systems often carry out several manipulations with the same reagent. These manipulations many include activation, conformation and other transformations. In the laboratory, it has now been possible to carry out biochemical oxidations, biochemical reductions and enzyme catalyed hydrolytic process. Different types of enzymes e.g. hydrolase, Lyases, isomerases, Ligases, transferases, oxidoreductases are available.

The biocatalytic conversions have many advantage in relevance to green chemistry. Some of these are –

- Most of the reactions are performed in aqueous medium at ambient temperature and pressure.
- The biocatalytic transformations normally involve only one step.
- Protection and deprotection of functional group in not necessary.
- The biocatalytic reactions are fast and the conversion are stereospecific.

Combinatorial Green Chemistry:

Combinatorial chemistry is a practice of being able to make a large number of chemical compounds rapidly on a small scale through reaction matrices. This practice is used on a large scale in the pharmaceutical sector. The pharmaceutical company identifies lead compound, which has considerable promise (as far as its biological activity is concerned) then the company would proceed in making a large number of derivatives of the lead compound and test their efficacy. In this way, the potential of a compound will be optimized. The combinatorial chemistry has enabled large number of substances to be made and screened for their activities without having any adverse effect on the environment. This approach is very useful to assess the biodegradability of the products. For example, if a company has struck on a biodegradable pesticide, the combinatorial approach will be helpful to make large number of other compounds, which will have the required pesticidal activity along with biodegradability.

4. Proliferation of Solventless Reactions: A large number of reactions occur in solid phase without the use of solvents are not harmful to the environment. In fact, a number of solventless reactions occur more efficiently with more selectivity compared to reactions carried out using solvents. Such reactions are simple to handle, reduce pollution and are comparatively cheaper to operate.

5. Non Covalent Derivatization: Any chemical synthesis involving formation and breaking of covalent bonds. The philosophy of making and breaking covalent bond must change. Infact, without bond making, physical / chemical properties can be modified and performance measured. Through the formation of dynamic complexation (which temporarily allow modification of the chemical structure) the properties of the molecules can be changed for in a short period of time to carry out a particular function. In this case no waste will be generated if full derivatization were implemented.

Green Chemistry in Sustainable Development:

Green chemistry can play a vital role sustainable development. Green chemistry as we know is environmentally benign synthesis. Chemical manufacturing is the source of many useful and enjoyable products, which has not only improved the quality of life of the people but also increased their life expectancy. Some of these products include antibiotics and other medicines, plastics, gasoline and other fuels, agricultural chemicals like fertilizers and pesticides, and a variety of synthetic fabrics including nylon, rayon and polyester. All these products are made by chemical industrial processes, which are mainly responsible for pollution of the environment. This in fact, green chemistry works toward sustainability by – Making chemical products that do not harm either the environment or our health.

- Using industrial processes that reduce or eliminate hazardous chemicals.
- Designing more efficient processes that minimize the production of waste materials.
- Using the most appropriate starting materials, reagents and catalysts.
- New products designed should be biodegradable.
- The waste products should be recycled as far as possible.

Directed Evolution', Green Chemistry and Biocatalysis

In 2016 the biochemical engineer Frances Arnold (CALTECH) received the Millennium Technology Prize (1 million Euros, awarded by Technology Academy Finland, Helsinki) in recognition of her discoveries and research on the field of _**directed evolut**ion‘, which mimics natural evolution to create new and better proteins (enzymes for biocatalysis) in the laboratory. This technology have solved many important synthetic industrial problems, often replacing less efficient synthetic methods and sometimes harmful technologies. Thanks to directed evolution, sustainable development and clean technology (biocatalysis) become available in many fields of chemical industry.

The 'Bionic Leaf'. Sunlight Splits Water and Bacteria Produce from Hydrogen Liquid Fuels

Hydrogen generated from solar-driven water-splitting has the potential to be a clean, sustainable and abundant energy source. Inspired by natural photosynthesis, artificial solar water-splitting devices are now being designed and tested for efficiency. Although sunlight-driven water splitting is a promising process to sustainable hydrogen (H2) production as fuel, widespread implementation is hampered by the expense of the photovoltaic and photoelectrochemical apparatus. Various catalysts and integrated systems have been used for the production of hydrogen from water.33,34 International teams of researchers have succeeded to increase the efficiency for direct solar water splitting with a tandem solar cell whose surfaces have been selectively modified with as new record of 14% efficiency.

At present there is in use of new generation of hydrogen fuel cell vehicles with zero emissions. The H2 car runs on compressed hydrogen fed into a fuel cell "stack" that produces electricity to power the vehicle. A fuel cell can be used in combination with an electric motor to drive a vehicle – quietly, powerfully and cleanly. Great attention has been focused on hydrogen as a potential energy vector and on the use of water-splitting technology as a clean and renewable means to generate hydrogen using solar energy. Numerous attempts have been made to develop photo-catalysts that work not only under UV light but also under visible-light illumination to efficiently utilize solar energy. Some potential sources of hydrogen are electrical, thermal, biochemical, photonic, electro-thermal, photo-thermal, photo-electric, photo-biochemical, and thermal-biochemical. Such forms of energy can be derived from renewable sources, and from energy recovery processes for hydrogen production purposes.

The Idea of the 'Bionic Leaf 2.0' for Photochemical Use of Sunlight

In the last decade new research activities introduced the idea of ―bionic leaf‖ for the efficient splitting of water by photochemical use of sunlight. This research started in the University of Harvard (Massachusetts, USA) and the goal has always been to harness sunlight and use it to create liquid fuel rather than electricity that must then be stored in a battery. The experimental set was designed to use solar power to separate oxygen atoms in water from hydrogen, which is then converted into isopropyl alcohol by bacteria. But prior efforts had used a nickel-molybdenum-zinc (NiMoZn) catalyst and the resulting reactive oxygen species (reactive oxygen species, ROS) would destroy the bacteria‗s DNA.

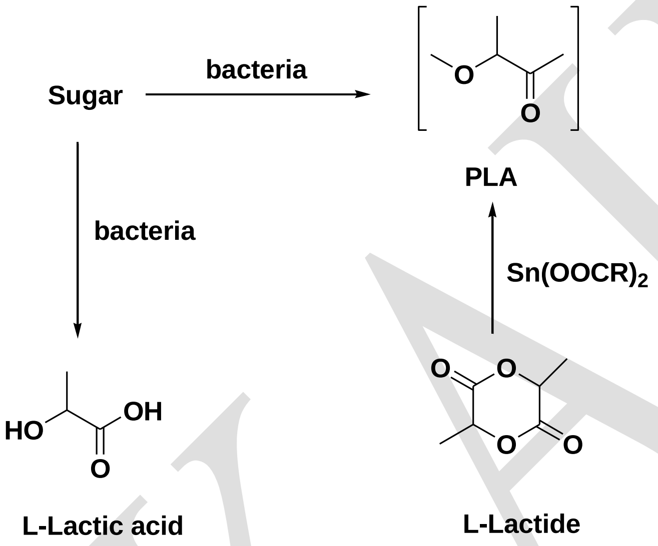
Green Biocatalysis for the Pharmaceutical Industry

Aftrer an initial lag phase the pharmaceutical industry embraced Green Chemistry from the beginning for economic and prestige purposes with emphasis in greener synthetic methods, less solvents and environmental protection. In the last decades biocatalysis has established itself as a scalable and green technology for the production of a broad range of pharmaceutical compounds and intermediates. Biocatalysts employed on large scale in pharmaceutical synthesis deliver cost- and quality- advantages to the pharmaceutical industry. To this respect there are many discoveries of innovative biocatalytic processes using hydrolases, reductases, transaminases, oxidases etc., which are used for the preparation of therapeutic agents. A recent review included 25 recent biocatalysis case studies for pharmaceuticals manufacture. Innovative enzymes used for biocatalysis offered substantial economic benefits to the pharmaceutical industry.

New Developments in Degradable and Recycled Polymers

The green economy strives to promote sustainability and alternative methods for reduction of the demand for raw material resources and energy, to minimize wastes, to prevent environmental pollution and hazards, to reduce greenhouse gas emissions, to optimize manufacturing processes, and effective recycling of end-of-life products and wastes. In the first decades of industrial processes the polymer production was using mainly petroleum raw materials, high energy inputs, and produced non-degradable plastics and large amounts of waste. In the 1930s, the first industrial process for making polyethylene (PE) required temperatures above 150°C and very high pressures exceeding 1000 bar. Catalytic olefin polymerization was discovered during the 1950s with low pressures below 10 bar and at temperatures below 100 °C.

In 1997, scientists working for the chemical company Dow formed a joint venture aiming at converting PolyLactic Acid (PLA) into a commodity plastic which was biodegradable. The L-lactic acid monomer was produced by fermentation of dextrose from forage maize or other plant sources for sugar without requiring genetically modified plants. The PLA was globally marketed in 2003 by the newly formed company NatureWorks under the trade name IngeoTM. In 2009, NatureWorks established an annual nameplate production capacity of 140.000 tons of the Ingeo biopolymer. The biodegradable PLA applications included packaging, durable plastics, and fibers. Like the paper waste PLA does not degrade in landfills.



Green synthesis of plastic (poly lactic acid) made from corn.

Today, polymers and materials used for food packaging consist of a variety of petrochemical-based polymers, metals, glass, paper, and board, or combinations hereof. The durability and degradability of packaging materials are two contradictory subjects; the 1st is desirable for packaging stability and protection for its contents during shelf life and the 2nd for its rapid degradation in the environment.

Advantages of petrochemical-based polymers, which encouraged industries to use them are: (a) low cost and high-speed production;
(b) high mechanical performance;
(c) good barrier properties; and
(d) good heat sealability.

On the other hand, several disadvantages include:
(a) declining oil and gas resources;
(b) increasing oil and gas prices during recent decades;
(c) environmental concerns for their degradation or incineration and global warming;
(d) uneconomical costs and cross-contaminations in their recycling; and
(e) consumer toxicity risks about their monomers or oligomers migrating to edible materials

Mechanical recycling (segregated plastics, mixed plastics), biological recycling (sewage, compost, soil), and energy recovery (incineration, pyrolysis) are 3 alternative ways for plastics waste management, with each having some advantages and disadvantages as to economical, processing, and technological aspects.

The above-mentioned concerns are negligible for biopolymers concerning the biodegradation process that takes place in nature. Biodegradation is defined as the degradation of a polymer in natural environments that includes changes in chemical structure, loss of mechanical and structural properties, and finally, changing into other compounds like water, carbon dioxide, minerals, and intermediate products like biomass and humic materials. The natural environments contain chemical, biological, and physical forces with impinging factors like temperature, humidity, pH, O_2 presence, and so on, which determine the rate and products of the biodegradation process.

Biopolymers are produced from natural resources and crude oil. Four categories of biopolymers are recognized:

(a) Extracted directly from natural raw materials, such as polysaccharides like starch and cellulose; proteins like gelatin, casein, and silk; and marine prokaryotes;

(b) Produced by chemical synthesis from bio-derived monomers such as poly-lactic acid (PLA), also known as poly(lactic acid) in the literature;

(c) Produced by microorganisms or genetically modified bacteria such as polyhydroxyalkanoates (PHA), polyhydroxybutyrate (PHB), hydroxyl-valerate (PHV), bacterial cellulose, xanthan, and pullan; and

(d) Produced from crude oil like aliphatic and aromatic polyesters, polyvinyl alcohol, and modifiedpolyolefins, which are sensitive to temperature and light.

It is highly impossible to avoid products made from synthetic plastics. In many cases, these strong, long-lasting materials have replaced natural substances such as wood and metal in a variety of applications. The marketing of cheap plastic items to the general public has led to the popularity of "single use" items that can be simply thrown away without any cleanup on the part of the consumer.

This being the situation what problem we face

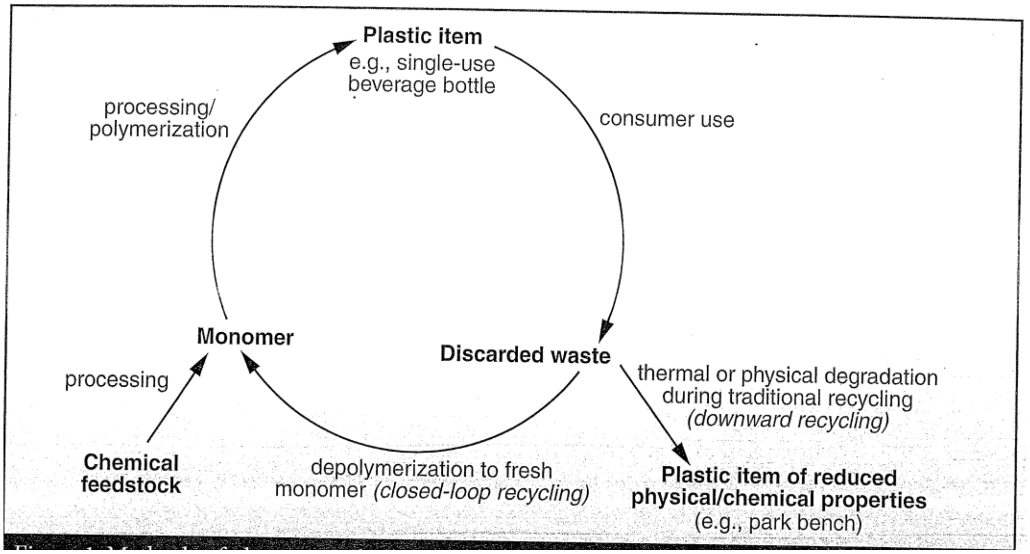
Almost all plastic products made today are made from crude oil which is a non-renewable source that is quickly being depleted. Eventhough some people encourage us to reuse and recycle plastic commodities, these practice will not permanently solve the problem generated by plastic waste. Many plastic items are designed for "single use" means which cannot be reused, while the physical process of recycling often degrades the quality of the second generation plastic.

Neither reusing or recycling is always beneficial as we are led to believe. Due to contamination many plastic items such as plastic food wrap and diapers simply cannot be reused, while the process of recycling often thermally or mechanically degrades polymer molecules leading to a reduction in their physical properties. For example polystyrene commonly used as a packing material undergoes 34% reduction in impact strength after three rounds of recycling.

Because of such issues as contamination and thermal degradation, most plastic products are downward recycled into a product with inferior quality. For example a plastic drink bottle that is recycled does not return to a consumer as a fresh drink bottle, but rather as an item such as plastic chair or plastic pots. Downward recycling prevents the bottle from entering the landfill, but fresh monomer is still required to create a new bottle.

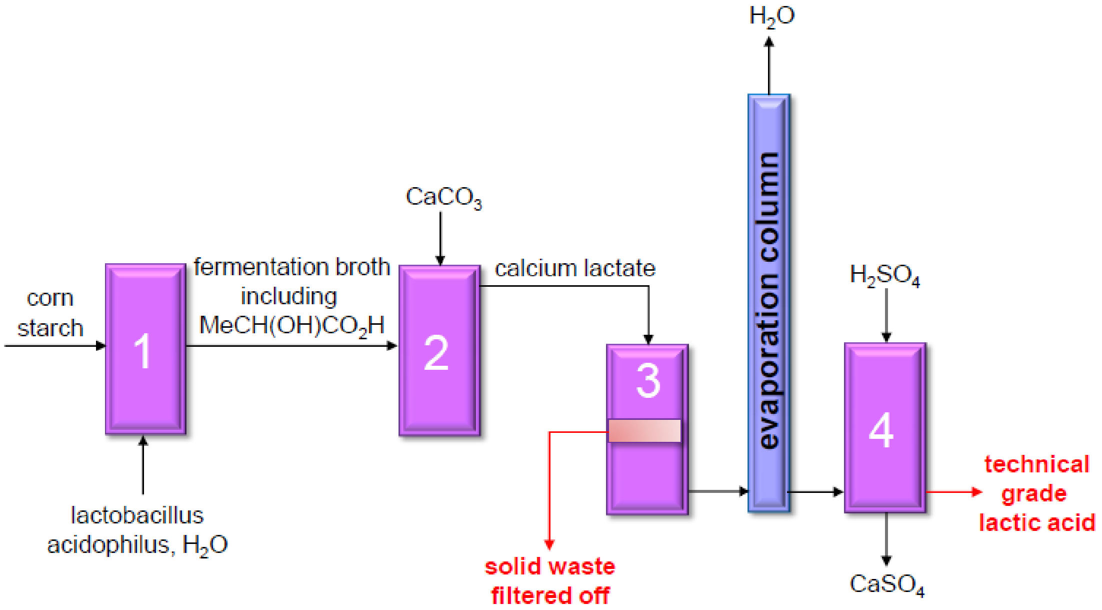
So what will the solution

'Polylactic acid' is a plastic made from the starch found naturally in plants. It can be used in many applications, including packaging, fabrics, and biomedical implants. The material is fully compostable and can be recycled back into pure starting materials to make virgin polylactic acid. Nature works LLC has developed a method for producing polylactic acid from corn. This synthesis uses a renewable resource to produce the monomer and also avoids using the organic solvents common to most synthesis of petrochemical based polymers.



Methods of recycling.

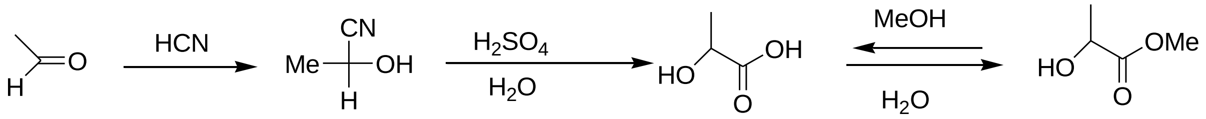
Biosynthesis from starch
Reactor 1: fermentation; 2: salt formation; 3: filtration; 4: hydrolysis



Poly(lactic acid) or **polylactic acid** or **polylactide** (**PLA**) is a biodegradable and bioactive thermoplastic aliphatic polyester derived from renewable resources, such as corn starch.There are several industrial routes to usable (i.e. high molecular weight) PLA. Two main monomers are used: lactic acid, and the cyclic di-ester, lactide.

Chemical synthesis of lactic acid

Lactic acid can also be synthesised from acetaldehyde.



The advantages of this synthetic method is that

1. all the reactions involved are fast and high yielding reactions

2. MeOH generated in final step is recycled
3. Produces high purity lactic acid (99%)

The disadvantages are

1. HCN is highly toxic; acetaldehyde and MeOH are also toxic
2. Waste stream of Ammonium sulphate is produced(but can be used as a fertilizer)
3. Several energy intensive distillations required.

Biochemical Process

The advantages are 1. Renewable feedstock 2. Uses non-hazardous materials

The disadvantages are

1. Slow process (every cycle takes 4-6 days)
2. Quantity of product per reactor volume is low
3. Evaporation is required (due to low salt concentration)
4. Technical grade lactic acid(85 % purity) produced. In order to produce high purity product, the material has to undergo the methanol transesterification process.
5. Waste stream of $CaSO_4$ produced and very large quantities of waste water.

PLA Production

Lactic acid (2-hydroxy propionic acid), the single monomer of PLA, is produced via fermentation or chemical synthesis. Its two optically active configurations, the L(+) and D(−) stereoisomers are produced by bacterial (homofermentative and heterofermentative) fermentation of carbohydrates. Industrial lactic acid production utilizes the lactic fermentation process rather than synthesis because the synthetic routes have many major limitations.

1. Limited capacity due to the dependency on a by-product of another process,
2. Inability to make only the desirable L-lactic acid stereoisomer, and
3. High manufacturing costs.

The homofermentative method is preferably used for industrial production because its pathways lead to greater yields of lactic acid and to lower levels of by-products. The general process consists of

a. Using species of the *Lactobacillus* genus such as *Lactobacillus delbrueckii*, *L.amylophilus*, *L. bulgaricus, and L. leichmanii*,
b. pH range of 5.4 to 6.4,
c. Temperature range of 38 to 42 °C, and
d. Low oxygen concentration.

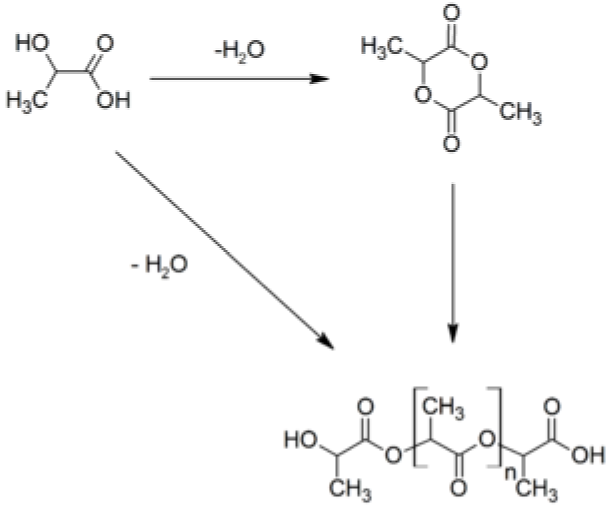
Generally, pure L-lactic acid is used for PLA production.

The most common route to PLA is the ring-opening polymerization of lactide with various metal catalysts(typically tin octoate) in solution, in the melt, or as a suspension. The metal-catalyzed reaction tends to cause racemization of the PLA, reducing its stereoregularity compared to the starting material (usually corn starch).

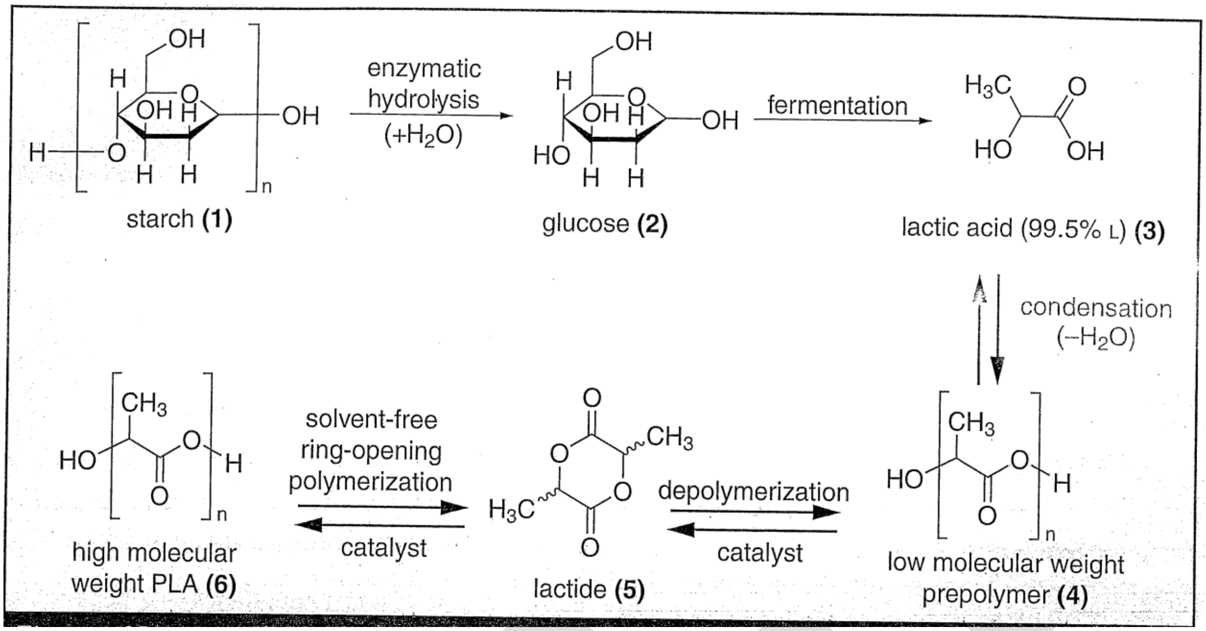
Another route to PLA is the direct condensation of lactic acid monomers. This process needs to be carried out at less than 200 °C; above that temperature, the entropically favoured lactide monomer is generated.

This reaction generates one equivalent of water for every condensation (esterification) step, and that is undesirable because water causes chain-transfer leading to low molecular weight material. The direct condensation is thus performed in a stepwise fashion, where lactic acid is first oligomerized to PLA oligomers. Thereafter, polycondensation is done in the melt or as a solution, where short oligomeric units are combined to give a high molecular weight polymer strand.

Water removal by application of a vacuum or by azeotropic distillation is crucial to favour polycondensation over transesterification. Molecular weights of 130 kDa can be obtained this way. Even higher molecular weights can be attained by carefully crystallizing the crude polymer from the melt. Carboxylic acid and alcohol end groups are thus concentrated in the amorphous region of the solid polymer, and so they can react. Molecular weights of 128–152 kDa are obtainable thus.



NatureWorks exclusively uses corn starch as raw material for lactic acid production via lactic fermentation. Many studies have been conducted to find other sources of carbohydrates for lactic acid production. The use of a specific carbohydrate feedstock depends on its price, availability, and purity. Some agricultural by-products, which are potential substrates for lactic acid production include, cassava starch, lignocellulose/hemicellulose hydrolysates, cottonseed hulls, Jerusalem artichokes, corn cobs, corn stalks, beet molasses, wheat bran, rye flour, sweet sorghum, sugarcane press mud, cassava, barley starch, cellulose, carrot processing waste, molasses spent wash, corn fiberhydrolysates, and potato starch.



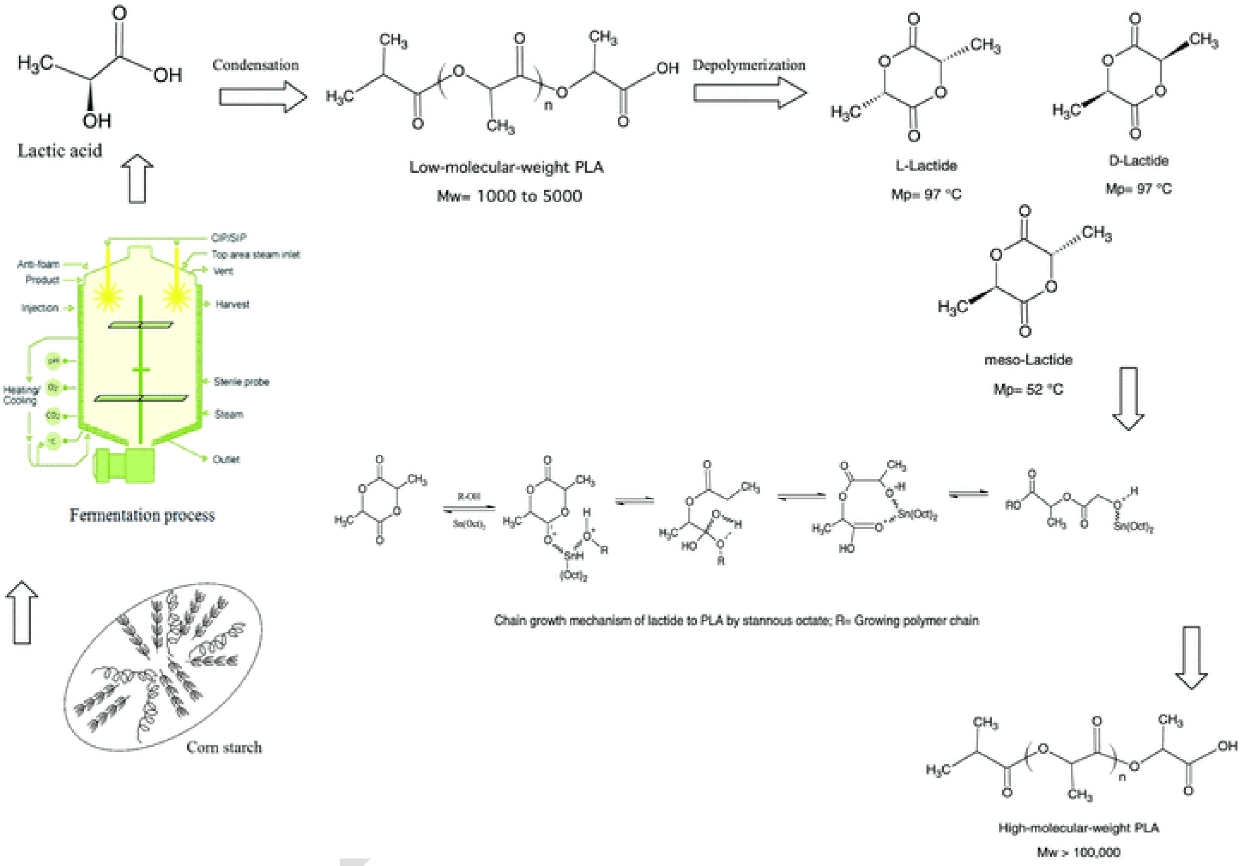
Production of PLA from starch

Other sources of carbohydrate for lactic acid production include kitchen wastes, fish meal wastes, and paper sludge. By using kitchen wastes, concerns about waste management in crowded cities could be automatically eased. Additionally, some parts of carbohydrates from wastes will return to the production cycle of lactic acid and, as a result, decrease a large amount of corn consumption. By using other carbohydrate sources rather than corn, the criticisms and debates about utilizing a food source as packaging material will be defused.

Producing high molecular weight PLA polymers by direct polycondensation in an azeotropic solution and also application of some catalysts is more practicable. The azeotropic solution helps to decrease the distillation pressures and facilitates PLA separation from the solvent by application of molecular sieves.

Lactide purification is accomplished by vacuum-distillation of high temperatures. After the vacuum-distillation of L-lactide, high molecular weight PLA with a controlled optical and crystal purity is formed by ring-opening polymerization. Ring-opening polymerization of lactide can be carried out in melt or solution by cationic, anionic, and coordination mechanisms, depending on the initiator utilized. The most considered active initiator for the L-lactide ring-opening polymerization is stannous octoate (bis 2-ethyl hexanoate, $SnOct_2$), which causes a low degree of racemization at high temperature. It has a low toxicity and is accepted by FDA.

Figure 1 shows PLA production steps by ring-opening polymerization using stannous octoate as an initiator.



Current production steps for PLA.

New ideas for decreasing PLA final price and making production processes more eco-friendly, in comparison to earlier production process, include

1. Usage of crop residue (stems, straw, husks, and leaves) from corn or, potentially, other crops, and use of unfermentable residues as a heat source,
2. Substituting some part of electricity energy by wind power energy.

These approaches decrease the consumption of fossil fuels and corn starch as raw materials and also diminish polluting air, water, and waste emissions to the environment.

One of the most positive points of PLA production in comparison with the other hydrocarbon-based polymers is the decrease of CO_2 emission. Carbon dioxide is believed to be the most important contributor to global climate change and its warming. Because, carbon dioxide is absorbed from air when corn is grown, use of PLA has the potential to emit fewer greenhouse gases compared to competitive hydrocarbon-based polymers.

PLA or poly-lactide was discovered in 1932 by Carothers (at DuPont). He was only able to produce a low molecular weight PLA by heating lactic acid under vacuum while removing the condensed water. The problem at that time was to increase the molecular weight of the products; and, finally, by ring-opening polymerization of the lactide, high-molecular weight PLA was synthesized. PLA was 1st used in combination with polyglycolic acid (PGA) as suture material and sold under the name Vicryl in the U.S.A. in 1974.

In comparison to other biopolymers, the production of PLA has numerous advantages including:
(a) production of the lactide monomer from lactic acid, which is produced by fermentation of a renewable agricultural source corn;
(b) fixation of significant quantities of carbon dioxide via corn (maize) production by the corn plant;
(c) significant energy savings;

(d) the ability to recycle back to lactic acid by hydrolysis or alcoholysis;
(e) the capability of producing hybrid paper-plastic packaging that is compostable;
(f) reduction of landfill volumes;
(g) improvement of the agricultural economy; and
(h) the all-important ability to tailor physical properties through material modifications

Briefly, PLA is based on agricultural (crop growing), biological (fermentation), and chemical (polymerization) sciences and technologies.

PLA Processing Technologies

The methods of manufacture for biopolymers are all established polymer-manufacturing techniques, but the control and application of these methods must be varied to cope with certain factors associated with exploiting the advantages of biopolymers. The manufacturing routes all show certain fundamental similarities, with the major differences depending on whether a thermoset or thermoplastic biopolymer is to be processed.

The conditions in biopolymer processes such as injection molding are least damaging to polymer melts, and most problematic in continuous processes like extrusion, particularly in processes where the extrudate is stretched, such as film blowing. The limiting factors for processing conditions for biopolymers are the same as for petrochemical-based ones: degradation at the upper limits of temperature and shear, and lack of homogeneity at the lower limits. However, these limits are somewhat more tightly drawn at the upper limits for biopolymers. The results of exceeding these upper limits are degradation of the polymer, resulting in molding defects such as weld lines, discoloration, or a strong odor in the final product.

Commercial PLA resins are packaged in crystalline and amorphous pellet forms. Crystalline and amorphous pellets look significantly different. Semicrystalline pellets are opaque and amorphous pellets are transparent. Different types of PLA resins with different application ranges are being produced and each customer should specify packaging demands. In Table 2, available commercial PLA resins for food packaging applications are characterized.

Table 2 Commercial PLA resins adapted by NatureWorks

Product code	**Applications**	**Usages**
2002D	Extrusion, thermoforming	Dairy containers, food serviceware, transparent food containers, blister packaging, cold drink cups
3001D 3051D	Injection molding for applications with heat deflection temperatures lower than 55 °C (130 °F)	Cutlery, cups, plates, and saucers, and outdoor novelties
3251D	Injection molding, having higher melt flow capability than other PLA resins for easier molding of thin-walled parts	Injection molding applications, both clear and opaque, requiring high gloss, UV resistance, and stiffness
4032D	Biaxially oriented films with use temperatures up to 150 °C (300 °F), barrier to flavor and grease, and oil resistance	Laminations, printed films with higher curing temperatures, other packaging applications
4042D	Biaxially oriented films with use temperatures up to 130 °C (265 °F), barrier to flavor and grease, and superior oil resistance	Candy twist-wrap, salad, and vegetable bags, window envelope film, lidding film, label film, other packaging applications
4060D	Heat sealant with a seal initiation temperature of 80 °C	Can be coextruded with other PLA resin to form a sealant layer for biaxially- oriented PLA film

Product code	**Applications**	**Usages**
7000D	Injection stretch blow molding, for 1:2 stage operations	Fresh dairy, edible oils, fresh water
7032D	Injection stretch blow molding, for 1:2 stage operation	Fruit juices, sports drinks, jams, and jellies

The processing technologies for producing different packaging applications with PLA resins are mentioned here.

PLA production is a popular idea as it represents the fulfillment of the dream of cost-efficient, non-petroleum plastic production. **The huge benefit of PLA as a bioplastic is its versatility and the fact that it naturally degrades when exposed to the environment.** For example, a PLA bottle left in the ocean would typically degrade in six to 24 months. Compared to conventional plastics (which in the same environment can take several hundred to a thousand years to degrade) this is truly phenomenal. Accordingly, there is a high potential for PLA to be very useful in short lifespan applications where biodegradability is highly beneficial (e.g. as a plastic water bottle or as a container for fruit and vegetables). Of note, despite its ability to degrade when exposed to the elements over a long time, PLA is extremely robust in any normal application (e.g. as a plastic electronics part).

Chemical and physical properties

Due to the chiral nature of lactic acid, several distinct forms of polylactide exist: poly-L-lactide (**PLLA**) is the product resulting from polymerization of L,L-lactide (also known as L-lactide).

PLLA has a crystallinity of around 37%, a glass transition temperature 60–65 °C, a melting temperature 173–178 °C and a tensile modulus 2.7–16 GPa. Heat-resistant PLA can withstand temperatures of 110 °C. PLA is soluble in chlorinated solvents, hot benzene, tetrahydrofuran, and dioxane.

Polylactic acid can be processed like most thermoplastics into fiber (for example, using conventional melt spinning processes) and film. PLA has similar mechanical properties to PETE polymer, but has a significantly lower maximum continuous use temperature. The tensile strength for 3-D printed PLA was previously determined.

The melting temperature of PLLA can be increased by 40–50 °C and its heat deflection temperature can be increased from approximately 60 °C to up to 190 °C by physically blending the polymer with PDLA (poly-D-lactide). PDLA and PLLA form a highly regular stereocomplex with increased crystallinity. The temperature stability is maximised when a 1:1 blend is used, but even at lower concentrations of 3–10% of PDLA, there is still a substantial improvement. In the later case, PDLA acts as a nucleating agent, thereby increasing the crystallization rate. Biodegradation of PDLA is slower than for PLA due to the higher crystallinity of PDLA.

There is also poly(L-lactide-*co*-D,L-lactide) (PLDLLA) – used as PLDLLA/TCP scaffolds for bone engineering.

What is PLA, and what is it used for?

Polylactic Acid (PLA) is different than most thermoplastic polymers in that it is derived from renewable resources like corn starch or sugar cane. Most plastics, by contrast, are derived from the distillation and polymerization of nonrenewable petroleum reserves. Plastics that are derived from biomass (e.g. PLA) are known as “bioplastics.”

Polylactic Acid is biodegradable and has characteristics similar to polypropylene (PP), polyethylene (PE), or polystyrene (PS). It can be produced from already existing manufacturing equipment (those designed and originally used for petrochemical industry plastics). This makes it relatively cost efficient to produce. Accordingly, PLA has the second largest production volume of any bioplastic (the most common typically cited as thermoplastic starch).

There are a vast array of applications for Polylactic Acid. Some of the most common uses include plastic films, bottles, and biodegradable medical devices (e.g. screws, pins, rods, and plates that are expected to biodegrade within 6-12 months). PLA constricts under heat and is thereby suitable for use as a shrink wrap material.

What Are The Different Types of Polylactic Acid and Why is it Used so Often?

There are several different types of Polylactic Acid to include Racemic PLLA (Poly-L-lactic Acid), Regular PLLA (Poly-L-lactic Acid), PDLA (Poly-D-lactic Acid), and PDLLA (Poly-DL-lactic Acid). They each have slightly different characteristics but are similar in that they are produced from a renewable resource (lactic acid: $C_3H_6O_3$) as opposed to traditional plastics which are derived from nonrenewable petroleum.

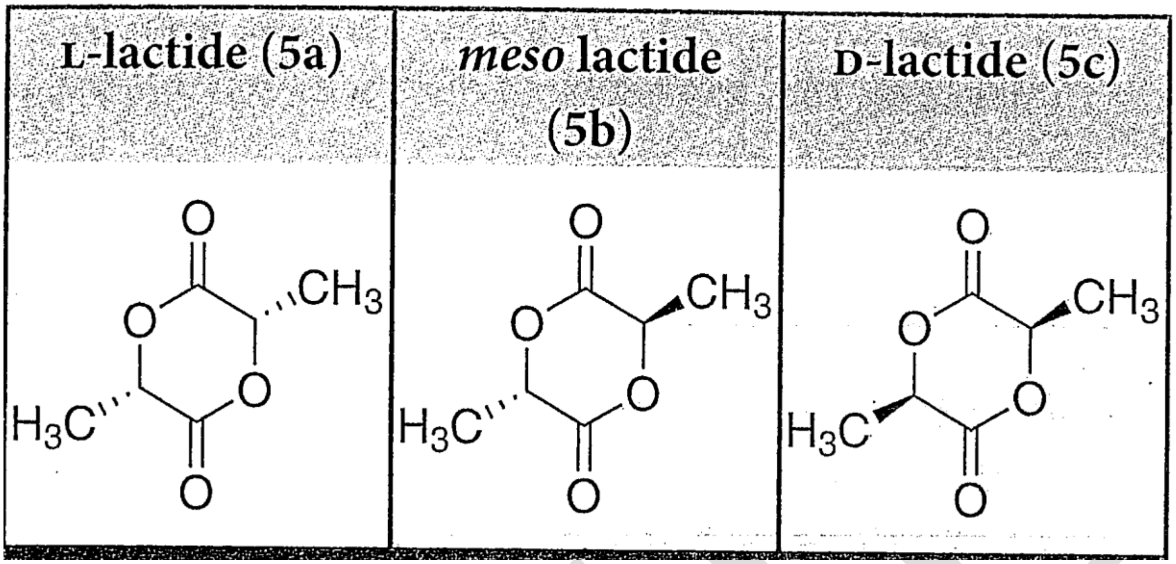
Is PLA toxic?

In solid form, no. In fact, Polylactic Acid (PLA) is biodegradable. It is often used in food handling and medical implants that biodegrade within the body over time. Like most plastics, it has the potential to be toxic if inhaled and/or absorbed into the skin or eyes as a vapor or liquid (i.e. during manufacturing processes). Be careful and closely follow handling instructions for molten polymer in particular.

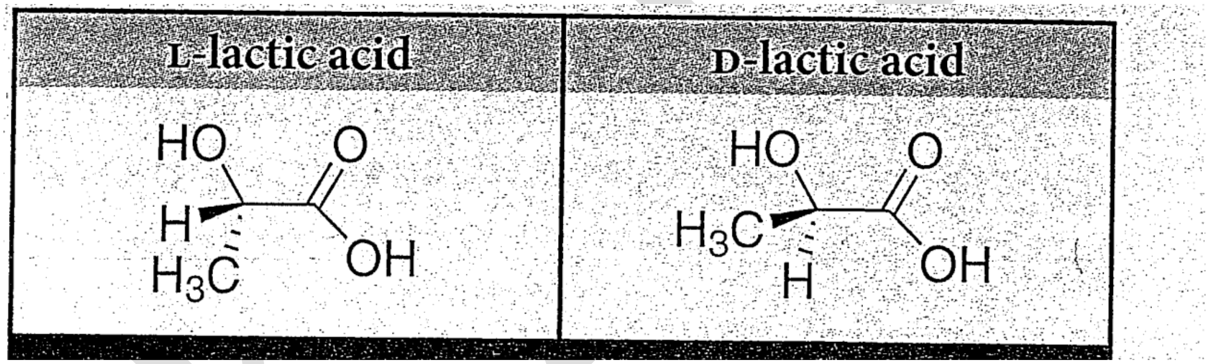
What are the Disadvantages of Polylactic Acid?

PLA has a relatively low glass transition temperature (typically between 111 and 145 °F). This makes it fairly unsuitable for high temperature applications. Even things like a hot car in the summer could cause parts to soften and deform.

Polylactic Acid is a little bit more brittle than ABS for 3D prototyping but it has some advantages as well. For a full comparison of the two plastics as they relate to 3D printing read here.



Isomers of Lactide



Isomers of lactic acid

Due to its biocompatibility, the medical community has used PLA for many years for making bone screws, sutures, surgical staples and tissue scaffolding.

PLA’s physical properties like high gloss, clarity, printability, heat sealability, oil and grease resistance and its ability to act as a flavour and odour barrier, are comparable or superior than that of polystyrene and polyethylene terephthalate(PET).

The process of producing PLA designed by Nature works received a presidential Green chemistry Challenge award in the year 2002. Unlike most other polymer synthesis that use crude oil as a chemical feedstock, Nature Work process uses starch harvested from corn. Besides the obvious advantage of using renewable source, the use of corn as the feed stock provides the economic benefit of not having a market price directly linked to the rising cost of the crude oil. Starch is a biopolymer produced in plants by the linking of glucose molecules. Glucose is the product of photosynthesis, and therefore one might consider carbon di oxide and water as the required feedstock for the preparation of PLA.

The Nature works process begins by reactingwater enzymatically with the corn derived starch, which cleaved the starch glycosidic linkage to form glucose, the monomer of starch. The glucose is then converted into lactic acid via fermentation. This process involves the generation of pyruvate (as in glycolysis) which is then converted into lactic acid (99.5% L-lactic acid). Lactic acid is then polymerised in to an oligomeric ‘pre- polymer’ in a mild solventless condensation polymerization. We should recognise the reaction between the lactic acid carboxylic acid functionality with hydroxyl functionality as esterification. The low molecular weight prepolymer that is formed is then catalytically broken down into a cyclic dimer (two linked monomers) of lactic acid called lactide with three possible stereochemical isomers which undergoes actual polymerization.

PART B (2 Mark Questions)

1. What Advantages of petrochemical-based polymers, which encouraged industries to use them
2. What are the disadvantages of petrochemical-based polymers, which discouraged industries to use them
3. Mention any three alternative ways for plastics waste management.
4. Neither reusing or recycling of plastic is always beneficial as we are led to believe. Comment on the statement.
5. Explain the method of recycling of a plastic material.
6. How lactic acid is synthesized in the laboratory. What are its advantages and disadvantages.
7. Suggest some New ideas for decreasing PLA final price and making production processes more eco-friendly, in comparison to earlier production process.
8. In comparison to other biopolymers, the production of PLA has numerous advantages. Justify the statement.
9. What is PLA, and what is it used for?
10. Is PLA toxic. Comment on the statement.
11. What are the disadvantages f PLA.
12. What are starch rich plants that could be used to produce PLA
13. Nature Works market the product as “compositable” and not as “Biodegradable”. What is the difference between these two terms.
14. What compounds would you expect PLA to degrade to in the environment.

PART C (8 Mark Questions)

1. What Are The Different Types of Polylactic Acid and Why is it Used so Often?
2. What are the possible monomers of prepearing PLA. Draw their structres.
3. The development of Nature works PLA won the presenditial Green Chemistry award. Look up the three focus areas for this award and determine which focus area this case best fits into.
4. List out any two of the twelve principles of green chemistry that are addressed by the green chemistry developed by Nature Works PLA.
5. What is the stereochemical relationship between the two forms of lactic acid and three forms of Lactide.
6. Propose a mechanism for the formation of PLA “pre-polymer” from lactic acid in aqueous acidic environment. Why is this reaction referred to condensation.
7. When composted, PLA releases carbon di oxide into the atmosphere. Does this carbon di oxide add to the global greenhouse effect. Why or why not.
8. What are bio-polymers. How many different types of biopolymers were recognized from nature.
9. What is polylactic acid. Explain its biosynthesis from starch.

10. Explain the biochemical process of preparing lactic acid. What are its advantages and disadvantages.
11. Explain the manufacturing process of PLA from corn. What are the advantages.

Questions	A	B	C	D	Answers
Which are considered as renewable starting materials ?	CO_2	methane gas	CO	CO_2 & methane gas	CO_2 & methane gas
Known deposits of a material that can be extracted profitably are called	resources.	undiscovered reserves.	identified deposits.	reserves.	reserves.
Which of the following is the most abundant fossil fuel?	oil	natural gas	coal	gasoline	coal
Which of the following is not a renewable energy source?	biomass conversion	solar	hydroelectric	oil	oil
What are the main constituents of natural gas?	CO	CO2	CH4 & C_2H_6	NO_2	CH4 & C_2H_6
What is the name of the porous Teflon base of the reaction vessel?	Frit	Test tube	Flask	Filter	Frit
What term is used to describe the release of molecules from the resin in combatorial chemistry?	Bond breaking	Synthesis	Cleavage	Decomposition	Cleavage
How many compounds are there in a library?	384	96	1000	12	384
How many reaction vessels are there in the standard teflon reaction	1000	12	312	96	96

vessel block?					
Where may receptor molecules be found?	On the outer side of the cell	Inside the flu virus	Inside the cell	On the surface of the flu virus	On the outer side of the cell
What quantities of compounds can be made in the pilot plant?	Up to 100 tonnes	Up to 100 kg	Up to 100 mg	Up to 100 g	Up to 100 kg
What is the name of the process by which compounds related to a promising compound are made on a larger scale?	Computational chemistry	Combinational chemistry	Lead optimisation	Improvement	Lead optimisation
Combinatorial and parallel synthesis can be useful at various stages of the drug design / development process. Which of the following is not such a stage?	Finding a lead compound	Optimising a lead compound	Structure determination of the lead compound	Structure-activity relationships of the lead compound	Structure determination of the lead compound
What is meant by a linker or an anchor?	The bond which links a molecule to a solid support.	A reactive functional group on the solid support which allows a molecule to be attached to the solid support.	A molecular unit which is attached to the solid support and which contains a reactive functional group that allows attachment of a starting material.	The functional group on the starting material which is used to attach the molecule to the solid support.	A molecular unit which is attached to the solid support and which contains a reactive functional group that allows attachment of a starting material.
What is meant by a scaffold?	The lead compound	The carbon skeleton of a	The core structure of a molecule that is	The pharmacophore	The core structure of a molecule that is

		compound	common to a series of compounds		common to a series of compounds
According to EPA of USA, the following is not one of the six major pollutants?	Ozone	Carbon monoxide	Nitrogen oxides	Carbon di-oxide	Carbon di-oxide
The Pollution Standard Index (PSI) scale has span from	0-200	0-300	0-400	0-500	0-500
Which of the following is an organic gas?	Hydrocarbons	Aldehydes	Ketones	Ammonia	Ammonia
Ozone of found in	Mesosphere	Ionosphere	Stratosphere	Exosphere	Stratosphere
Ozone is formed in the upper atmosphere by a photochemical reaction with	Ultra violet solar radiation	Infra red radiation	Visible light	All of the above	Ultra violet solar radiation
The principal source of volatile organics (Hydrocarbons) is	Transportation	Industrial processes	Stationary fuel combustion	Volcanoes	Industrial processes
The function of automobile catalytic converter is to control emissions of	carbon dioxide and hydrogen	carbon monoxide and hydrogen	carbon monoxide and carbon dioxide	carbon monoxide and nitrogen dioxide	carbon monoxide and hydrogen
The threshold concentration of sulphur dioxide in any industrial activity should not be permitted beyond	2ppm	3ppm	4ppm	5ppm	5ppm
The threshold limit of	15ppm	20ppm	25ppm	30ppm	25ppm

benzene is					
Which of the following is used as antiknock compound in gasoline?	tetramethyl lead	tetraethyl lead	trimethyl lead	triethyl lead	tetraethyl lead
Which of the following is a fermentation product of molasses?	Methano	Formaldeyde	Ammonia	Acetone	Acetone
The boiler flue gas is source of	HCl	NO	HF	Volatile organic compounds	NO
Which of the following is true about carbon monoxide?	single largest source is from internal combustion engines	results from the actions of ultraviolet light on ozone	causes acid rain	leading cause of cancer in smokers	single largest source is from internal combustion engines
Sulfur dioxide contributes to all of the following problems except	damage to buildings	acid rain.	death of vegetation	photochemical smog.	photochemical smog.
What percentage of total world production of carbon dioxide do the developed countries contribute?	about 25%	about 50%	about 75%	almost 100%	about 75%
Which of the following is not a major contributor to the greenhouse effect?	carbon dioxide	carbon monoxide	chlorofluorocarbons	methane gas	carbon monoxide
Which of the following enzyme groups can catalyse oxidation	phosphorylases	isomerases	hydrolases	dehydrogenases	dehydrogenases

reactions?					
Enzymes differ from inorganic catalysts in that they are highly specific.Which property of an enzyme is responsible for this specificity?	The insoluble nature of enzymes.	The high molecular mass of enzymes.	The surface configuration of enzymes.	The absence of metallic ions in an enzyme.	The surface configuration of enzymes.
Which of the following is an extracellular enzyme?	catalase	DNA polymerase	keratin	trypsin	trypsin
Which one of the following conditions is least likely to denature an enzyme?	a high temperature	an extreme pH	heavy metal ions	a low temperature	a low temperature
Which type of enzyme catalyses the conversion of a dipeptide into two separate amino acids?	decarboxylase	dehydrogenase	hydrolase	oxidoreductase	hydrolase
An example for a renewable resource	Crude oil	petroleum	diesel	biomass	biomass
Example for a biocatalyst	enzymes	Metallic salts	Raney Nickel	Coordination compounds	enzymes
Using a biocatalyst in a reaction makes it	Environmentally friendly	unattractive	Economically unviable	Environmentally unviable	Environmentally friendly
Using a biocatalyst in a reaction makes it	Environmentally un friendly	unattractive	Economically unviable	Environmentally viable	Environmentally viable
d-glucose is used to prepare adipic acid is a	Renewable source	Non-renewable source	Environmentally friendly gas	Biological catalyst	Renewable source
The catalyst used for	E.Coli	Pen-acylase	Environmentally	zymase	E.Coli

the preparation of adipic acid from d-glucose is			friendly gas		
d-glucose is used to prepare adipic acid is manufactured from	Corn starch	Animal protein	Raney Nickel	Animal fats	Corn starch
d-glucose is used to prepare adipic acid is manufactured from	Agricultural wastes	Animal protein	petroleum	Animal fats	Agricultural wastes
In conventional method for the preparation of Adipic acid, it produces	N_2O	N_2O_2	NO	NO_2	N_2O
N_2O is produced during the preparation of	Adipic acid	Succinic acid	Tattaric acid	Lactic acid	Adipic acid
N_2O is produced during the preparation of adipic is a	Greenhouse gas	Laughing gas	Environmentally friendly gas	Dry liquid	Greenhouse gas
N_2O is produced during the preparation of adipic is a	Ozone depleting gas	Laughing gas	Environmentally friendly gas	Dry liquid	Ozone depleting gas
In conventional method for the preparation of Adipic acid, it uses the catalyst	Ni-Al_2O_3 catalyst	C0 -Al_2O_3 catalyst	Raney Nickel	palladium	Ni-Al_2O_3 catalyst
In the greener method for the preparation of adipic acid the raw material used is	benzene	coal	petroleum	d-glucose	d-glucose
d-glucose is used to prepare	Adipic acid	Succinic acid	Tattaric acid	Lactic acid	Adipic acid

d-glucose is used to prepare adipic acid is a	Renewable source	Non-renewable source	Environmentally friendly gas	Biological catalyst	Renewable source
The catalyst used for the preparation of adipic acid from d-glucose is	E.Coli	Pen-acylase	Environmentally friendly gas	zymase	E.Coli
d-glucose is used to prepare adipic acid is manufactured from	Corn starch	Animal protein	Raney Nickel	Animal fats	Corn starch
d-glucose is used to prepare adipic acid is manufactured from	Agricultural wastes	Animal protein	petroleum	Animal fats	Agricultural wastes
A biocatalyst works under	a mild reaction condition	High temperature reaction condition	High pressure	High pressure and high temperature	a mild reaction condition
A biocatalyst works under	Physiological PH	High temperature reaction condition	High pressure	High pressure and high temperature	Physiological PH
A biocatalyst works under	Physiological temperature	High temperature reaction condition	High pressure	High pressure and high temperature	Physiological temperature
Microwave radiation is also called as	Ultraviolet radiation	Infrared radiation	Electromagnetic radiation	Radiofrequency radiation	Electromagnetic radiation
The microwave heating the molecules with excess potential energy is converted into kinetic	Collision among the molecules	Interaction among the molecules	No interaction among the molecules	Vibration Collision among the molecules	Collision among the molecules

energy through					