KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed University Established Under Section 3 of UGC Act 1956)

COIMBATORE-21

DEPARTMENT OF CHEMISTRY

I M.Sc Chemistry
Syllabus

Semester-I

ELECTIVE I

17CHP105-A	**GREEN CHEMISTRY**	**4H 4C**
Instruction Hours/week: L:4 T:0 P:0	**Marks: Internal:40 External: 60 Total:100**	

Scope

Green chemistry is the “design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances.” Green chemistry places equal importance on the development of science with the effects the development has on the environment and the global population. Green chemistry breaks away from the traditional methods that solely considered the treatment or abatement of pollution after it was created, and considers alternative routes obviating the need to produce the waste.

Programme Outcome

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.

Methodology

Blackboard teaching, Powerpoint presentation and group discussion.

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, calculation of atom economy of the rearrangement, addition, substitution and elimination reactions. Green solvents– supercritical fluids, water as a solvent for organic reactions, ionicliquids, fluorous biphasic solvent, PEG, solvent less processes, immobilized solvents and how to compare greenness of solvents.

UNIT III

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 (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:

Text Books:

1. Ahluwalia, V. K., & Kidwai, M. (2012). *New Trends in Green Chemistry* (III Edition). New Delhi: Anamalaya Publisher.
2. Asim K. Das, 2015, Environmental Chemistry with Green Chemistry, Books and Allied (P) Ltd, Kolkata-700010
3. Anastas, P. T., & Warner, J. C. (1998). *Green Chemistry: Theory and Practice*. Oxford: Oxford University Press.
4. Matlack, A. S. (2001). *Introduction to Green Chemistry.* New York: Marcel Dekker.
5. Cann, M. C., & Connely, M. E. (2000). *Real-World cases in Green Chemistry*. Washington: American Chemical Society.

Reference Books:

1. Ryan, M. A., & Tinnesand, M. (2002). *Introduction to Green Chemistry*, Washington: American Chemical Society.
2. Lancaster, M. (2010). *Green Chemistry: An Introductory Text* (II Edition). Cambridge: RSC Publishing.
3. Clark, J. H, & Macquarrie, D. J. (2002). *Handbook of Green Chemistry & Technology*. Abingdon: Blackwell Publishing.
4. Roger Arthur Sheldon, Isabel Arends, and Ulf Hanefeld, 2007, Green Chemistry and Catalysis, WILEY-VCH Verlag Gmbh & Co. KGaA.

Programme Learning Outcome

After the completion of the course the student will know about the concept and principles of green chemistry. Further he will have an idea to apply the principles of green chemistry in the reaction or process to determine “Greener” alternatives or to improve industrial processes.

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COIMBATORE-21

DEPARTMENT OF CHEMISTRY

I M.Sc Chemistry

LECTURE PLAN

ODD SEMESTER- JUNE 2017

INCHARGE STAFF: Dr.G. AYYANNAN

CLASS: I M.Sc. CHEMISTRY

TITLE: GREEN CHEMISTRYSUBJECT CODE: 17CHP105A

TOTAL HOURS: 62

UNIT-I

Hour's required-12

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	T2:683-685
4		Limitations of green chemistry	T2:684-685
5	1	Twelve principles of green chemistry(1) with explanations	T1:2, 3
6	1	Twelve principles of green chemistry(2) with explanations	T1: 3
7	1	Twelve principles of green chemistry(3 and 4) with explanations	T1:3, 4
8	1	Twelve principles of green chemistry(5 and 6) with explanations	T1:5, 6
9	1	Twelve principles of green chemistry(7 and 8) with explanations	T1:6, 7
10	1	Twelve principles of green chemistry(9 and 10) with explanations	T1:8, 9
11	1	Twelve principles of green chemistry(11 and 12) with explanations	T1:10, 11
12	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-13

S.No	Lecture Hour	Topics	Support Material
1	1	Designing a Green synthesis using these principles	T2: 665-667
2	1	Prevention of waste/ byproducts	T2: 667-669
3	1	Atom economy-calculation of atom economy	T1: 2-3
4	1	Atom economy of rearrangement reaction	T1: 3
5	1	Atom economy of addition reaction	T1: 3,4
6	1	Atom economy of substitution reactions	T1: 4-6
7	1	Atom economy of elimination reactions	T1: 6,7
8	1	Green solvents- Supercritical fluids	T2: 669, 695-696, 699
9	1	Water as solvent for organic reactions	T1: 251
10	1	Ionic liquids, Fluorous biphasic solvent	T1:15
11	1	PEG, solvent less processes	T1:66
12	1	Immobilized solvents, comparison of greenness solvents	T1: 267,268
13	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-12

S.No	Lecture Hour	Topics	Support Material
1	1	Introduction of alternative sources of energy	R2:22
2	1	Use of microwave and ultrasonic energy	T2: 692-695
3	1	Microwave assisted reactions in water	T1:227-229
4	1	Hoffmann elimination reactions	T1:171
5	1	Methyl benzoate to benzoic acid	T1:171, 172
6	1	Oxidation of toluene and alcohols	R1:170-171
7	1	Microwave assisted reactions in organic solvents	R2:401
8	1	Diels-Alder reactions	T1:116
9	1	Decarboxylation reaction	T1:117
10	1	Ultrasound assisted reactions	T1:16, 30, 296
11	1	Simmons-smith reaction	T1:217
12	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, 2007, Green Chemistry and Catalysis, WILEY-VCH Verlag Gmbh& Co. KGaA.

UNIT-IV

Hour's required-11

S.No	Lecture Hour	Topics	Support Material
1	1	Introduction of green synthesis	R2:310-314
2	1	Green starting materials	R2:314
3	1	Green reagents	T2:694
4	1	Green solvents	T2:695
5	1	Green reaction conditions	T2:696, 697
6	1	Green catalysis	R2:316
7	1	Green synthesis-Real world cases (traditional processes and green ones)	R2:284
8	1	Synthesis of Ibuprofen	T2:690-691
9	1	Synthesis Adipic acid	T2:693, 715
10	1	Synthesis disodium iminodiacetate (alternative to strecker synthesis)	T2: 694, 727
11	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, 2002, Hand Book of Green Chemistry and Technology, Blackwell Science Ltd.

UNIT-V

Heterocyclic compounds: **Hours required-14**

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	R1: 14, 15
4	1	Biomimetic reagents	R1: 18
5	1	Multifunctional reagents	R1: 18-20
6	1	Proliferation of solvent less reactions	T1: 267
7	1	Noncovalent derivatization	T1: 267, 268
8	1	Combinatorial green chemistry	T1: 269
9	1	Biomass conversion	T2: 661, R2: 355
10	1	Emission control	T2: 200-201
11	1	Bio catalysis	R1: 29
12	1	Recapitulation and discussion of important questions	
13	1	Previous year ESE question paper discussion	
14	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, 2007, Green Chemistry and Catalysis, WILEY-VCH Verlag Gmbh & Co. KGaA.

R2. James Clark & Duncunm Macquarrie, 2002, Hand Book of Green Chemistry and Technology, Blackwell Science Ltd.

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.

Introduction

Sustainable development is now accepted by governments, industry and the public as a necessary goal for achieving the desired combination of environmental, economic and societal objectives. The challenge for chemists and others is to develop new products, processes and services that achieve all the benefits of sustainable development. This requires a new approach whereby the materials and energy input to a process are minimised and thus utilised at maximum efficiency. The dispersion of harmful chemicals in the environment must be minimised or, preferably, completely eliminated. We must maximise the use of renewable resources and extend the durability and recyclability of products, and all of this must be achieved in a way that provides economic benefit to the producer (to make the greener product and process economically attractive) and enables industry to meet the needs of society.

We can start by considering the options for waste management within a chemical process. The hierarchy of waste management techniques now has prevention, through the use of cleaner processes, as by far the most desirable option. Recycling is considered to be the next most favourable option and, from an environmental standpoint, is particularly important for products that do not dissipate rapidly and safely into the environment. Disposal is certainly the least desirable option. The term ‘cleaner production’ encompasses goals and principles that fall nicely within the remit of waste minimisation. The United Nations Environmental Programme describes cleaner production as:

‘The continuous application of an integrated preventative environmental strategy to processes and products to reduce risks to humans and the environment. For production processes, cleaner production includes conserving raw materials, and reducing the quality and toxicity of all emissions and wastes before they leave a process.’

Cleaner production and clean synthesis fall under the heading of waste reduction at source and, along with retrofitting, can be considered as the two principal technological changes. Waste reduction at source also covers good housekeeping, input material changes and product changes.

“Science is making **chemical** processes more sustainable by reducing the amount of compounds used and reducing and/or eliminating the amount of toxic substances we produce. Researchers have made **important** progress in **Green Chemistry** in recent years.”

A Brief History of Green Chemistry

Green chemistry traces back several decades and can be linked to impactful environmental activists, such as Rachel Carson. Her 1962 publication, “Silent Spring,” helped direct the public’s awareness to pesticides and their ties to environmental pollution. Less than a decade later, The Environmental Protection Agency (EPA) was formed in 1970. The EPA references its existence as the extended shadow of Rachel Carlson who is considered a leading innovator of environmental protection, a cause that has paved the way to current green chemistry practices.

President Richard Nixon’s efforts for environmental sustainability lead to the creation of the Citizen’s Advisory Committee on Environmental Quality and a Cabinet-level Environmental Quality Council in 1969. In his speech announcing the creation of the council, Nixon urged the new council and the committee “to examine the full range of variables which affect environmental quality.” Nixon’s efforts were criticized for not being forceful enough. Eventually efforts led to the development of the NEPA, the National Environmental Policy, which called for a Council on Environmental Quality.

Recognizing the need to shift from end-of-pipeline control to pollution prevention, by the 1980s, the EPA established the Office of Pollution Prevention and Toxics. Two decades after the implementation of the EPA, **The Pollution Prevention Act** (1990), (http://www.epa.gov/p2/pubs/p2policy/act1990.htm), was created to enforce eco-friendly strategies, and provide grants to states in the effort to reduce source waste. President Bill Clinton devised the **Presidential Green Chemical Challenge Awards** during his presidency to reward those practicing sustainable chemistry. By the end of the 1990s, “Twelve Principles of Green Chemistry” was published. The guidelines serve as a reference for processes and practices to lessen negative environmental impact. These principles are Prevention i.e., It’s better to prevent waste than to treat or clean waste after it’s been created, Atom Economy, Less Hazardous Chemical Syntheses, Designing Safer Chemicals, Safer Solvents and Auxiliaries, Design for Energy Efficiency, Use of Renewable Feedstocks, Reduce

Derivatives, Catalysis, Design for Degradation, Real-time analysis for Pollution Prevention and Inherently Safer Chemistry for Accident Prevention.

As reflected in the previous decade spanning to today, there has been a shift in the emergence of green chemistry trends. As eco-awareness spreads to the consumer market and as the hazards of certain materials and chemicals become better known, companies and manufacturers are working to revamp the way they use chemicals in their products. These practices include:

- Reducing formaldehyde (a gas linked to various health issues including cancer) use in the production of products.
- Eliminating/reducing dyes in manufacture.
- Eliminating ozone-depleting CFC's in widely used products.
- Development of technology through chemicals that lessens green impact (i.e. converting sustainable plant-based materials to low-carbon chemicals).
- Creating a patented system to formalize and phase out raw materials for fabrication processes.
- Developing sustainable technology used in agrichemical treatment for farming.

A Timeline of Green Chemistry Highlights

- **1962** - Rachel Carson, writer, biologist and environmental conservation icon, publishes the first of three instalments of "Silent Spring,"—literature that is historically tied to the launch of the environmental movement. The publication helped spread public awareness of the hazards of environmental pollution and pesticides to the environment.
- **1969** - President Richard Nixon establishes the Citizen's Advisory Committee on Environmental Quality and a Cabinet-level Environmental Quality Council. (http://www.presidency.ucsb.edu/) Later that year, Nixon expanded his environmental efforts by appointing the White House Committee to determine whether an environmental agency should be developed.
- **1970** -The Environmental Protection Agency (EPA) is born.
- **1980s/1988** - Shift from end-of-pipeline control to pollution prevention is recognized, leading to the Office of Pollution Prevention and Toxics in 1988.
- **1990 -** The Pollution Prevention Act under the George H.W. Bush Administration is passed.

- **1993** -The EPA implements the Green Chemistry Program, which serves as a precedent for the design and processing of chemicals that lessen the negative environmental impact.
- **1995 & 1996** - In 1995, President Bill Clinton established the Presidential Green Chemical Challenge Awards, which served to encourage those involved with the manufacture and processes of chemicals to incorporate environmentally sustainable design and processes in their practices. The following year, the first recipient receives the award, the only award issued by the president that honors work in chemistry.
- **1997** - The Green Chemistry Institute is launched. Its vision is "…to advance the broader chemistry enterprise and its practitioners for the benefit of Earth and its people."
- **1998** - "Twelve Principles of Green Chemistry" is published by Paul Anastas (of the EPA) and John Warner.
- **2000s-Present** - In the past decade, some major green chemistry achievements include the **California Green Chemistry Initiative**. Governor Arnold Schwarzenegger signed the bills to in 2008, which serve to develop policy options for green chemistry. Source: http://www.dtsc.ca.gov One year later, President Obama nominated Paul Anastas (of Yale) as head of Research and Development at the EPA.

Today and the Future

- After all of the research advancements in green chemistry and engineering, mainstream chemical businesses have not yet fully embraced the technology. Today, more than 98% of all organic chemicals are still derived from petroleum.
- Green chemists and engineers are working to take their research and innovations out of the lab and into the board room through the creation of viable industrial products that can be embraced by today's industry leaders.
- The ACS Green Chemistry Institute continues to be a clearing-house of information, connection, and research sharing through The Nexus Newsletter and Blog, the annual GC&E Conference, industrial roundtables, and a growing number of educational and research programs.

What is Green Chemistry?

Green chemistry, also called sustainable **chemistry**, 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.

The limitations of a command and control system for environmental protection have become more obvious even as the system has become more successful. In industrialized societies with good, well-enforced regulations, most of the easy and inexpensive measures that can be taken to reduce environmental pollution and exposure to harmful chemicals have been implemented. Therefore, small increases in environmental protection now require relatively large investments in money and effort. Is there a better way? There is, indeed. The better way is through the practice of green chemistry.

Green chemistry can be defined as the practice of chemical science and manufacturing in a manner that is sustainable, safe, and non-polluting and that consumes minimum amounts of materials and energy while producing little or no waste material. The practice of green chemistry begins with recognition that the production, processing, use, and eventual disposal of chemical products may cause harm when performed incorrectly. In accomplishing its objectives, green chemistry and green chemical engineering may modify or totally redesign chemical products and processes with the objective of minimizing wastes and the use or generation of particularly dangerous materials. Those who practice green chemistry recognize that they are responsible for any effects on the world that their chemicals or chemical processes may have. Far from being economically regressive and a drag on profits, green chemistry is about increasing profits and promoting innovation while protecting human health and the environment.

To a degree, we are still finding out what green chemistry is. That is because it is a rapidly evolving and developing subdiscipline in the field of chemistry. And it is a very exciting time for those who are practitioners of this developing science. Basically, green chemistry harnesses a vast body of chemical knowledge and applies it to the production, use, and ultimate disposal of chemicals in a way that minimizes consumption of materials, exposure of living organisms, including humans, to toxic substances, and damage to the environment. And it does so in a manner that is economically feasible and cost effective. In one sense, green chemistry is the most efficient possible practice of chemistry and the least costly when all of the costs of the practice of chemistry, including hazards and potential environmental damage are taken into account.

Green chemistry is sustainable chemistry. There are several important respects in which green chemistry is sustainable:

- Economic: At a high level of sophistication green chemistry normally costs less in strictly economic terms (to say nothing of environmental costs) than chemistry as it is normally practiced.
- Materials: By efficiently using materials, maximum recycling, and minimum use of virgin raw materials, green chemistry is sustainable with respect to materials.
- Waste: By reducing insofar as possible, or even totally eliminating their production, green chemistry is sustainable with respect to wastes.

Need for Green Chemistry:

There is increasing pressure from both society and governments for **chemistry**-based industries to become more sustainable through development of eco-friendly products and processes that both reduce waste and prevent toxic substances from entering the environment.

Goals of Green Chemistry:

Design synthetic methodologies that reduce or eliminate the use and or generation of toxic products All possible routes may be examined. Most appropriate route (without hazardous starting materials and or products) should be used. No chemical accidents. Eg: synthesis of Adipic acid Used for making nylon, PU, lubricants, plasticizers.

1. To reduce adverse environmental impact, try appropriate and innovative choice of material & their chemical transformation.
2. To develop processes based on renewable rather than non-renewable raw materials.
3. To develop processes those are less prone to obnoxious chemical release, fires & explosion.
4. To minimize by-products in chemical transformation by redesign of reactions & reaction sequences.
5. To develop products that is less toxic.
6. To develop products that degrades more rapidly in the environment than the current products.
7. To reduce the requirements for hazardous persistent solvents & extractants in chemical processes.
8. To improve energy efficiency by developing low temperature & low pressure processes using new catalysts.

9. To develop efficient & reliable methods to monitor the processes for better & improved controls.

ADVANTAGES OF GREEN TECHNOLOGY

- Does not emit anything harmful into the air
- Can bring economic benefits to certain areas.
- Requires less maintenance so you don’t have to shell out a lot of money to operate it
- Renewable this means we will never run out.
- Can slow the effects of global warming by reducing CO_2 emissions.

DISADVANTAGES TO ADOPTING GREEN TECHNOLOGIES

- High implementing costs.
- Lack of information.
- No known alternative chemical or raw material inputs
- No known alternative process technology
- Uncertainty about performance impacts
- Lack of human resources and skills

Principles of Green Chemistry

Green Chemistry aims to eliminate hazards right at the design stage. The practice of eliminating hazards from the beginning of the chemical design process has benefits for our health and the environment, throughout the design, production, use/reuse and disposal processes. Practitioners of Green Chemistry strive to protect the environment by cleaning up toxic waste sites and by inventing new chemical methods that do not pollute and that minimize the consumption of energy and natural resources. In 1998, two US chemists, Dr. Paul An astas and Dr John Warner outlined Twelve Principles of Green Chemistry to demonstrate how chemical production could respect human health and the environment while also being efficient and profitable. Guidelines for developing Green Chemistry technologies are summarized in the “***Twelve Principles of Green Chemistry***,” shown in the following.

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 sol ubility. 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 CO_2), 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 31^oC, 7280 kPa, or 72 atmospheres). Supercritical CO_2 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 CO_2 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 CO_2.

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 $AlCl_3$, 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 a shorter 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.

$$\underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} + KCN(aq) \longrightarrow \underset{\text{Benzyl cyanide}}{C_6H_5CH_2CN} + KCN$$

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,

$$C_6H_5CONHC_6H_5 \xrightarrow{\text{MW,12 mins}} C_6H_5COOH$$

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

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

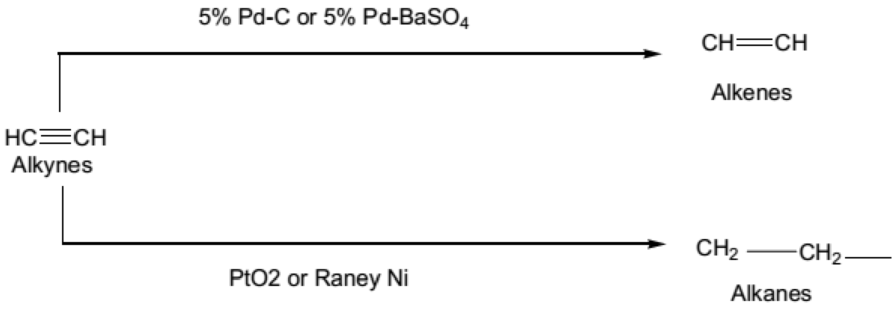
Non reversible or depleting sources can exhausted by their continual use. So these are not regarded as sustainable from environmental point of view. The starting materials which are obtained agricultural or biological processes are referred to as renewable starting materials. Substances like carbon dioxide (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 biogas and 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 presen t 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.

UNIT I

Possible Questions

PART A – Objective type questions (Each carry 1 mark)

1. Green chemistry aims to?

   a) Design chemical products and process that maximize profits

   b) Design safer chemical products and processes that reduce or eliminate the use and generation of hazardous substances

   c) Design chemical products and processes that work most efficiently

   d) Utilize non-renewable energy

2. In a reaction the auxiliary substance is

   a. Reactants b. Products c. catalyst d. **solvent**

3. Which among the following is a green solvent

   a. Chloroform b. Dichloromethane c. **water** carbon tetrachloride

4. Greener synthetic methods should be carried out under the condictions

   a. **Ambient temperature and Pressure** b. High temperature

   c. Low Temperature d. High pressure.

5. Green chemists reduce risk by?

   a. Reducing the hazard inherent in a chemical product or process

   b. Minimizing the use of all chemicals

   c. Inventing technologies that will clean up toxic sites

   d. Developing recycled products

6. Which is used in the Strecker synthesis

   a. **Formaldehyde** b. Diethanol amine c. DMC d. Potassium carbonate

7. The raw material used in the greener synthesis of Disodium iminoacetate

   a. Formaldehyde b. HCN c. Ammonia d. **Diethanolamine**

8. Which of the following is a challenge for green chemists?

   a. Awareness of the benefits of green chemistry

   b. Developing chemicals that are recyclable

   c. Training for cleaning up chemical spills

   d. Knowing when to reduce and eliminate hazardous waste

9. Which of the following is the greenest solvent?

   a. Formaldehyde b. Benzene c. Ethanol **d. Water**

10. In Friedel Crafts reaction, the greener catalyst used is

    a. **Zeolites** b. $AlCl_3$ c.CuO d. BF_3

11. The Neat reaction takes place

    a. **In the absence of solvent** b. In the absence of a solid support

    c. In the absence of a catalyst d. In presence of a solvent

12. Claisen Rearrangement is an example for

    a.**Neat Reaction** b. Solid supported reaction

    c. Microwave assisted reaction d. Ultrasound assisted reaction.

13. Benzene, a _______ substance, is an important industrial solvent used in the production of pharmaceuticals, plastics, and dyes?

    a. Odorless b. Non-flammable c. Biodegradable **d. Carcinogenic**

14. Which is used in the Strecker synthesis

    a. **Formaldehyde** b. Diethanol amine c. DMC d. Potassium carbonate

15. The raw material used in the greener synthesis of Disodium iminoacetate

    a. Formaldehyde b. HCN c. Ammonia d. **Diethanolamine**

16. Salicylaldehydes undergo Knoevenagel condensation with a variety of ethyl acetate derivatives under basic conditions to afford

    a. Coumarins b. Flavanoids c. Alkaloids d. Terpenes

PART B (Each carry 6 marks)

1. What do you mean by “Green Chemistry”? What are the main objectives of practising green chemistry?
2. Illustrate the atom economy with suitable examples.
3. Give the twelve principles of Green Chemistry.
4. What are the obstacles in the pursuit of the green chemistry?
5. Why catalytic reagents are superior to stoichiometric reagents? Explain.
6. Describe any three principles of green chemistry.
7. Explain the following principles of green chemistry

   (i) Prevention waste (ii) Safer synthesis and (iii) Safer chemicals
8. How do you prepare adipic acid from renewable and non-renewable sources? Illustrate with suitable example.
9. Why need of renewable feedstock rather than non-renewable feedstock? Give the explanations.

PART C (Each carry 10 marks)

1. What do you mean by the concept of atom economy? Illustrate with examples.
2. Explain the principles of green chemistry with suitable examples

UNIT I (Objective type questions)

	Option A	Option B	Option C	Option 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 green chemistry legislation promising to remove politics from the evaluation of disputed chemicals?	Oregon	California	Newyork	Florida	California
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 with plantation and overcoming greenhouse effect is	Biochemistry	Organic chemistry	Environmental chemistry	Inorganic chemistry	Environmental chemistry
Our bodies cannot produce	minerals	proteins	vitamins	carbohydrates	vitamins
Maximum amount of ozone (O_3) 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 (O_3) has	unpleasant odor	pleasant odor	no odor	orange color	unpleasant odor
Amount of Nitrogen (N_2) 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 (CH_4N_2O) 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 process that maximize 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
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 could also involve which of the following?	High temperature	Dichloromethane	Fossil fuels	Microwave	Microwave
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	CO_2 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	O_3	CH_4	H_2O 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 from the dehydration of ethanol can best be described as	an addition reaction	an elimination reaction	an oxidation reaction	a substitution reaction	an elimination 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

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, ionicliquids, fluorous biphasic solvent, PEG, solvent less processes, immobilized solvents and how to compare greenness of solvents.

Introduction:

Green chemistry for chemical synthesis addresses our future challenges in working with chemical processes and products by inventing novel reactions that can maximize the desired products and minimize by-products, designing new synthetic schemes and apparati that can simplify operations in chemical productions, and seeking greener solvents that are inherently environmentally and ecologically benign.

Over the past two centuries, fundamental theories and reactivities in chemistry have been soundly established. Such theories and reactivities have provided the foundations for the chemical enterprise that generates critical living needs such as food for the world's population, achieves various medical wonders that save millions of lives and improve people's health, and produces materials essential to the present and future needs of mankind. Just less than two centuries ago, organic compounds were believed to be only accessible through biological processes under the influence of “vital forces”. Today, many molecules of great complexity can be synthesized readily. The total syntheses of natural products with extremely high complexity such as vitamin B_{12} and palytoxin in the laboratory are testimonials of achievements comparable to the construction of the great pyramids at the molecular scale. However, despite such enormous achievements, we are facing great challenges in future chemical synthesis. The present state-of-the-art processes for synthesizing chemical products are highly inefficient. The concept of atom economy was created to emphasize the importance of this inefficiency. The E factor provided a quantifiable measure of such inefficiency and showed that, for every kilogram of fine chemical and pharmaceutical products produced, 5–100 times that amount of chemical waste is generated.

Such low efficiency in state-of-the-art organic syntheses presents great challenges in resource conservation and draws environmental and health concerns related to the chemical wastes.

Since its birth over a decade ago the field of Green Chemistry has been specifically designed to meet such challenges in chemical synthesis. To address these challenges, innovative and fundamentally novel chemistry is needed throughout the synthetic processes: feedstocks, reactions, solvents, and separations.

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

Prevention of waste Our production and consumption lead to large quantities of waste. An important element in work on eco-cycles is therefore sustainable waste management. Articles that circulate in society contain large quantities of different materials. Many are energy-demanding to produce and contain substances that exist in limited quantities. It is therefore necessary that we manage joint resources in a long-term manner to achieve sustainable cycles in society. Many articles additionally contain substances that are toxic or hazardous and should not be released into the environment. This necessitates phasing out the most harmful substances and handling correctly those substances that continue to be used. There is a eco-cycle strategy in Sweden linked to the Swedish environmental objectives. The strategy is aimed at bringing about a society with non-toxic and resource-efficient cycles. This includes prevention of waste, changed patterns of consumption, more efficient production methods and waste management with a greater focus on recycling. The natural cycle strategy looks at materials and products throughout their lifecycle in order to provide as complete a picture as possible of their environmental impact. Consumption of energy for a product also has to be weighed into the assessment. Sweden considers it necessary for the volume of waste to decrease if we are to come close to sustainable management of waste. Producers must already take account of a product's environmental impact in a lifecycle perspective when it is manufactured. Design and material selection, as well as energy consumption in manufacturing and use must be taken into account. In addition, sustainable cycles can only be achieved if a greater proportion of waste can be reused and recycled. This saves both materials and energy, while also reducing the use of hazardous chemicals and environmental problems in waste management.

By-product is a substance or object, resulting from a production process, the primary aim of which is not the production of that item. By-products can come from a wide range of business sectors, and can have very different environmental impacts. An incorrect classification could be the cause of environmental damage or unnecessary costs for business.

Waste minimisation is a process of elimination that involves reducing the amount of waste produced in society and helps to eliminate the generation of harmful and persistent wastes, supporting the efforts to promote a more sustainable society. Waste minimisation involves redesigning products and/or changing societal patterns, concerning consumption and production, of waste generation, to prevent the creation of waste.

The most environmentally resourceful, economically efficient, and cost effective way to manage waste is to not have to address the problem in the first place. Waste minimisation should be seen as a primary focus for most waste management strategies. Proper waste management can require a significant amount of time and resources; therefore, it is important to understand the benefits of waste minimisation and how it can be implemented in all sectors of the economy, in an effective, safe and sustainable manner.

The basic concept behind waste management is the waste hierarchy, where the most effective approaches to managing waste are at the top. Waste management is in contrast to waste minimisation. Waste management focuses on processing waste after it is created, concentrating on re-use, recycling, and waste-to-energy conversion rather than eliminating the creation of waste in the initial phases of production. Waste minimisation involves efforts to minimize resource and energy use during manufacture. For the same commercial output, usually the less material are used, the less waste is produced. Waste minimisation usually requires knowledge of the production process, cradle-to-grave analysis (the tracking of materials from their extraction to their return to earth) and detailed knowledge of the composition of the waste.

The main sources of waste vary from country to country. In the UK, most waste comes from the construction and demolition of buildings, followed by mining and quarrying, industry and commerce. Household waste constitutes a relatively small proportion of all waste. Reasons for the creation of waste sometimes include requirements in the supply chain. For example, a company handling a product may insist that it should be packaged using particular packing because it fits its packaging equipment.

ATOM ECONOMY

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

The second principle of green chemistry can be simply stated as the “atom economy” of a reaction. Atom economy, which was developed by Barry Trost1, asks the question “what atoms of the reactants are incorporated into the final desired product(s) and what atoms are wasted?”

Definition of the fundamental difference in the manner in which the reaction and the atom economy yields are generated

$$\text{Reaction Yield} = \frac{\text{quantity of product isolated}}{\text{theoretical quantity of product}} \times 100\%$$

$$\text{Atom Economy} = \frac{\text{molecular wt. of desired product}}{\text{molecular weight of all products}} \times 100\%$$

The reaction yield is only concerned with the quantity of the desired product that is isolated, relative to the theoretical quantity of the product. Atom economy takes all used reagents and unwanted side products into account along with the desired product. For example, substitutions and eliminations represent the vast majority of uneconomical classical reactions in which inherent wastes are unavoidable.

ATOM ECONOMY: A Measure of the Efficiency of a Reaction

Efficiency of a Reaction

Percentage Yield

Although the efficiency of a reaction can be measured in many ways, by far the most common way is to calculate the yield (percentage yield). Students are often required, especially in laboratory, to determine the theoretical yield based upon the limiting reagent and then to calculate the percentage yield based upon the ratio of the actual yield/theoretical yield X 100. In general organic chemists consider yields of 90% or better as excellent while 20% or less are poor.

Theoretical yield = (moles of limiting reagent)(stoichiometric ratio; desired product/limiting reagent)(MW of desired product)

Percentage yield= (actual yield/theoretical yield) X 100

In order to illustrate the calculation of the percentage yield (and the measurement of the efficiency of a reaction) consider the following acid promoted nucleophilic substitution reaction. A typical procedure[1] for this reaction begins with dissolving

Equation1

$$\underset{(1)}{CH_3CH_2CH_2CH_2OH} + \underset{(2)}{NaBr} + \underset{(3)}{H_2SO_4} \longrightarrow \underset{(4)}{CH_3CH_2CH_2CH_2Br} + \underset{(5)}{NaHSO_4} + \underset{(6)}{H_2O}$$

Table 1: Reagents

Reagent	MW	Weight Used (g)	Moles Used	Theoretical Moles Needed	Density	Bp (^oC)
(1) C_4H_9OH	74.12	0.80	0.0108	0.0108	0.810	118
(**2**) NaBr	102.91	1.33	0.0129	0.0108		
(**3**) H_2SO_4	98.08	2.0	0.0200	0.0108	1.84	

Table 2 **Desired Product Table**

Compound	MW	Theoretical Yield (Moles)	Theoretical Yield (Grams)	Actual Yield (Grams)	% Yield	Density	Bp (^oC)
(**4**) C_4H_9Br	137.03	0.011	1.48 (100%)	1.20	81	1.275	101.6

1.33 g of sodium bromide (**2**) in 1.5 mL of water, followed by addition of 0.80 mL of 1-butanol (**1**) and 1.1 mL (2.0 g) of concentrated sulfuric acid (**3**). The following Reagents Table (Table 1) and Desired Product Table (Table 2) can then be setup. Dividing the weight of each reactant that is used, by the molecular weight of the reactant, gives the number of moles of each reagent used. From the stoichiometry of the reaction (Equation 1a) it is clear that one mole of each reactant is required to produce one mole of product (1-bromobutane) and since 1-butanol (0.0108 mole) is used in the smallest amount it is the limiting reagent. Calculation of the (as shown below) theoretical yield of 1-bromobutane gives 1.48 g. This means that using the

Theoretical yield =

=(moles of limiting reagent)(stoichiometric ratio; desired product /limiting reagent)(MW of desired product)

= (moles of 1-butanol)(stoichiometric ratio; 1-bromobutane/1-butanol)(MW of 1-bromobutane)

=(0.0180 mole)(1 mole / 1 mole)(137.03 g/mole)=1.48g

above quantities of reagents the maximum amount (assuming 100% yield) of 1-bromobutane that can be produced is 1.48 g. In fact no reaction ever proceeds with 100% yield due to such factors as the formation of side products, incomplete conversion of the starting materials, loss upon workup of the reaction mixture, and loss upon isolation and purification of the desired product. This reaction typically produces actual yields of 1-1.2 g. Assuming that the actual yield is 1.20 g calculation of the % yield is as follows. Thus 81% of the theoretical yield is actually isolated, which is a very respectable yield, that would please most chemists.

Percentage yield = (actual yield/theoretical yield) X 100

= (1.20 g/1.48 g) X 100 = 81%

Atom Economy in Rearrangement Reactions

The acid (H^+) used in this reaction is not incorporated into the desired product it is used only in catalytic amounts and therefore indicated in black (not green or brown) and it is not considered in the **atom economy** table or the **calculation** of the **atom economy**.

Rearrangement reactions involve reorganization of the atoms of a molecule. Because neither elimination, addition or substitution of atoms is taking place, in the molecule undergoing rearrangement, the atom economy of rearrangement reactions is 100% and they are environmentally preferable reactions from an atom economy standpoint. To illustrate this, consider the acid catalyzed rearrangement of 3,3-dimethyl-1-butene (12) to 2,3-dimethyl-2-butene (13). In this case the atoms of the reactant 12 are all shown in green since they are all incorporated into the desired product 13. As in the previous examples one can set up an atom economy table and calculate the % atom economy. Although the acid (H^+) used in this reaction is not incorporated into the desired product it is used only in catalytic amounts and therefore indicated in black (not green or brown) and it is not considered in the atom economy table or the calculation of the atom economy. As was predicted above for rearrangements, the % atom economy of this reaction is 100%.

Equation 2

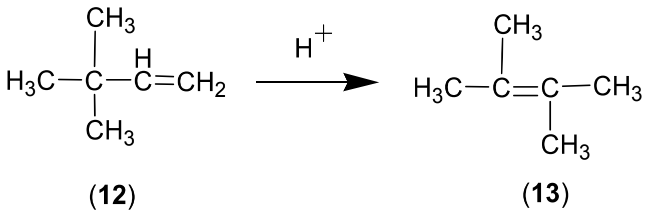


Table 3 Atom Economy Equation 2

Reagents Formula	Reagents FW	Utilized Atoms	Weight of Utilized Atoms	Unutilized Atoms	Weight of Unutilized Atoms
(**12**) C_6H_{12}	84	6C,12H	84	—	0
Total 6C,12H	84	6C,12H	84	—	0

% Atom Economy = (FW of atoms utilized/FW of all reactants) X 100

= (84/84) X 100 = 100%

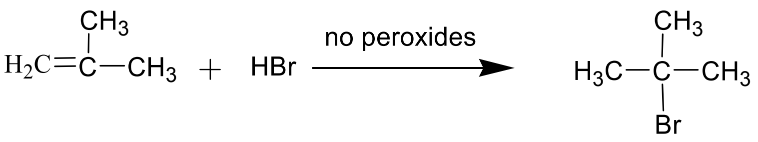
Virtually all organic reactions fall into the categories of substitution, addition, elimination or rearrangement reactions. From the perspective of atom economy, addition and rearrangement reactions are environmentally preferable, with substitution reactions next, while eliminations are the least environmentally preferable. As one encounters reactions, in the study of chemistry, one should examine each reaction from the point of not only the yield, but also the atom economy of the reaction.

Atom Economy in Addition Reactions

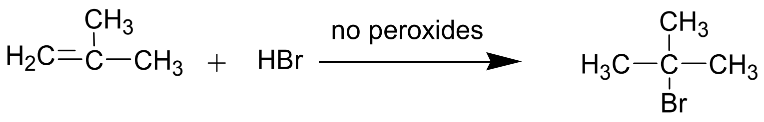
The addition reactions in general lead to the incorporation of all the **atoms** of the reactants into the final desired products, **addition reactions** result in high **atom economy**.

Because addition reactions in general lead to the incorporation of all the atoms of the reactants into the final desired products, addition reactions result in high atom economy. From an atom economy point of view, addition reactions are thus environmentally preferable to elimination and substitution reactions. As a case in point consider the following addition of hydrogen bromide to methyl propene. In this example all the atoms of the reactants (9 and 11) are shown in green since all of these atoms are utilized in the final desired product (7). The table of atom economy (Table 4) and the calculation of 100% atom economy further emphasize the excellent atom economy of this reaction.

Equation 3



Equation 4



(9) (11) (7)

Reagents Formula	Reagents FW	Utilized Atoms	Weight of Utilized Atoms	Unutilized Atoms	Weight of Unutilized Atoms
(9) C_4H_8	56	4C,8H	56	—	0
(11) HBr	81	HBr	81	—	0
Total 4C,9H,Br	137	4C,9H,Br	137	—	0

Table 4 Atom Economy Equation 3

% Atom Economy = (FW of atoms utilized/FW of all reactants) X 100
= (137/137) X 100 = 100%

Atom Economy In A Substitution Reaction

Atom Economy in Rearrangement **Reactions**. Because neither elimination, addition or **substitution** of **atoms** is taking place, in the molecule undergoing rearrangement, the **atom economy** of rearrangement **reactions** is 100% and they are environmentally preferable **reactions** from an **atom economy** standpoint.

As indicated previously most chemists have traditionally measured the efficiency of a reaction by the percentage yield, however this only tells part of the story. If one considers the above reaction where a total of 4.13 g of reactants (0.8 g of 1-butanol, 1.33 g of NaBr and 2.0 g of H_2SO_4) was used, and that at best this reaction will only yield 1.48 g of the desired product, the question might be asked "what happens to the bulk (4.13 g -1.48 g = *2.7 g*) of the mass of reactants?". The answer is they end up in side products ($NaHSO_4$ and H_2O) that may be unwanted, unused, toxic and/or not recycled/reused. The side products are oftentimes treated as wastes and must be disposed of or otherwise treated. At best only 36% (1.48 g/4.13 g X 100) of the mass of the reactants end up in the desired product. If the actual yield is 81% then only 29% (.81 X .36 X 100) of the mass of the reactants actually ends up in the desired product!

In an effort to foster awareness of the atoms of reactants that are incorporated into the desired product and those that are wasted (incorporated into undesired products), Barry Trost developed the concept of ***atom economy***. In 1998 Trost was awarded a Presidential Green Chemistry Challenge Award for the concept of atom economy. In light of the concept of atom economy, the above acid promoted nucleophilic substitution must now be reconsidered. In Equation 1 we have illustrated the atom economy of this reaction by showing all of the reactant atoms that are incorporated into the desired product in green,

Equation 4

$$\underset{1}{CH_3CH_2CH_2CH_2OH} + \underset{2}{Na\,Br} + \underset{3}{H_2SO_4} \longrightarrow \underset{4}{CH_3CH_2CH_2CH_2Br} + \underset{5}{NaHSO_4} + \underset{6}{H_2O}$$

while those that are wasted are shown in brown. Likewise the atoms of the desired product are in green and the atoms composing the unwanted products are in brown. Table 3 provides another view of the atom economy of this reaction. In columns 1 and 2 of this table, the formulas and formula weights (FW) of the reactants are listed. Shown in green (columns 3 and 4) are the atoms and weights of the atoms of the reactants that are incorporated into the desired product (4), and shown in brown (columns 5 and 6) are the atoms and weights of atoms of the reactants that end up in unwanted side products. Focusing on the last row of this table it can be seen that of all the atoms of the reactants (4C, 12H, 5O, 1Br, 1Na and 1S) only 4C, 9H, and 1Br are utilized in the desired product and the bulk (3H, 5O, 1Na, 1S) are wasted as components of unwanted products. This is an example of poor atom economy! A logical extension of Trost's concept of atom economy is to calculate

Table 5 Atom Economy of equation 4

Reagents Formula	Reagents FW	Utilized Atoms	Weight of Utilized Atoms	Unutilized Atoms	Weight of Unutilized Atoms
1 C_4H_9OH	74	4C,9H	57	HO	17
2 NaBr	103	Br	80	Na	23
3 H_2SO_4	98	——	0	2H,4O,S	98
Total 4C,12H,5O,BrNaS	275	4C,9H,Br	137	3H,5O,Na,S	138

The percentage atom economy: This can be done by taking the ratio of the mass of the utilized atoms (137) to the total mass of the atoms of all the reactants (275) and multiplying by 100. As shown below this reaction has only 50% atom economy.

% Atom Economy = (FW of atoms utilized/FW of all reactants) X 100
= (137/275) X 100 = 50%

Thus at best (if the reaction produced 100% yield) then only half of the mass of the reactants would be incorporated into the desired product while the rest would be wasted in unwanted side products.

Atom Economy In Elimination Reactions

Atom Economy in Rearrangement **Reactions**. Because neither **elimination**, addition or substitution of **atoms** is taking place, in the molecule undergoing rearrangement, the **atom economy** of rearrangement **reactions** is 100% and they are environmentally preferable **reactions** from an **atom economy** standpoint.

In all of the remaining discussions of the efficiency of a reaction, the discussion will be limited to the atom economy based on the stoichiometry of the reaction. When one encounters these reactions in the laboratory it may also be prudent to calculate the atom economy based on the quantities of the reagents used (experimental atom economy). In addition one may also want to consider matters such as toxicity, energy use, the use of auxiliary substances, catalytic versus stoichiometric reagents and renewable versus nonrenewable feedstocks.

In the substitution reaction above (Equation 1a) it was revealed that the poor atom economy resulted from the fact that the atoms of the leaving group (OH) that is being replaced, the counterion (sodium) of our nucleophile (bromide), and the sulfuric acid that is required for this reaction all are wasted in forming unwanted products in this reaction. By virtue of the fact that elimination reactions require only the loss of atoms (while gaining none) from the reactant, means that elimination reactions are in general even worse, in terms of their atom economy, than substitution reactions.

As an example consider the atoms of the following elimination reaction. Base promoted dehydrohalogenation of alkyl halides is a common method of producing alkenes from alkyl halides via elimination. In Equation 2 the formation of methyl propene is accomplished by the reaction of 2-bromo-2-methylpropane (7) with sodium ethoxide (8). In this reaction, the atoms of the reactants that are incorporated into the desired product (9) and the atoms of the desired product are indicated in green, while the unutilized atoms of the reactants are shown in brown as are the atoms in the unwanted products of the reaction. Table 6 illustrates the atom economy of this reaction and calculation of the % atom economy gives a very poor 27%. The poor atom

Equation 5

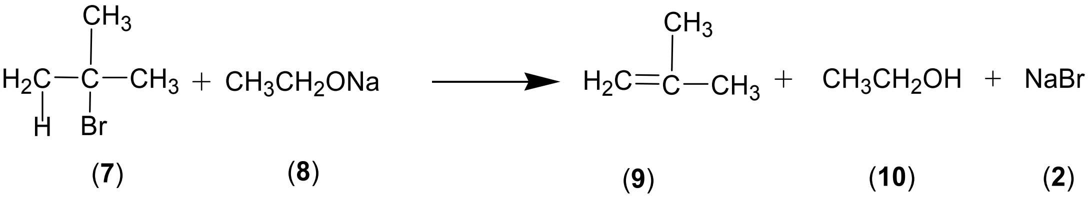


Table 6 Atom Economy Equation 5

Reagents Formula	Reagents FW	Utilized Atoms	Weight of Utilized Atoms	Unutilized Atoms	Weight of Unutilized Atoms
(7) C_4H_9Br	137	4C,8H	56	HBr	81
(8) C_2H_5ONa	68	—	0	2C,5H,O,Na	68
Total 6C,14H,O,Br,Na	205	4C,8H	56	2C,6H,O,Br,Na	149

% Atom Economy = (FW of atoms utilized/FW of all reactants) X 100

= (56/205) X 100 = 27%

economy is a result not only of the loss of the HBr but also because this is a base promoted reaction and all of the atoms of the sodium ethoxide base are found in unwanted side products.

Green solvents are environmentally friendly **solvents** or bio-solvents, which are derived from the processing of agricultural crops. The uses of petrochemical solvents are the key to the majority of chemical processes but not without severe implications on the environment.

What are Green Solvents?

Green solvents are environmentally friendly solvents or bio-solvents, which are derived from the processing of agricultural crops.

Organic Synthesis in Water

Although water is considered a problem for organic synthesis and the purification processes and drying in final products is very cumbersome, in recent years water is considered a good solvent for organic reactions. A good example is the synthetic routes of the Diels-Alder reactions in which the hydrophobic properties of some reagents makes water an ideal solvent. Water as a solvent accelerates some reactions because some reagents are not soluble and provides selectivity. The low solubility of Oxygen is also an advantage for some reactions where metal catalysts are used. In the last years water is used in many methods for organic reactions.

A **supercritical fluid** (SCF) is any substance at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist. It can effuse through solids like a gas, and dissolve materials like a liquid.

In general terms, supercritical fluids have properties between those of a gas and a liquid. In Table 1, the critical properties are shown for some components, which are commonly used as supercritical fluids.

Table 1. Crticial properties of various solvents

Solvents	Molecular mass	Critical temperature	Critical pressure	Critical density

	g/mol	K	MPa (atm)	g/cm^3
Carbon di oxide	44.01	304.1	7.38	0.469
Water	18.015	647.096	22.064	0.322
Methane	16.04	190.4	4.60	0.162
Ethane	30.07	305.3	4.87	0.203
Propane	44.09	369.8	5.04	0.215
Propylene	42.08	364.90	4.60	0.232
Methanol	32.04	512.6	8.09	0.272
Ethanol	46.07	513.9	4.70	0.278
Nitrous oxide	44.013	306.57	7.35	0.452

Table 2 shows density, diffusivity and viscosity for typical liquids, gases and supercritical fluids.

Table 2 Comparision of gases, supercritical fluids and liquids

	Density (kg/m^3)	Viscosity (μPa.S)	Dissusivity (mm^2/s)
Gases	1	10	1-10
Supercritical fluids	100-1000	50-100	0.01-0.1
Liquids	1000	500-1000	0.001

In addition, there is no surface tension in a supercritical fluid, as there is no liquid/gas phase boundary. By changing the pressure and temperature of the fluid, the properties can be "tuned" to be more liquid-like or more gas-like. One of the most important properties is the solubility of material in the fluid. Solubility in a supercritical fluid tends to increase with density of the fluid (at constant temperature). Since density increases with pressure, solubility tends to increase with pressure. The relationship with temperature is a little more complicated. At constant density, solubility will increase with temperature. However, close to the critical point, the density can drop sharply with a slight increase in temperature. Therefore, close to the critical temperature, solubility often drops with increasing temperature, then rises again.

All supercritical fluids are completely miscible with each other so for a mixture a single phase can be guaranteed if the critical point of the mixture is exceeded. The critical point of a binary mixture can be estimated as the arithmetic mean of the critical temperatures and pressures of the two components,

$$T_{c(\text{mix})} = (\text{mole fraction } A) \times T_cA + (\text{mole fraction } B) \times T_cB.$$

For greater accuracy, the critical point can be calculated using equations of state, such as the Peng Robinson, or group contribution methods. Other properties, such as density, can also be calculated using equations of state.

Supercritical carbon dioxide and supercritical water A supercritical liquid is at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist. The supercritical liquid can effuse through solids like a gas, and dissolve materials like a liquid. In addition, close to the critical point, small changes in pressure or temperature result in large changes in density, allowing many properties of a supercritical fluid to be "fine-tuned". Supercritical liquids are suiTable as a substitute for organic solvents in a range of industrial and laboratory processes. Carbon dioxide and water are the most commonly used supercritical fluids. Supercritical CO_2 and water are considered “green” solvents in many industrial processes, providing high yields in many reactions, and there are many examples of their use in the scientific literature.

Water as a solvent for organic reactions

Despite the fact that it is the cheapest, safest and most non toxic **solvent** in the world, its presence is generally avoided through the dehydrative drying of substrates and **solvents**.

The use of **water** as a medium for **organic reactions** is therefore one of the latest challenges for modern **organic** chemists.

Organic Synthesis in Water

Although water is considered a problem for organic synthesis and the purification processes and drying in final products is very cumbersome, in recent years water is considered a good solvent for organic reactions. A good example is the synthetic routes of the Diels-Alder reactions in which the hydrophobic properties of some reagents makes water an ideal solvent. Water as a solvent accelerates some reactions because some reagent are not soluble and provides selectivity. The low solubility of Oxygen is also an advantage for some reactions where metal catalysts are used. In the last years water is used in many methods for organic reactions Water plays an essential role in life processes, however its use as a solvent has been limited in organic synthesis. Despite the fact that it is the cheapest, safest and most non toxic solvent in the world, its presence is generally avoided through the dehydrative drying of substrates and solvents.

1. Oxidations
2. Dehydrogenation, Hydrogenation, Halogenation and Dehalogenation
3. Allylations
4. Coupling of Acyl Chlorides and Alkynes
5. Heck Reaction
6. Wittig Reaction
7. Mannich-type Reactions
8. Intramolecular Diels-Alder Reaction
9. Deprotection of Functional Groups
10. Acetates, Alkyl Ethers and Acetals

IONIC LIQUIDS

An ionic liquid (IL) is a salt in the liquid state. In some contexts, the term has been restricted to salts whose melting point is below some arbitrary temperature, such as 100 °C (212 °F). While ordinary liquids such as water and gasoline are predominantly made of electrically neutral molecules, ionic liquids are largely made of ions and short-lived ion pairs. These substances are variously called liquid electrolytes, ionic melts, ionic fluids, fused salts, liquid salts, or ionic glasses. They are known as "solvents of the future" as well as "designer solvents".

Ionic liquids are described as having many potential applications. They are powerful solvents and electrically conducting fluids (electrolytes). Salts that are liquid at near-ambient temperature are important for electric battery applications, and have been considered as sealants due to their very low vapor pressure.

Any salt that melts without decomposing or vaporizing usually yields an ionic liquid. Sodium chloride (NaCl), for example, melts at 801 °C (1,474 °F) into a liquid that consists largely of sodium cations ($Na+$) and chloride anions ($Cl−$). Conversely, when an ionic liquid is cooled, it often forms an ionic solid—which may be either crystalline or glassy.

The ionic bond is usually stronger than the Van der Waals forces between the molecules of ordinary liquids. For that reason, common salts tend to melt at higher temperatures than other solid molecules. Some salts are liquid at or below room temperature. Examples include compounds based on the 1-Ethyl-3-methylimidazolium (EMIM) cation and include: EMIM:Cl, EMIM dicyanamide, $(C_2H_5)(CH_3)C_3H_3N+2·N(CN)−2$, that melts at −21 °C (−6 °F);[4] and 1-butyl-3,5-dimethylpyridinium bromide which becomes a glass below −24 °C (−11 °F).

Low-temperature ionic liquids can be compared to ionic solutions, liquids that contain both ions and neutral molecules, and in particular to the so-called deep eutectic solvents, mixtures of ionic and non-ionic solid substances which have much lower melting points than the pure compounds. Certain mixtures of nitrate salts can have melting points below 100 °C.

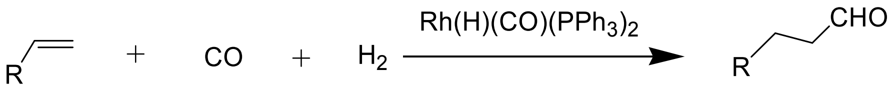
Fluorous biphasic solvent:

Fluorous chemistry involves the use of perfluorinated compounds or perfluorinated substituents to facilitate recovery of a catalyst or reaction product. Perfluorinated groups impart unique physical properties including high solubility in perfluorinated solvents.

Fully fluorinated solvents (e.g. C_6F_{14}) are non-polar and immiscible with organic solvents. Ideal if reactants are non-polar, but products are polar:

Example:

Hydroformylation:



PEG (polyethylene glycol):

In recent years, polyethylene glycol (PEG) has attracted special attention as a green and inexpensive solvent in various chemical transformations. The current critical review deals with breakthrough achievements for the applications of PEG as an alternative reaction media for well-known coupling reactions such as Suzuki, Heck, Stille, Sonogashira, Hiyama and some challenging organic reactions for carbon–carbon bond formation.

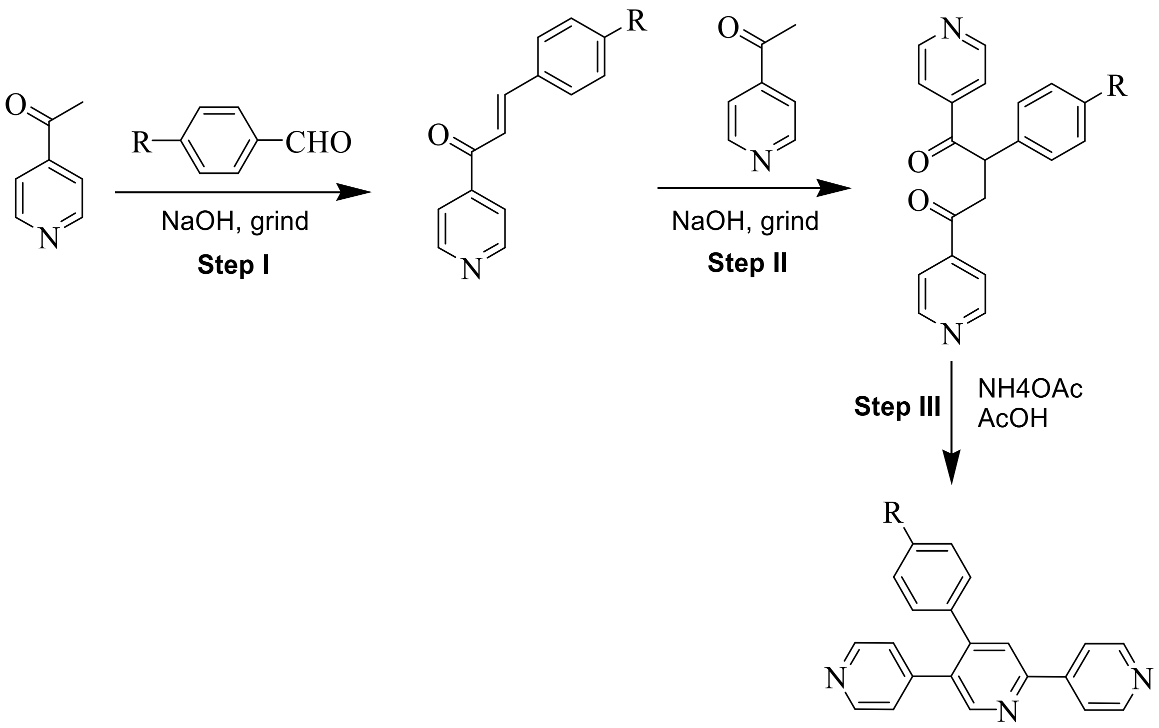
Polyethylene glycol (PEG) is an eco-friendly solvent.

- Various metal-catalyzed carbon–carbon bond formation reactions can conduct in PEG
- Reactions have excellent compatibility in both thermal and microwave irradiations
- Reactions have excellent compatibility in both thermal and microwave irradiations

Solvent less process

The toxicity and volatile nature of many organic solvents, particularly chlorinated hydrocarbons that are widely used in huge amounts for organic reactions have posed a serious threat to the environment. Thus, design of solvent less catalytic reaction has received tremendous attention in recent times in the area of green synthesis. 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 to achieve high degree of stereo selectivity in the products, to reduce by-products, to maximize rate of reaction. We illustrate the environmentally benign approach to 1,2-Oxazine-2- oxides, Michael addition, Wohl–Ziegler reaction, Acylation, Heck reaction, Tishchenko reaction, Diels–Alder reaction, Reformatsky and Luche Reaction, Oxidative coupling Reaction, Synthesis of chalcones, Synthesis of Dihydropyrimidinones and etc.

Example for solvent free synthesis process:



Step 1: Aldol condensation reaction - no solvent required

Step 2: Michael Addition reaction - no solvent required

Step 3: The only stage that requires solvent, but no purification of the dione precursor is required

- Both steps 1 and 2 are fast and quantitative, (in EtOH, yields of both steps are 50%)

Advantages

- Energy-efficient because Process reduces primary energy consumption by over 75%, compared with conventional Process
- Environmentally friendly because it eliminates the need to use hazardous organic solvents
- Likely to result in new tackifier products made with a mixture of resins having different melting points and different solubility properties
- Cost-effective because it allows adhesives to be made in a single step
- Adaptable because process can be used with commercially available equipment, yielding further cost savings
- Could open new markets for manufacturers of tackifiers or resins because dry, pulverized resins can be shipped instead of emulsions
- Faster than conventional processes

Disadvantages of solvent-free syntheses:

- Solvents are often still required during work-up (e.g. extraction)

- Poor heat transfer in the solid state (although this may be overcome using microwaves)

UNIT II

Possible Questions

PART A – Objective type questions (Each carry 1 mark)

1. Benzyl alcohols are selectively oxidized to carbonyl compounds using

   a. 35%MnO_2 doped silica b. 35%MnO_2 doped alumina

   c. 95%MnO_2 doped silica d. 55%MnO_2 doped alumina

2. In Friedel Crafts reaction, the greener catalyst used is

   a. **Zeolites** b. $AlCl_3$ c. CuO d. BF_3

3. The Neat reaction takes place

   a. In the absence of solvent b. In the absence of a solid support

   c. In the absence of a catalyst d. In presence of a solvent

4. Claisen Rearrangement is an example for

   a. Neat Reaction b. Solid supported reaction

   c. Microwave assisted reaction d. Ultrasound assisted reaction.

5. In the conventional method for the preparation of ibuprofen, the atom economy is

   a. 10% b. 77% c. 50% d. **40%**

6. Example for a anti-inflammatory drug is

   a. **Ibuprofen** b. MMA c. DMC d. DMS

7. Microwave radiation is selectively absorbed by the

   a. Non polar molecules b. **Polar Molecules**

   c. Asymmetric molecules d. Crystalline substances

8. The safer reagent for methylation is

   a. Methyl iodide b. Dimethyl sulfate **c. Dimethyl carbonate** d. Methyl bromide

9. Methyl methacrylate is widely used as

   a. **Monomer** b. drug c. pesticide d. catalyst

10. In a reaction the auxiliary substance is

    a. Reactants b. Products c. catalyst d. s**olvent**

11. In the greener method for the preparation of ibuprofen, the atom economy is

    a. 10% b. **77%** c. 50% d. 40%

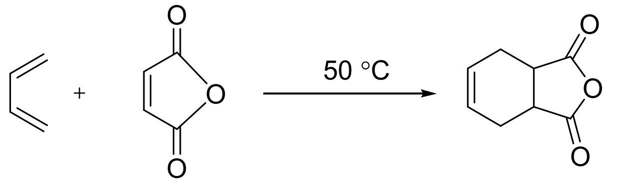
12. Microwave radiation is selectively absorbed by the

    a. Non polar molecules b. **Polar Molecules**

    c. Asymmetric molecules d. Crystalline substances

PART B (Each carry 6 marks)

1. What are ionic liquids? Explain advantage of ionic liquids in synthesis? Write the synthesis of some the common ionic liquids by giving specific example.
2. Describe the atom economy of rearrangement and substitution reactions
3. With suitable examples show that the atom economy of addition reactions are more than elimination reactions.
4. Illustrate the solvent less reactions with the suitable examples.
5. Explain about 100% atom economy reactions with examples.
6. What are green solvents? Explain why water is considered as green solvents
7. What are the different types of ionic liquids? Illustrate with an example the synthesis in presence of an ionic liquid.
8. Calculate the atom economy of addition and elimination reactions.
9. Calculate the atom economy of the following reactions

i) 

ii) $(CH_3)_3C\text{-}Br \xrightarrow{EtONa} (CH_3)_3C{=}CH_2 + C_2H_5OH + NaOH$

10. Explain the term water as solvent by giving suitable examples.

PART C (Each carry 10 marks)

1. What do you mean by the concept of atom economy? Illustrate with examples.
2. What are the different types of ionic liquids? Illustrate with an example the synthesis in presence of an ionic liquid.

UNIT II (Objective type questions)

	Option A	**Option B**	**Option C**	**Option 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 methylation is	Methyl iodide	Dimethyl sulfate	Dimethyl carbonate	Methyl bromide	Dimethyl 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 melting point?	Low molecular weight	No ionic bonding	High lattice energy	Large ions and shape mismatch between them	Large ions and 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 should be carried out under the conditions	Ambient temperature and Pressure	High temperature	Low Temperature	High pressure.	Ambient temperature and Pressure

UNIT III

ENERGY REQUIREMENTS FOR REACTIONS

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 (Ultrasonic alternative to iodine).

Introduction

Consider now what happens at the molecular level when a reaction takes place. Bonds between the atoms in the reacting molecules break, and new bonds form to combine the atoms in a different way. For this reaction to occur, the reacting molecules must collide. Together they must have enough kinetic energy (energy of motion) to overcome the repulsion between the clouds of electrons that surround the molecules. As they collide, the two reacting molecules must be oriented so that those atoms that will be bonded together in the product are next to each other. Without this molecular orientation, the molecules will retreat from the collision without reacting. A collision that takes place with enough energy and with the correct molecular orientation is called an effective collision. Needless to say, not all collisions are effective.

Alternative energy sources for reactions

Running reactions can be energy intensive. When chemists boil a reaction, they simultaneously cool the solvent vapours .The resulting droplets fall into the reaction so that the reaction never runs dry .But this standard process requires energy to both heat and cool the reaction, in addition to the water being constantly run through a condenser.

Therefore, some green chemists look to new energy sources to drive reactions. Microwave assisted reactions can be run in water at a small scale, often with accelerated rates due to temperature and pressure effects .Reactions to build oxygen-, nitrogen- or sulfur-containing rings common in medicinal chemistry can also be driven using microwaves, though these reactions aren’t running on a process scale yet. Alternatively, the energy from grinding reagents together using a mortar and pestle or a ball grinder can be enough to trigger a reaction.

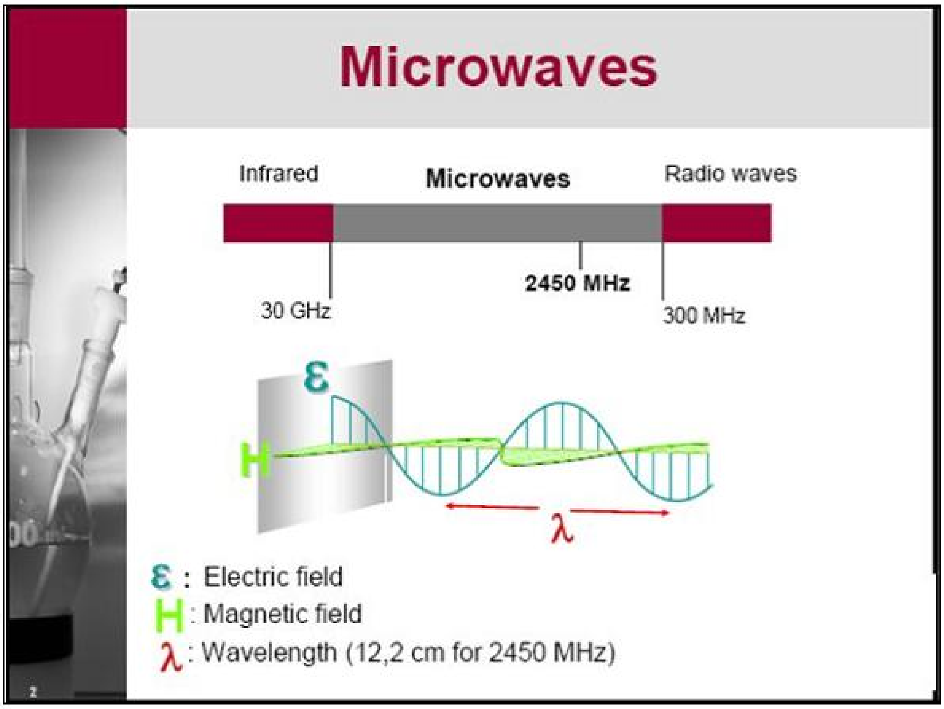
Ultrasound sonication is another energy source with useful applications such as deprotecting an amine, protecting hydroxyls on sugars, or reducing an α,β-unsaturated ketone in a steroid. The sound waves create areas of high and low pressure, much like ripples in a pond, as they travel through liquid .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.

Microwave Chemistry

Microwave chemistry involves the use of microwave radiation to conduct chemical reactions, and essentially pertains to chemical analysis and chemical synthesis. Microwave radiation has been successfully applied to numerous industrial applications (drying, heating, sintering, etc.).

This section provides a basic overview of microwave chemistry. It starts with an insight into the scientific principle governing the function of microwave radiation and its use in chemical analysis and synthesis. It also discusses the mechanism of microwave heating and provides a background to the evolution of microwave chemistry, enumerating its benefits and limitations, while briefly delving into the controversy pertaining to the ‘microwave effect’.

Microwaves lie in the electromagnetic spectrum between infrared waves and radio waves. They have wavelengths between 0.01 and 1 metre, and operate in a frequency range between 0.3 and 30 GHz. However, for their use in laboratory reactions, a frequency of 2.45 GHz is preferred, since this frequency has the right penetration depth for laboratory reaction conditions. Beyond 30 GHz, the microwave frequency range overlaps with the radio frequency range.



Microwaves

Infrared
Microwaves
Radio waves
30 GHz
2450 MHz
300 MHz
ε
H
λ

ε : Electric field
H : Magnetic field
λ : Wavelength (12,2 cm for 2450 MHz)

Fig. Range of frequencies of electromagnetic radiation

Use of microwaves energy:

1. Compared to conventional heating, microwave heating enhances the rate of certain chemical reactions by 10 to 1,000 times
2. Heating by means of microwave radiation is a highly efficient process and results in significant energy saving
3. In certain chemical reactions, microwave radiation produces higher yields compared to conventional heating methods, for example, micro wave synthesis of fluoresce in results in an increase in the yield of the reaction, from 70% to 82%.
4. Microwave radiation, unlike conventional heating methods, provides uniform heating throughout a reaction mixture.
5. Selective heating is based on the principle that different materials respond differently to microwaves.
6. Reactions conducted through microwaves are cleaner and more environmentally friendly than conventional heating methods.
7. Reactions with microwave heating are more reproducible compared to conventional heating because of uniform heating and better control of process parameters.

Ultrasonic energy

Sonication is the act of applying sound energy to agitate particles in a sample, for various purposes. Ultrasonic frequencies (>20 kHz) are usually used, leading to the process also being known as ultrasonication or ultra-sonication.

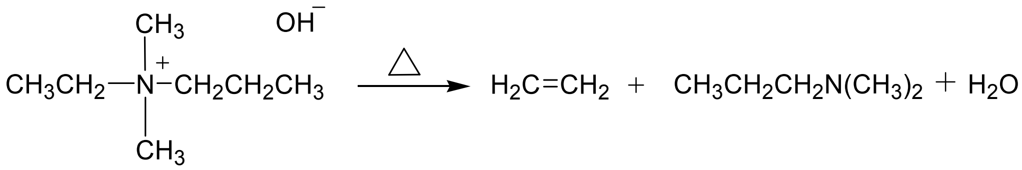
The chemical effects of ultrasound derive primarily from acoustic cavitation. Bubble collapse in liquids results in an enormous concentration of energy from the conversion of the kinetic energy of the liquid motion into heating of the contents of the bubble. The high local temperatures and pressures, combined with extraordinarily rapid cooling, provide a unique means for driving chemical reactions under extreme conditions. A diverse set of applications of ultrasound to enhance chemical reactivity has been explored with important uses in synthetic materials chemistry.

The ever increasing awareness of the need to protect natural resources through the development of environmentally sustainable processes and the optimization of energy consumption has guided the actions of both the private and governmental sectors of society. Economic planning has been strongly impacted by this new paradigm, which has led to increasing demands by society for products produced in a sustainable way and to more stringent governmental regulatory policies. Thus, while in the past profit was often the major concern, in the current economic context more sustainable production processes are preferred. This has triggered a demand in both industry and academy for the development of new, cleaner technologies.

In the field of chemistry and chemical technology, the 12 principles of Green Chemistry provide a set of clear guidelines for the development of new synthetic methodologies and chemical processes and for the evaluation of their potential for environmental impact. As a consequence, in organic chemistry, numerous investigations now routinely use non-tradicional synthetic methodologies such as solvent-free reactions, the application of alternative activation techniques like microwaves or ultrasound, the replacement of volatile organic solvents by water, ionic liquids, or supercritical CO_2, etc.

Hofmann elimination

Hofmann elimination reaction used to synthesis the olefins from quaternary ammonium hydroxides.

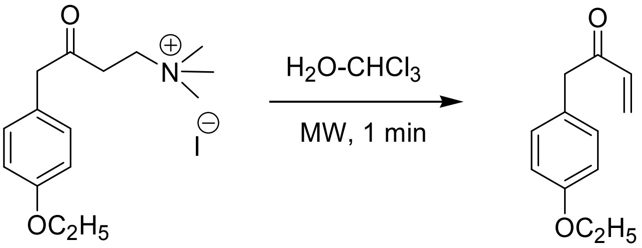


$$CH_3CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{\overset{+}{N}}}-CH_2CH_2CH_3\ \ OH^- \xrightarrow{\triangle} H_2C{=}CH_2 + CH_3CH_2CH_2N(CH_3)_2 + H_2O$$

This reaction results in the formation of a double bond between α-carbon and β-carbon atom.

Hofmann elimination under Microwave Irradiation

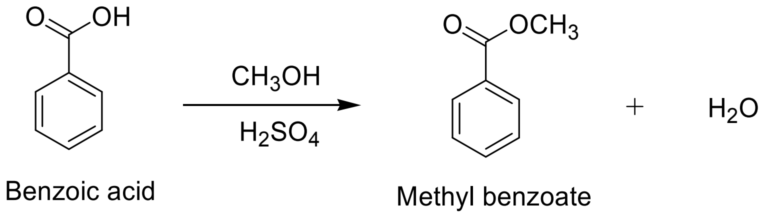
On microwave irradiation reactions carried out in water-chloroform mixture solvent, the quaternary ammonium salts converted into an olefin compound.



From the microwave irradiation reaction, the yields are twice than those obtained by traditional methods.

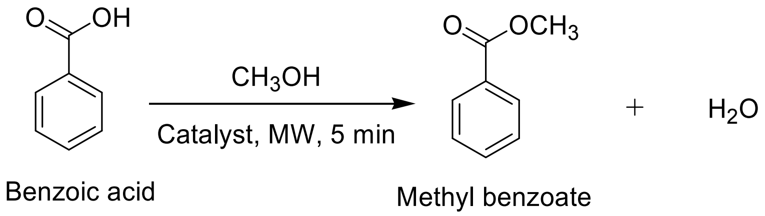
Methyl benzoate to benzoic acid

Esters can be prepared by the reaction of a carboxylic acid with an alcohol in the presence of a catalyst such as concentrated sulfuric acid (or) hydrogen chloride (or) p-toluenesulfonic acid.



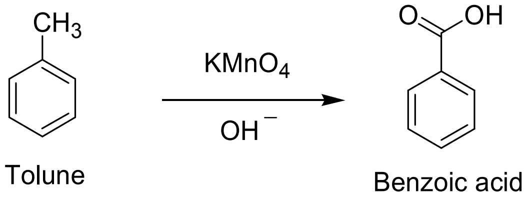
Microwave synthesis of Methyl benzoate

Benzoic acid, dry alcohol and the catalyst (0.5g) were mixed in a glass tube with a loosely held stopper. The reaction was performed in the microwave oven at an engaged power of 360 W in an alumina bath and reaction time of 5 min. The alcohol was removed using a vacuum evaporator. Compared with traditional method more yield obtained.



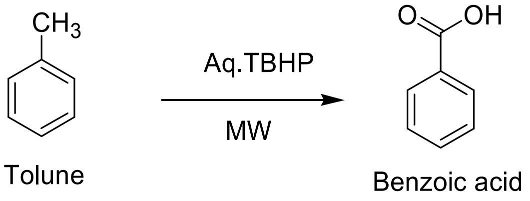
Oxidation of Toluene

Basic conditions are preferred for the oxidation of aromatic alkyl side chains by potassium permanganate. $KMnO_4$ is the extremely powerful oxidizing species involved in this reaction and this ion is stable in basic solutions.



Oxidation of Toluene in microwave condition

The microwave-assisted (MW) solvent-free oxidation of toluene was carried out. the reaction mixture was closed, placed in the microwave reactor and maintained under stirring and under irradiation (5–10W), at 30–100°C for 15–120 min. Finally, the crude product of benzoic acid obtained.



Aq.TBHP = tert-Butyl hydroperoxide solution
Metal and solvent free reaction

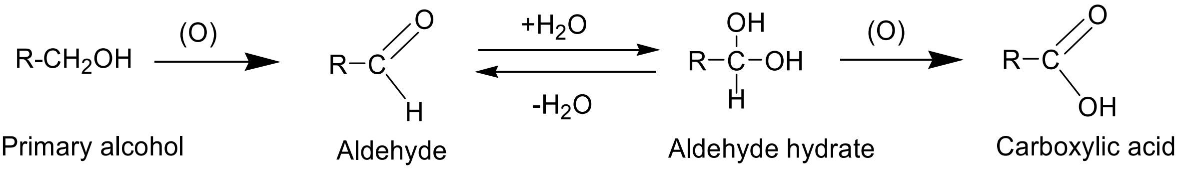
Oxidation of alcohols

Alcohol oxidation is an important organic reaction. Primary alcohols (R-CH_2-OH) can be oxidized either to aldehydes (R-CHO) or to carboxylic acids (R-COOH), while the oxidation of secondary alcohols (R_1R_2CH-OH) normally terminates at the ketone ($R_1R_2C=O$) stage. Tertiary alcohols ($R_1R_2R_3$C-OH) are resistant to oxidation.

The indirect oxidation of primary alcohols to carboxylic acids normally proceeds via the corresponding aldehyde, which is transformed via an **aldehyde hydrate** (R-CH$(OH)_2$) by reaction with water .The oxidation of a primary alcohol at the aldehyde level is possible by performing the reaction in absence of water, so that no aldehyde hydrate can be formed.

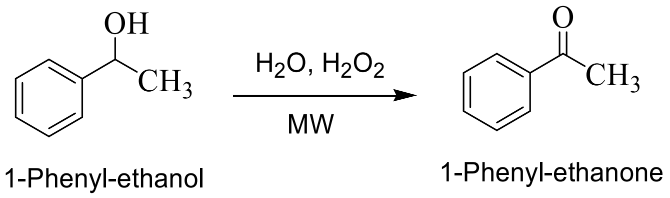
Primary alcohols

Primary alcohols can be oxidised to either aldehydes or carboxylic acids depending on the reaction conditions. In the case of the formation of carboxylic acids, the alcohol is first oxidised to an aldehyde which is then oxidised further to the acid.



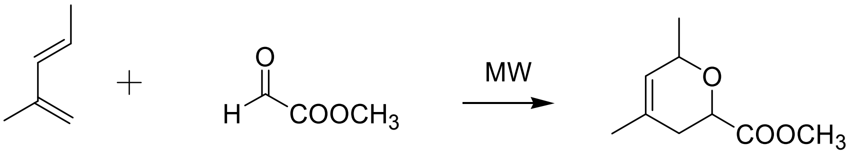
Secondary alcohols

Secondary alcohols are oxidised to ketones.



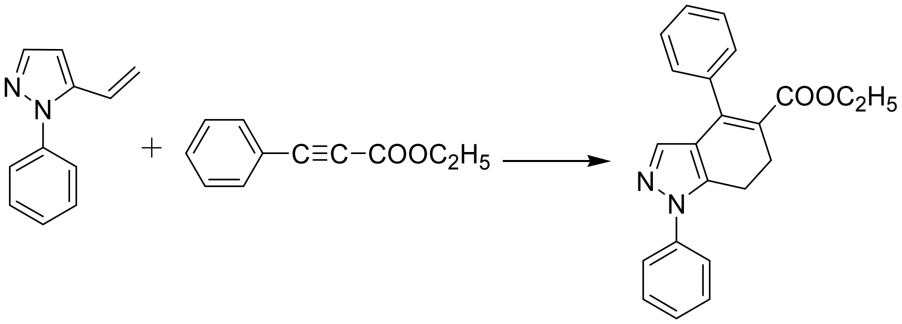
Microwave assisted Diels-Alder reaction

Diels-Alder reactions were carried out methylgloxylate in water at 140ºC gives 82% adduct product obtained after 3 hours. Whereas, microwave irradiation reactions reduce the reactions time to 8 minutes.



Solvent: H_2O, Time: 8 min, Yield: 80
Solvent: No Solvent, Time: 10 min, Yield: 96

The microwave assisted cycloaddition of pyrazole with the poorly reactive dienophile ethylphenyl-propiolate is significant, under the classical thermal reaction conditions (140˚C, 6 days) only polymerization or decomposition product were obtained.



Reaction conditions	Product (Yield %)
140˚C, 6 days	0
MW, 180˚C, 15 min	19

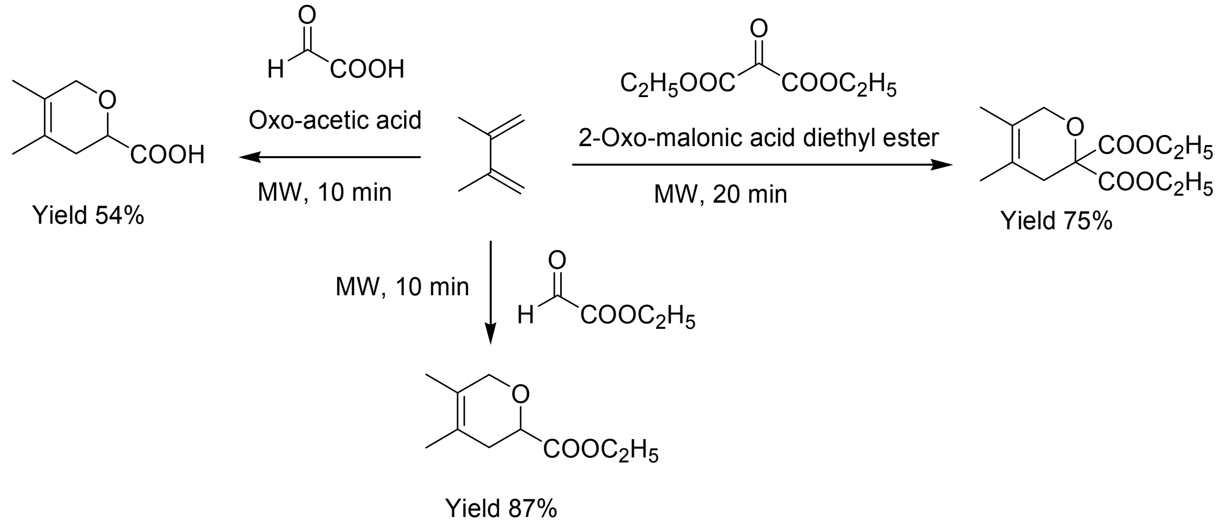
Advantage and Disadvantage of Microwaves

Advantages

- Rapid reactions
- High purity of products Less side-products
- Improved yields Simplified and improved synthetic procedure
- Wider usable range of temperature
- Higher energy efficiency
- Sophisticated measurement and safety technology
- Modular systems enable changing from mg to kg scale.

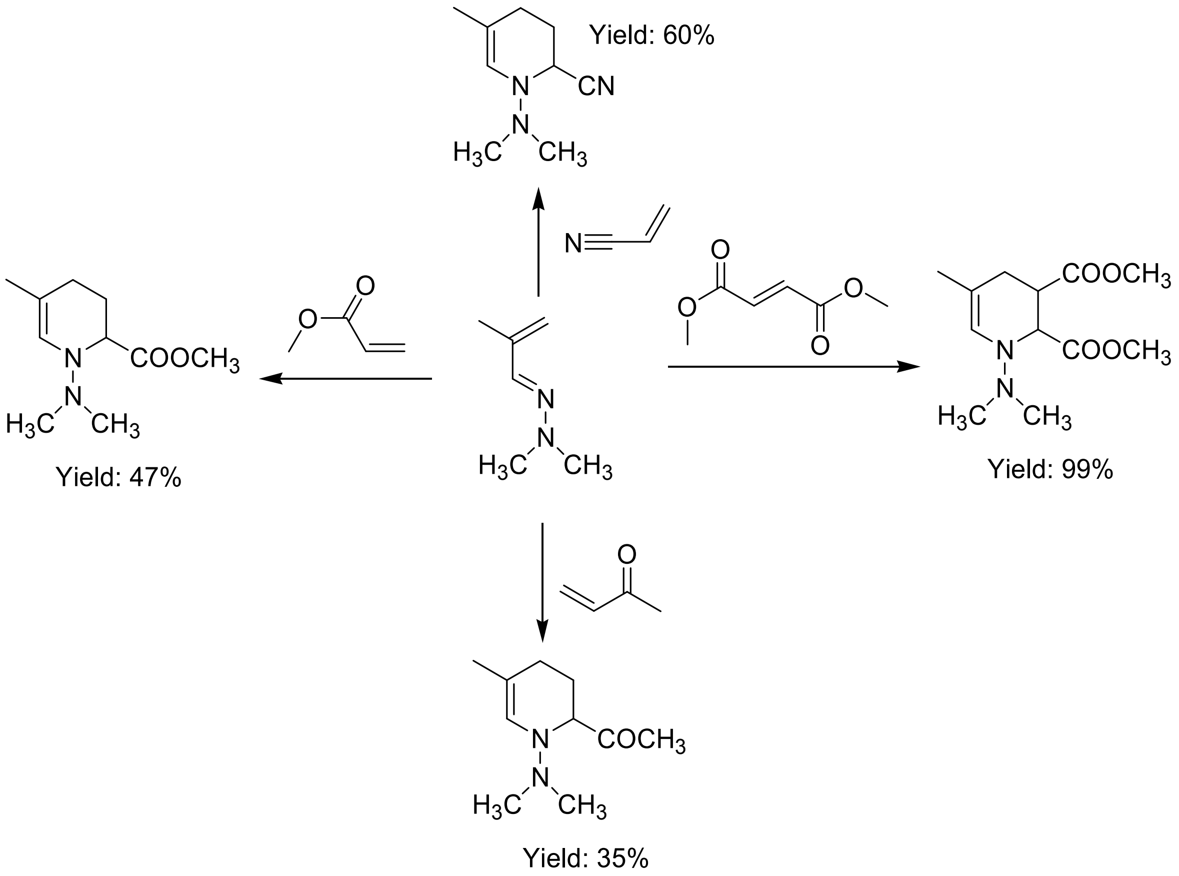
Disadvantages

- Heat force control is difficult
- Water evaporation
- Closed container is dangerous because it could be burst

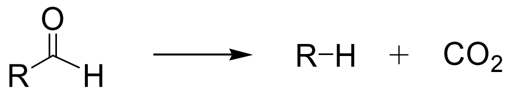


Ultrasound-Assisted Diels-alder reactions

Sonication of Diels-Alder reactions of 1-dimethylamino-3-methyl-azadiene with electron-deficient dienohiles by using diene as solvent or in acetonitrile. Ultrasound irradiation which allows mild reaction condition gave good yields.



Decarboxylation reaction



$$RCHO \longrightarrow R{-}H + CO_2$$

UNIT I

Possible Questions

PART A – Objective type questions (Each carry 1 mark)

1. In the greener synthesis of ibuprofen which is not used as a catalyst

   a. HF b. Raney Ni c. Pd d. Aluminium chloride

2. Which is not a tool of green chemistry

   a. Auxillary substances b. renewable feed stock

   c.High atom economy d. **Energy saves**

3. Which of the following are among the 12 principles of green chemistry?

   a. Design commercially viable products b. Use only new solvents

   c. Usecatalysts,not stoichiometric reagents d.Re-use waste

4. Green chemistry synthesis could also involve which of the following?

   a. High temperature b. Dicholoromethane **c. microwave oven** d. fossil fuels

5. Which among the following is a green solvent?

   a.Chloroform b. Dichloromethane **c.water** d. carbon tetrachloride

6. Greener synthetic methods should be carried out under the condictions

   a. **Ambient temperature and Pressure** b. High temperature

   c. Low Temperature d. High pressure.

7. An example for a renewable resource

   a. Crude oil b. Petroleum c. Disel d. **Biomass**

8. Which of the following are among the 12 principles of green chemistry?

   a. Design commercially viable products b. Use only new solvents

   c. Use **catalysts but not stoichiometric reagents** d.Re-use waste

9. For methylation reaction the greener alternative is

   a. Methyl halides b. Dimethyl sulfate c. **Dimethyl carbonate** d. Methyl oxalate

10. Example for green oxidants

    a. Oxygen and hydrogen peroxides b. chromates c. permanganates d. ethers

11. In the conventional method for the preparation of ibuprofen, the atom economy is

    a. 10% b. 77% c. 50% d. **40%**

12. Example for a anti-inflammatory drug is

    a. Ibuprofen b. MMA c. DMC d. DMS

13. Example for green oxidants

    a. oxygen and hydrogen peroxides b. chromates

    c. permanganates d. ethers

PART B (Each carry 6 marks)

1. How will you carried out Simmons-Smith reaction under sonification. Give the important applications.
2. Explain the microwave reactions in organic solvents.
3. Explain the Diels-Alder reactions under microwave irradiation.
4. Describe the oxidation reactions of toluene and alcohol.
5. What are the advantages of ultrasound synthesis?
6. What is polyethylene glycol? Give the Suzuki coupling reaction in polyethylene glycol.
7. Write Diels alder reaction on the basis of microwave and ultra sound assisted synthesis.
8. Illustrate the Hoffmann elimination reaction.
9. Microwave heating is more efficient than ordinary heating-explain.
10. Explain the principles of sonochemistry. Write any three of the important ultrasonic promoted synthesis.

Part C

1. Give the detailed account on Diels-Alder reactions under microwave and ultra sonification methods.
2. Compare and contrast the conventional and greener synthesis of Ibuprofen. What are the major advantages in this greener synthesis?

UNIT III (Objective type questions)

	Option A	**Option B**	**Option C**	**Option D**	**Answer**
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
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 preferred over other methods of	Cyclopropanation	cyclopentation	cycloheptane	cyclobutane	Cyclopropanation
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 glycol	supercritical water	dimethyl sulphaoxide	dimethyl 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
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).

Green synthesis definition:

"Green Chemistry is the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products."

Synthesis of a substance without badly affects the environment. Green chemistry aims at carrying out a traditional synthesis procedure or a new procedure following the principles of green chemistry. Use green solvent (water) instead of organic solvent, minimise waste and hazardous products, utilise waste etc.

Green starting materials

Polysaccharides polymers: polymers are a very important class of compounds that have broad applications and a wide array of compounds can be exploited. They have their hazardous effects. In order to use starting materials more environmentally we must use polysaccharides as the feedstock. These are biological feedstock, and as such have the advantage of being renewable, as opposed to those feedstocks which are the product of petroleum. On the other hand these have no chronic toxicity to human health and environment.

Commodity chemicals from glucose: glucose is another alternative for commodity chemicals. Using biotechnological techniques to manipulate the schkimic acid pathway (responsible for making aromatic compounds), compounds such as hydroquinone, catechol, and adipic acid, all of which are important, can be synthesized. Benzene is the starting material for these substances, by using glucose in place of benzene, can help in minimizing the use of certain reagents with certain toxicity. The conduction of synthesis in water instead of organic solvents is more beneficial

Green reagents:

- Green oxidative transmission complexes: many oxidative processes have negative ecological consequences. The metal ion contamination can be minimized by using molecular oxygen as the primary oxidant. Many ligands which are stable towards oxidative decomposition in oxidizing environments have been developed. Now, stable high oxidation state transition metal complexes can be synthesized.
- Liquid oxidation reactor: it allows safe oxidation of organic chemicals with pure oxygen. The amount of vent gas has been reduced because of use of oxygen. The use of can make reaction to occur at low temperature is beneficial.
- Non phosgene isocynate synthesis: polyurethanes are important polymers that are widely used for variety applications. These are generally prepared with the help of phosgene. But phosgene is an extremely toxic gas whose acute end point is lethality. A method of synthesis is developed in which poly-urethanes and their isocynate precursors are synthesized without using phosgene.

Green solvents:

"Green solvents are environmentally friendly solvents or bio-solvents, which are derived from the processing of agricultural crops. The uses of petrochemical solvents are the key to the majority of chemical processes but not without severe implications on the environment".

Green solvent research in academic labs is targeted at finding new solvents. Scientists also develop applications for interesting liquids like water, supercritical carbon dioxide (CO_2), and ionic liquids. Water is often not thought of as a potential solvent for organic reactions, because many reagents are water-sensitive or insoluble in water. But some reactions, like an aqueous Diels-Alder reaction between cyclopentadiene and butanone, run faster in water than in organic solvents like methanol. Often the rate enhancement is due to hydrophobic effects and hydrogen bonds that stabilize transition states. Running a reaction in water makes it possible to use enzyme catalysts as well.

A 2007 analysis of green solvents that includes life cycle impacts ranks water and supercritical CO_2 as promising green alternatives to traditional organic solvents. Many chemicals do not dissolve in these solvents, but the researchers write that that fact is "more than counterbalanced" by the ease of handling and separating these solvents, as well as their low environmental impact.

Supercritical CO_2 has properties between that of a gas and a liquid. It's commonly used as a dry cleaning solvent or to extract caffeine from coffee beans. Scientists can control what compounds dissolve in the supercritical fluid by adjusting its density to tune its polarity. The volatility of CO_2 means that the supercritical fluid is easily removed after a reaction.

Ionic liquids are mentioned in almost half of the green solvent research published in Green Chemistry in 2010. The structure of positive and negative ions in these liquid salts control solubility and guide a reaction. Ionic liquids work as solvents for a variety of reactions, and they can be designed to catalyze reactions too. While ionic liquids might be interesting substances from the perspective of basic research, their potential utility in industry is unclear due to as-yet-to-be-determined disposal protocols on a large scale.

The amount of research into various green solvents doesn't match predicted needs for solvents to reduce environmental damage, writes Philip Jessop of Queen's University in Canada, in a 2011 perspective in Green Chemistry. While Jessop supports basic research into solvents, he asks his colleagues to consider their research topics carefully if they wish to reduce solvent caused environmental damage.

Of course, the best way to reduce solvent use is to not use solvents in the first place. It's often thought that a solvent is needed to increase catalyst efficiency or improve the enantioselectivity of a catalyzed reaction .Some asymmetric reactions, however, can be run just by mixing the reagents together.

The need for alternative solvents:

- Play a major role in many areas of technology
- Provide many opportunities for improvement of environmental aspects.
- Represent a very large proportion of the volatile organic compounds (VOCs) released into the atmosphere.
- UK solvents market - £4,000 million p.a.
- £1,000 million spent on environmental technology, much of which is end of pipe equipment and associated operating costs to clean up emissions and air.

Alternative Solvents for Synthesis

Widely used throughout the chemical industry

- ❖ Synthetic Chemistry
  - ➢ Reaction medium on laboratory and industrial scale
  - ➢ Extensively used in work-up and purification (usually more than for reaction medium)

- Analytical Chemistry
  - Sample extraction and preparation (Spectroscopy)
  - Chromatography mobile phase (HPLC, TLC etc.)
- Crystallisation
  - Recrystallisation to purify compounds and prepare crystals suitable for analysis

Green solvent and reaction conditions:

- ***Super critical fluids***: The use of CO_2 as a substitute for organic solvent already represents a tool of waste reduction in chemical industry. Of the wide range of supercritical carbon dioxide reactions that have been explored, one class of reaction has shown exceptional promise; it was found that asymmetric catalytic reactions, particularly hydrogenation and hydrogen transfer reactions can be carried out in supercritical carbon dioxide with selectivity compared or superior to those observed in conventional solvents.
- ***Immobilized solvents***: With solvents being of extremely high volume and very broad breadth of applicability, their potential for negative impact on human health and the environment is very large. Therefore, the immobilization of such solvents helps in reduction of hazards. Immobilized solvents or solvent molecules tethered to a polymeric backbone follow the same logic as the ionic liquids. By creating a system where a known solvent, e.g., THF, is tethered properly, it can still maintain its solvency but is incapable of manifesting any hazard by exposing humans or the environment. These types of solvents are expensive and difficult to handle.
- aqueous reaction conditions
- Irradiative reaction conditions.

Green catalysis:

It is not only the "green" solvents that will change the face of synthetic organic reactions, but also the use of "green catalysts" will improve substantially the efficiency of many industrial processes. The use of catalysts is one of the principles of Green Chemistry. Catalysis is considered a cornerstone for innovative changes in chemical processes. Catalysts will affect energy use and reaction time, will increase yield, reduce use of solvents, and lower production of by-products and waste. Catalysis with "green" catalysts (which can be recycled) is considered a very important step in the direction of Green Chemistry for many industrial processes.

Recently, growing attention is being directed towards the development of innovative catalytic systems with high performance from the point of environmentally greener processes, economical efficiency and minimum consumption of resources. The application of catalysis to reduce toxicity and renewable energy systems, and efficiency makes it a central focus area for green chemistry research.

Green Catalysis is a subtitle of green chemistry but the most important one and one of the urgently needed challenges facing engineers now is the design and use of environmentally benign catalysts. Green and sustainable catalyst should possess, higher activity, higher selectivity, efficient recovery from reaction medium, durability or recyclability, cost effectiveness.

In recent years the development of catalysts for processes to replace conventional ones has made a significant contribution to the reduction of environmental pollutants. Thus, there is an increasing interest on the topic of green catalysis recently. It not only includes developing new catalysts which can offer stable, highly effective catalytic performances, but considers the application of environmentally friendly catalyst preparations.

Enzymes are commonly used as catalysts in industry, particularly pharmaceuticals, because they work at ambient temperatures and pressures in water. That makes them safe to handle on a process scale. One example is the three-step enzymatic route to the key chiral building block used to make the active ingredient in the cholesterol-lowering drug Lipitor. The process won enzyme company Codex is an EPA Presidential Green Chemistry Challenge Award in 2006 .Previous routes to the key intermediate involved separating enantiomers in the first step (at 50% maximum yield) and a final step plagued with byproducts. The enzymatic process gives the desired intermediate in a greater than 90% isolated yield. The overall process has an E-factor about five times smaller than a typical pharmaceutical designed with green chemistry principles.

But in practice, biocatalysts are not necessarily “greener” than chemical catalysts .A streamlined LCA comparing a metal catalyst to an enzymatic reduction of a keto-ester revealed that some of the processes and reaction conditions most impacted the analysis. Including bioprocesses in LCA would help the pharmaceutical industry evaluate these catalysts.

Applications for enzymes can be found outside of the pharmaceutical industry, too. In 2012, a chemical company, Buckman International, won an EPA Presidential Green Chemistry Challenge Award for using enzymes to create stronger paper without added wood pulp or chemical additives .The enzymes connect the fibers of cellulose within the paper, resulting in a stronger end product .The enzymes also allow for increased production. Combined with energy reductions, the new process saves the company an estimated $1 million per year.

Green Synthesis:

"**Green Chemistry** is the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products"

Ibuprofen synthesis

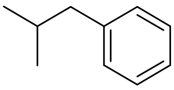
An elegant example of a process with high atom efficiency is provided by the manufacture of the over-the-counter, non-steroidal anti-inflammatory drug, ibuprofen. Two routes for the production of ibuprofen via the common intermediate, p-isobutyl acetophenone, are compared. The UK market for over-the-counter pain-killers (for headache, toothache, muscular aches, period pain etc) is worth about 300 million per year. In the UK, all such medicines are formulated from just four active ingredients-aspirin, paracetamol, codeine and ibuprofen. These may be sold separately under their own names, as a branded product (Aspro, Panadol, Nurofen etc), or as combined preparations containing two or more of these ingredients (Veganin contains aspirin, codeine and paracetamol, for example). Ibuprofen is the most recent addition to this list. It was patented by the Boots Company in the 1960s and became available without prescription in the UK in the mid-1980s. The skeletal formula of ibuprofen is given below.

Ibuprofen uses:

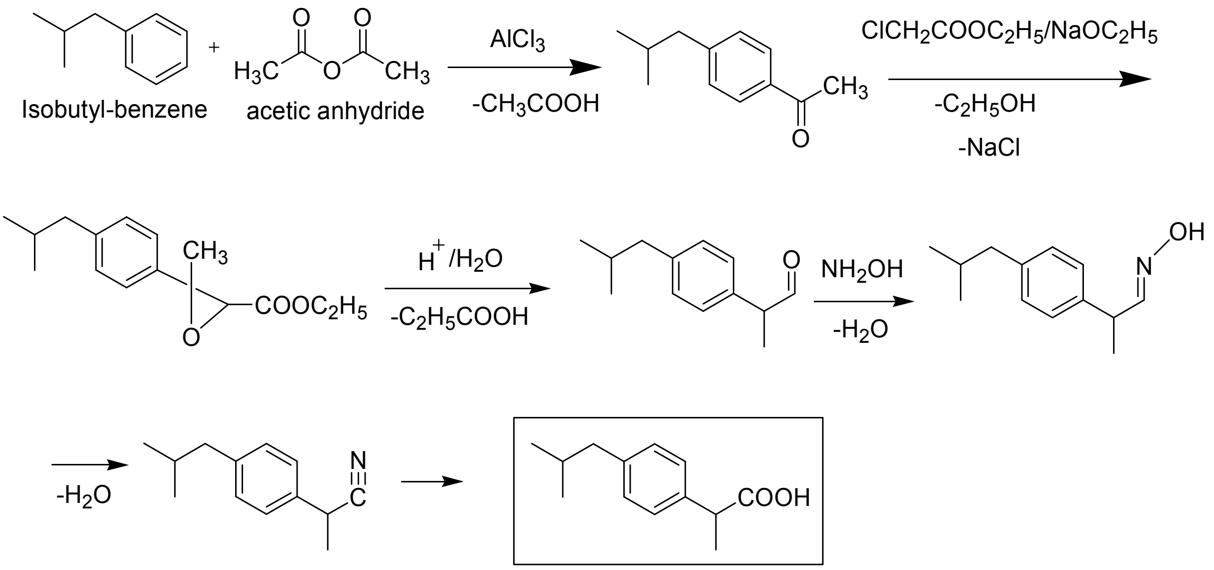
Ibuprofen is used to relieve pain from various conditions such as headache, dental pain, menstrual cramps, muscle aches, or arthritis. It is also used to reduce fever and to relieve minor aches and pain due to the common cold or flu. Ibuprofen is a nonsteroidal anti-inflammatory drug (NSAID)

Boots' synthesis of ibuprofen

Boots' method of making ibuprofen described in their patent starts from the compound 2-methylpropylbenzene that can be made from compounds separated from crude oil. This compound has a similar carbon skeleton to that of ibuprofen



2-methypropyl benzene



2-(4-Isobutyl-phenyl)-propionic acid

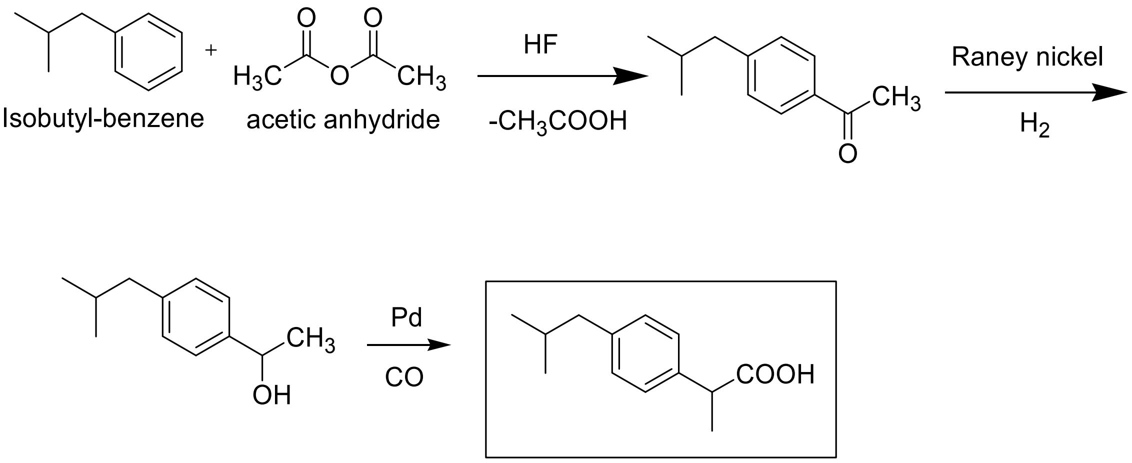
(Ibuprofen)

Atom economy = 40%

The overall figure is 40%. This means that more than half the materials used in the synthesis are wasted. Since the UK market for ibuprofen is about 3000 tonnes (3000 000 kg) per year this is an awful lot of waste

Green synthesis of ibuprofen

The ibuprofen patent ran out in the mid-1980s. Prior to that, only Boots had the right to make and sell the drug. The patent system protects the interests of companies that develop drugs, and allows them to sell patented drugs exclusively, normally for 20 years (although by the time the drug gets to the market, there is usually only about ten years left to run). This allows them to recoup the money spent on a drug' s development and also make a profit, some of which will go on investment in new drugs. After the patent ran out, any company could make and sell the drug. A new company, called BHC, was formed to develop a new 'green' synthesis of ibuprofen and to sell the pain-killer. This consortium developed an alternative synthesis of ibuprofen from the same starting material in just three steps. The calculation of the overall atom economy; it is 77% - almost double that of the Boots' synthesis.



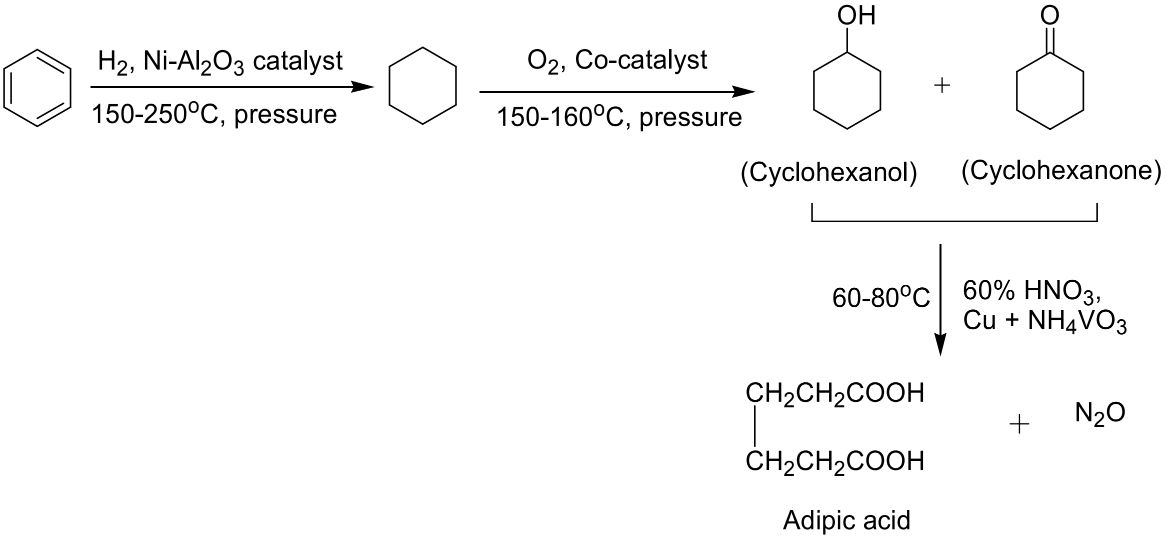
(Ibuprofen)

Atom economy = 77%

Adipic acid Synthesis

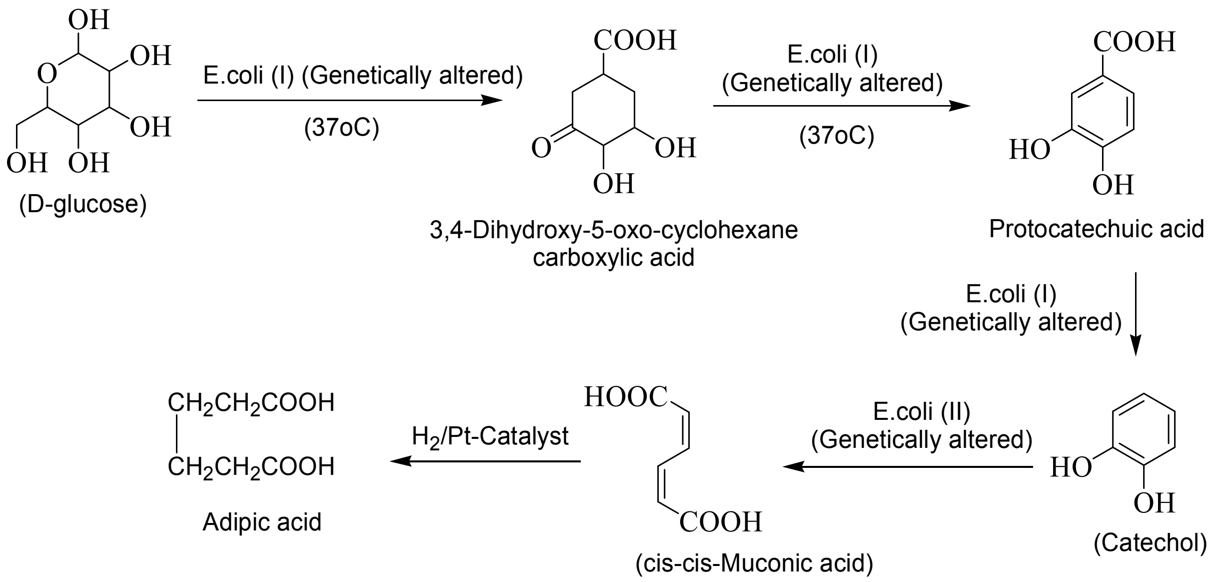
Conventional route of synthesis of adipic acid

Adipic acid synthesized from benzene using some hazards chemicals and catalyst.



Green synthesis of adipic acid

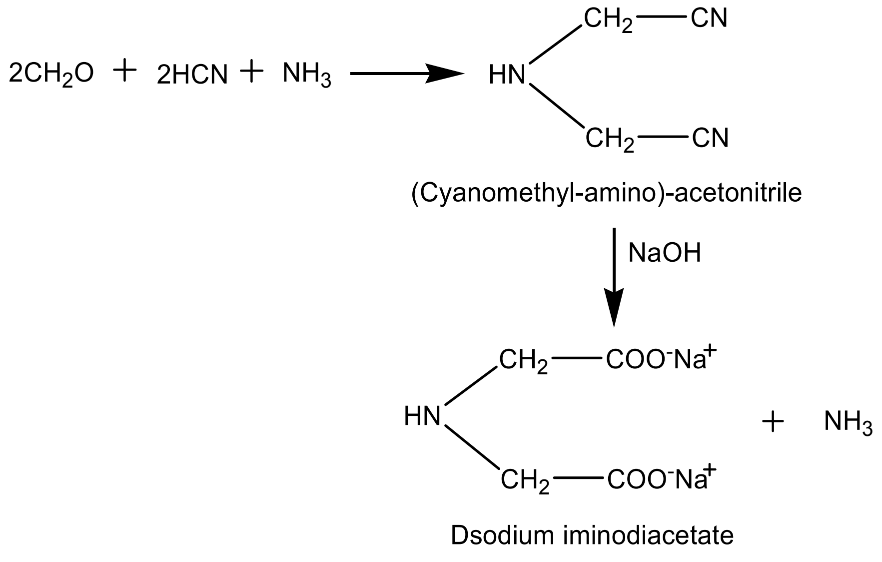
In green synthesis the adipic acid obtained from D-glucose and using biocatalyst like genetically altered E.coli (Escheerichia coli).



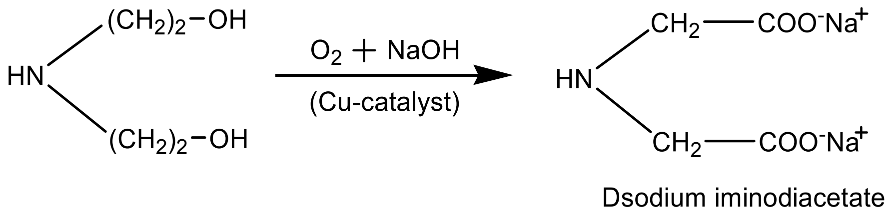
Disodium iminodiacetate (Na_2ida):

Disodium iminodiacetate is an essential reactant in manufacturing an herbicide. Conventional route uses the hazardous chemicals like formaldehyde and HCN while the green synthesis (developed by Monsanto) does not use any much hazardous substances.

Strecker Synthesis:



Green Synthesis of Disodium iminodiacetate:
(Alternative to Strecker synthesis)



UNIT IV

Possible Questions

PART A – Objective type questions (Each carry 1 mark)

1. Super critical carbon dioxide it behaves as a supercritical fluid

   a. Above its critical temperature b. Above its inversion temperature

   c. Above Boyle temperature d. Above its ignition temperature

2. The solubility of many extracted compounds in CO_2 varies

   a. **With pressure** b. with temperature c. with volume d. with density

3. Example for a biocatalyst

   a. **Enzymes** b. Raney Nickel c. Zeolites d. metallic salts

4. For the preparation of 6-aminopenicillanic acid the catalyst used is

   a. **Pen-acylase** b. Zymase c. invertase d. coordination compound

5. Green chemistry synthesis could also involve which of the following?

   a. High temperature b. dicholoromethane c**. microwave oven** d. fossil fuels

6. This 'green' chemical is used in household cleaners to remove stains and is also a favourite dressing on salads!?

   a. **Vinegar(acetic acid)** b. Citric acid c. Hydrochloric acid d. chloroform

7. Ionic liquids belongs to

   a. **Liquids composed entirely of anions and cations in contrast to molecular solvents**

   b. Organic compounds with low melting point

   c. Organic liquids with high boiling point

   d. Inorganic liquids with high boiling point

8. Which one belongs to a ionic liquid type

   a**. N-alkyl pyridinium based salts** b. Potassium salts

   c. Double salts d. Coordination compounds

9. This 'green' chemical is used in household cleaners to remove stains

   a. **Vinegar(acetic acid)** b. Citric acid c. Hydrochloric acid d. chloroform

10. The purpose of $AlCl_3$ in Friedel Crafts reaction is
    a.To provide the electrophile b. To provide the nuycleophile
    c. To provide the free radicals d. To provide the carbanions

PART B (Each carry 6 marks)

1. Discuss the green synthesis disodium iminodiacetate.
2. Explain the following (i) Green reagents and (ii) Green solvents
3. Explain in detail about green solvent synthesis.
4. Write notes on green starting materials.
5. What is meant by green-catalysis? Explain it with suitable examples
6. Illustrate the strecker synthesis with their mechanism.
7. Give the examples of green solvent, green catalyst and green reagents used in organic synthesis.
8. Discuss the green synthesis adipic acid.
9. Explain the synthesis of ibuprofen by conventional method.

PART C (Each carry 10 marks)

1. Outline the conventional route of synthesis of Ibuprofen. Give the greener synthesis of this drug? What are the major advantages in this greener synthesis?
2. What are green solvents? Explain why water is considered as green solvents? Explain the limitations of green solvents.

UNIT IV (Objective type questions)

	Option A	Option B	Option C	Option D	Answer
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	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 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
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, the atom economy is	10%	77%	50%	40%	40%
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 energy?	Catalysts	Selection of starting materials	Percentage atom utilization	Evaluating the type of reaction	Catalysts
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 statements about alcohols is incorrect?	Tertiary alcohols have lower boiling points than primary alcohols with an equivalent molecular weight	Alcohols undergo nucleophilic substitution.	Tertiary alcohols undergo dehydration more readily than primary alcohols	Tertiary alcohols are metabolised in the body to ketone	Tertiary alcohols are 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 Super critical carbon dioxide	72.9 atm	82.9 atm	Compressed liquid	102.9 atm	72.9 atm
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

Hazard assessment and mitigation in chemical industry

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.

Hazard assessment:

"A hazard assessment is an evaluation of a work place, or work situation, as to the potential for hazards that an employee may encounter while performing the job."

Requirements:

- Employers are required (by OSHA) to certify in writing that they have assessed the work place to determine if hazards that require personal protective equipment (PPE) are present or likely.
- Employers are also required to:

  -Select and provide properly fitted protection from injury or impairment, and

  -Train employees in work area hazards and the proper use of PPE.

Identify the Hazards:

- As you walk through the area and discuss work tasks with employees, look for the following hazards.
  - If you are unsure whether something should be included in your hazard assessment, contact EHSS for assistance or try using the reference material suggested on some of the slides.

Identify hazards in the workplace that could result in injury or illness. Evaluate the level of risk to help determine what controls to implement. Select an appropriate solution to control the hazard and/or protect the employee.

What are the common types of hazard assessments?

There are many ways to do a hazard assessment. Employers should customize the process based on their business operations. Two common types of hazard assessments are formal and site-specific. Formal and site-specific hazard assessments may work separately, but are most effective when they are used together.

A **formal hazard assessment** takes a close look at the overall operations of an organization to identify hazards, measure risk (to help prioritize hazards), and develop, implement and monitor related controls. Worker jobs or types of work are broken down into separate tasks. Formal hazard assessments are detailed, can involve many people, and will require time to complete

A **site-specific hazard assessment** (also called field-level) is performed before work starts at a site and at a site where conditions change or when non-routine work is added. This flags hazards identified at the location (e.g. overhead powerlines, poor lighting, wet surfaces, extreme temperatures, the presence of wildlife), or introduced by a change at the work site (e.g. scaffolding, unfamiliar chemicals, introduction of new equipment). Any hazards identified are to be eliminated or controlled right away, before work begins or continues.

Resources for Hazard Assessment & Alternatives Assessment

Two of the more well-known categories of tools using the principles of green chemistry are hazard assessment and alternatives assessment. A hazard assessment evaluates the health and environmental hazards of chemicals in use, as well as potential alternatives under consideration for substitution.

An alternatives assessment (AA) more fully evaluates the impacts of chemical hazards by including other assessment components, such as risk/exposure evaluation and social impact analysis. However, no standard presently exists that defines the components of an alternatives assessment, although there is consensus that a chemical hazard assessment is the foundation of any AA.

Various tools employ different frameworks for analysis, and it is important to choose the framework that will give the best information to suit the client’s needs. The use of alternatives assessments in particular, is growing. An AA helps companies seeking to replace problematic chemicals determine what alternatives exist and assures that any substitute selected is not worse than what it is replacing. This is sometimes known as “regrettable substitution” (which is, unfortunately, more common than one would expect).

The Interstate Chemicals Clearinghouse has developed an extensive document, the Alternatives Assessment Guide that is divided into modules to assist users as they determine what approach is most appropriate and then leads them through the assessment process in that module. The Toxics Use Reduction Institute (TURI) in Lowell, Massachusetts has also developed alternative assessment methodologies and case studies that are available online, as well as an Alternatives Assessment Framework in collaboration with Clean Production Action. BizNGO Network has published several guidance documents: Guide to Safer Chemicals, Chemical Alternatives Assessment Protocol and The Commons Principles for Alternatives Assessments. These are just a few examples of the many guidance publications emerging onto the landscape.

Many tools are available for performing a chemical hazard assessment. The U.S, EPA, for example, has a tool called TEST for estimating toxicity, and has developed tools to assist in the replacement of industrial solvents (PARIS III) and facilitate waste reduction (WAR). Other well-respected tools in this category include Green Screen for Safer Chemicals, Green WERCS, and the Quick Chemical Assessment Tool, more commonly known as QCAT. In addition, organizations such as the Green Chemistry and Commerce Council (GC3), the state of California, and others have put together databases, which include tools across a spectrum of needs.

The plethora of available tools makes navigating them challenging. There is also no standard definition for what comprises an effective alternatives assessment and/or accepted understanding of what differentiates it from other evaluation tools. Companies will often need assistance in matching their needs to the tools available.

Life-cycle Assessment

A life-cycle analysis (LCA) is a procedure for evaluating environmental impacts through all stages of a product's life, and most of the tools available for LCA are proprietary. However, the U.S. EPAhas an excellent webpage that covers many aspects of LCA and gives a good definition and grounding in what LCA is about. The California Department of Toxic Substance Control published a document, Hazard Assessment Tools and Methods, which includes an extensive review of LCA tools. Other resources include the Cradle to Cradle concept, and it's not-for-profit institute, the Cradle to Cradle Products Innovation Institute.

Tool Selectors

Essenscia, the Belgian Federation for Chemistry and Life Sciences Industries, has developed an online tool selector for searching for appropriate sustainability tools, called SUSCHEM compass. The site contains an inventory of tools that "measure the ecological and/or economic impact of products and/or processes and that are useful in the chemical value chain” - "eco-efficiency measurement methods." However, this toolkit also contains some tools that would assist with a hazard assessment, including life cycle, economic, and other ecological evaluation tools that would be useful in conducting an alternatives assessment.

The Organization for Economic Cooperation and Development (OECD) is in the process of developing a web-based selection tool that focuses on chemical hazard assessment methods, but will also contain tools that are applicable to alternatives assessments. At the time of this writing, a release date of 2014 is expected.

Hazard Mitigation in chemical industry

The opportunities for GHG mitigation in industry are somewhat different from those in other sectors because the greatest increases in the efficiency of energy and materials use often come not from direct efforts to reduce consumption, but rather from pursuing other goals such as improved product quality and lower production costs. Many investments undertaken for non-energy reasons yield energy-efficiency gains as a secondary consequence.

Industry is also different in that firms usually have an incentive to improve efficiency in order to reduce costs and maintain their profitability. The degree to which this incentive applies varies among countries depending on the nature of the economy. In the type of market economy toward which many developing and transition countries appear to be evolving, one can expect that industry will pursue a number of the available opportunities for improving the efficiency of resource use. Shortage of capital is a problem in many cases, but gradual improvement in efficiency is likely as investment takes place and new plants are built. Thus, mitigation strategies in industry can build upon and enhance efforts that may already be underway. Well-designed policies can have an important impact, but the overall economic and financial context is likely to be more significant in encouraging investment in energy efficiency than particular policies explicitly designed to have that effect.

Mitigation technology options

Actions by industry that can reduce emissions from energy use include more efficient use of energy, fuel switching, and improved use of materials that reduce energy requirements. In addition, policies that lessen the demand for energy-intensive commodities can reduce industrial energy consumption.

Energy efficiency is the most important category for mitigation analysis. There are many technologies and practices that could enhance industrial energy efficiency. Minor operational changes, such as housekeeping and maintenance, are typically the cheapest, easiest to implement, and least risky, but usually yield the smallest energy and cost savings. Production equipment changes and energy conservation add-on technologies involve larger investments, typically thousands to millions of dollars, and may or may not be justified by reduced energy costs alone. Major process changes often require building a new facility and are usually justified only by strategic market development concerns.

Industry consists of a vast array of activities involving thousands of different processes that are often site-specific in design. Whereas the buildings and transportation sectors can utilize a limited number of energy conservation measures that may be widely applied, the industrial sector requires more of a focus on options in specific industries. Generic technologies that cut across industries represent only part of the full range of opportunities, and even these generic technologies are typically customized for particular applications.

Because of the nature of decision-making in the industrial sector, it is useful to consider two basic classes of technical options: (1) actions for which energy-cost savings are the dominant criteria, and (2) actions for which broader criteria such as overall production cost and product quality are the dominant criteria. One could call the former "energy-cost-sensitive options," and the latter "non-energy-cost-sensitive options."

Future trends in Green Chemistry

- Oxidation reagent and catalysis: historically, many of the oxidation reagents and catalysts have been comprised of toxic substances such as heavy metals. Since these substances were often used in extremely large volumes required to convert millions of pounds of petrochemicals, there was a significant legacy of these metals being released to the environment and having substantial negative effect on human health and environment. It can be changed by the use of benign substances.
- Non covalent derivatization: use of chemicals is dependent upon formation and breaking of covalent bond. chemistry happening without bond making physical, chemical properties are modified and performance measures are enhanced by utilization of dynamic complexation which allows for the temporary formations of modified chemical structures, the properties of molecules can be changed for the

period of the necessary to carry out a particular function without all of the waste that would be generated if full derivatization is implemented.

- Supramolecular chemistry: Research is currently ongoing in the area of supramolecular chemistry to develop reactions which can proceed in the solid state without the use of solvents. The cycloaddition of trans-1,2-bis(4-pyridyl)ethylene is directed by resorcinol in the solid state. This solid-state reaction proceeds in the presence of UV light in 100% yield.
- Biometric multifunctional reagents: while synthetic catalysis and reagents for the most part have centered on carrying out one discrete transformation. The manipulations may include activation, conformational adjustments, and one or several actual transformations and derivitizations.
- Combinatorial green chemistry: it is the chemistry of being able to make large numbers of chemical compounds rapidly on a small scale using reaction matrices. The example is lead that has a large no of derivatives. This chemistry has enabled large no of substances to be made and their properties assessed without the magnitude of the effects of waste disposal.
- Energy focus: The environmental effect of energy usage are profound but have not been as visible and as direct as some of the hazards that have not been posed by materials used in manufacture, use and disposal of chemicals. The benefit of catalysis is dramatic in photochemistry. There is a need to design substances and materials that are effective, efficient and inexpensive at the capture, storage and transportation.
- Proliferation of solvent less reaction: one of the 'solvent alternatives' that is being: it is one of the solvent alternatives that are being developed in green chemistry is that of solvent less reaction system. The carrying of manufacturing process in solvent-less condition utilizes some non-traditional conditions. This helps in development of product isolation, separation and purification that will be solvent-less as well in order to maximize the benefits.

Biomimetics:

“*In biomimetic chemistry, we take what we have observed in nature and apply its principles to the invention of novel synthetic compounds that can achieve the same goals*”

Biomimetic materials are materials developed using inspiration from nature. This may be useful in the design of composite materials, or material structures. Natural structures have evolved many inspiring examples that have been used by man. Common examples are the honeycomb structure of the beehive, the fibre structure of wood, spider silks, nacre, bone, hedgehog quills.

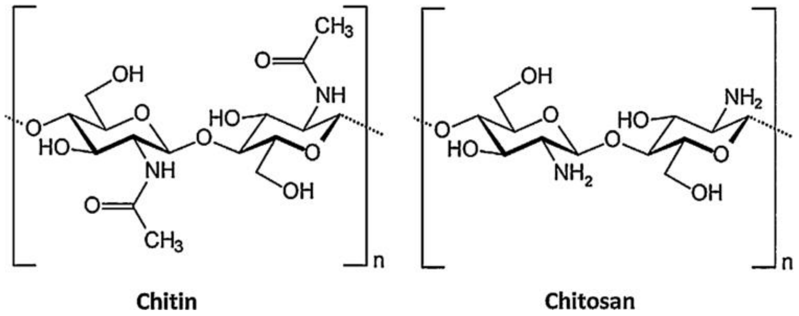
Biomimetic is the examination of nature, its models, systems, processes, and elements to emulate or take inspiration from in order to solve human problems. Similar terms include bionics. The term ‘biomimicry’, or imitation of nature, has been defined as, ‘copying or adaptation or derivation from biology’. The term ‘bionics’ was first introduced in 1960 by Steele as, ‘the science of systems which has some function copied from nature, or which represents characteristics of natural systems or their analogues’. The term ‘biomimetics’ introduced by Schmitt is derived from bios, meaning life (Greek) and mimesis, meaning to imitate. This ‘new’ science is based on the belief that nature follows the path of least resistance (least expenditure of energy), while often using the most common materials to accomplish a task. Biomimetics, ideally, should be the process of incorporating principles that promote sustainability much like nature does from ‘cradle to grave’, from raw material usage to recyclability, all in this physical world. Biomimetic material chemistry also refers to as bio-inspired chemistry which is an important diverse field such as bio-ceramic, bio-sensing, biomedical engineering, bio-nanotechnology and biologically driven self assembly.

Through the history of life on earth, nature has gone through a process of trial and error to refine the living organisms, processes, and materials on planet Earth. The emerging field of biomimetics has given rise to new technologies created from biologically inspired engineering at both the macro scale and nanoscale levels. Biomimetics is not a new idea. Humans have been looking at nature for answers to both complex and simple problems throughout our existence. Nature has solved many of today's engineering problems such as hydrophobicity, wind resistance, self-assembly, and harnessing solar energy through the evolutionary mechanics of selective advantages.

History of Biomemetic Materials

One of the early examples of biomimetic was the study of birds to enable human flight. Although never successful in creating a "flying machine", Leonardo da Vinci (1452–1519) was a keen observer of the anatomy and flight of birds, and made numerous notes and sketches on his observations as well as sketches of various "flying machines". The Wright Brothers, who succeeded in flying the first heavier-than-air aircraft in 1903, derived inspiration from observations of pigeons in flight. Otto Schmitt, an American academic and inventor, coined the term biomimetics to describe the transfer of ideas from biology to technology. The term biomimetics only entered the Websters Dictionary in 1974 and is defined as "the study of the formation, structure, or function of biologically produced substances and materials (as enzymes or silk) and biological mechanisms and processes (as protein synthesis or photosynthesis) especially for the purpose of synthesizing similar products by artificial mechanisms which mimic natural ones".

Chitin is one example where new uses for a biomolecule have been found. This polysaccharide can be found in algae, the cell walls of fungi, the exoskeletons of arthropods, etc and is one of the most abundant organic compounds on earth with a production that is estimated to be around 10^{11} tons each year. Chitin and its deacetylated form, chitosan, have several interesting properties; they are, among other things, non-toxic, nonallergenic, anti-microbial, and biodegradable, they have fiber- and film-forming properties and they adsorb metal ions. Chitosan is also suitableas a substrate for biomimetic polymers because the free amino groups in the polymer backbone are easily modified. In the medical field chitin and its derivatives have been used for drug delivery, contact lenses, wound dressing materials, suture materials, and tissue engineering, but they are also used in fields like cosmetics, textiles, nutritional supplements, water purification, foods and agriculture.



Economic Impact of Biomimetic Materials

The design strategies of biological materials are not immediately applicable to the design of new engineering materials, since there are some remarkable differences between the strategies common in engineering and those used by nature. The first major difference is in the range of choice of elements, which is far greater for the engineer. Elements such as iron, chromium and nickel are very rare in biological tissues and certainly not used in metallic form, as would be the case for steel. Iron is found in red blood cells, for instance, as an ion bound to the protein haemoglobin and its function is certainly not mechanical but rather to bind oxygen. Most of the structural materials used by nature are polymers or composites of polymers and ceramic particles. Such materials would generally not be the first choice of an engineer to build strong and long-lasting mechanical structures. Nevertheless, nature uses them to build trees and skeletons. The second major difference is the way in which materials are made. While the engineer selects a material to fabricate a part according to an exact design, nature goes the opposite way and grows both the material and the whole organism (a plant or an animal) using the principles of (biologically controlled) self-assembly. This provides control over the structure of the material at all levels of hierarchy and is certainly a key to the successful use of polymers and composites as structural materials.

Multifunctional reagents

The artificial contact action and reagents for the foremost half have targeted on concluding one distinct transformation. The manipulations could embrace activation, conformational changes, and one or many actual transformations and derivitizations.

Infection control on abiotic surfaces remains a longstanding challenge, which becomes particularly important considering that infection is one of the leading causes of orthopaedic implant failure. Continuous innovation has been made to modify material surfaces for preventing bacterial colonisation, *e.g.*, by grafting polyethylene glycol or other hydrophilic molecules to minimise bacterial adhesion, or incorporating antibiotics into implant materials or coating layers for controlled release to kill bacteria. While their efficiency in infection control has been demonstrated, there is no obvious evidence to show that these approaches would promote tissue growth. Tissue-integration with implant surface is not required for those implants for the temporary fracture fixation; however, it becomes highly crucial for long-term implants such as hip prostheses. It is recognised that the fate of long-term orthopaedic implants mainly depends on the surface race between successful osseointegration and unwanted bio film formation and an ideal surface for such orthopaedic implants should be repulsive to bacteria while adhesive to bone tissue cells. Following this concept, efforts to modify the surface with differential functionality for preventing bio film formation and promoting bone tissue formation will be of great benefit. Up to now, very limited progress has been made in designing such multifunctional surfaces. Seminal efforts were made to functionalise titanium substrates with covalently grafted chitosan, hyaluronic acid or their derivatives to suppress bacterial adhesion, while enhancing osseointegration with immobilised RGD peptides or growth factors. With promising evidence in reducing bacterial adhesion and enhancing osteogenesis, the involvement of two chemical modification steps in this approach could potentially complicate its application. Thus, more cost effective approaches are preferred.

Combinatorial green chemistry:

Definition:

'Combinatorial chemistry defined as preparation of a large number of different compounds at the same time'.

Conventional Reaction: **A + B $\longrightarrow$ A-B**

Combinatorial Chemistry: **A(1-n) + B(1-n) $\longrightarrow$ A(1-n) – B(1-n)**

Combinatorial chemistry-a technology for creating molecules en masse and testing them rapidly for desirable properties-continues to branch out rapidly. Compared with conventional one-molecule-at-a-time discovery strategies, combinatorial chemistry is a better way to discover new drugs, catalysts, and materials.

Combinatorial chemistry began with amino acids. In 1963, R. Bruce Merrifield developed a way to make peptides by solid-phase synthesis. But the field in its modern dimensions only began to take shape in the 1980s, when H. Mario Geysen, developed a technique to synthesize arrays of peptides on pin-shaped solid supports and Houghten developed a technique for creating peptide libraries in tiny mesh "tea bags" by solid phase parallel synthesis. It becomes the basis for the explosion of solid phase organic synthesis, whereby molecular diversity can be introduced by producing a nearly infinite variety of heterocycles, steroids, carbohydrates, and soon, organometallics, all while tethered by one reversible link to a suitable polymeric support. Soon after the discovery of high –Tc superconductors (HTSC), a huge number of investigators in many fields of science and technology expended huge amounts of energy and time on the preparation and characterization of mixed and sintered compounds with the presumed possibility of a higher Tc. Some groups started applying the combinatorial approach to identify the superconductive materials. Thus the application of combinatorial chemistry to inorganic materials started here.

Combinatorial synthetic methods:

The parallel synthetic methods described in the previous paragraph considerably speed up preparation of compounds used for different purposes. The advent of the real combinatorial processes accelerated the preparation of new compounds to never dreamed speeds.

Although there are compounds that can be prepared in a single reaction step most substances are synthesized in a multi-step process. Such substances are built upstepwise from building blocs. The building blocks of a peptide, for example, are the amino acids that are linked together step by step. The real combinatorial methods can be used in multi-step processes and their most important characteristic feature is that make possible to prepare in a single run all structural derivatives that can be theoretically deduced from the structures of the building blocks. The number of operations and number of reaction vessels relative to the number of synthesized compounds are drastically reduced.

Most combinatorial synthetic methods are based on solid phase approach but there are versions that can be realized in solution, too. Among the solid phase carriers most often the bead form resin is applied but surfaces of solid materials are also used.

Proliferation of solventless reactions:

Aristotle believed that "***No reaction occurs in the absence of solvent***."

(This is not true!)

Introduction

The earlier belief that no reaction is possible without the use of a solvent is no more valid. It has been found that a large number of reactions occur in solid state without the solvent. Infact in a number of cases, such reactions occur more efficiently and with more selectivity compared to reactions carried out in solvents. Such reactions are simple to handle, reduce pollution, comparatively cheaper to operate and are especially important in industry. It is believed that solvent free organic synthesis and transformations are industrially useful and largely green. Green chemistry, also called sustainable chemistry, is a chemical philosophy encouraging the design of products and processes that reduce or eliminate the use and generation of hazardous substances.

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.

Need of solvents in chemical reactions:

- 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 in reactions:

- 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:

- Use of solventless reactions
- Use of “non-organic” solvents
- Processing technology

Advantages to Solventless 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.

Solvent-Free synthesis

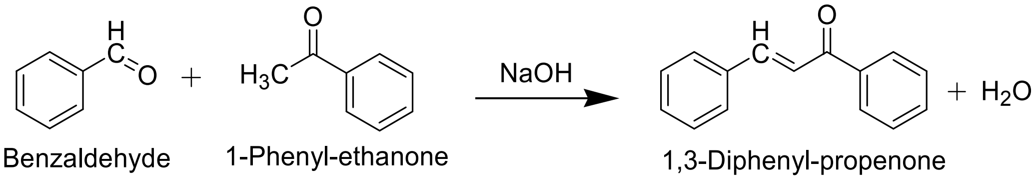
- Neat – reagents react together in the liquid phase in the absence of a solvent.
- Solid-state synthesis– two macroscopic solids interact directly and form a third, solid product without the intervention of a liquid or vapour phase.

➢ Generally solventless reactions are atom efficient reaction:

Solvent free synthesis of chalcones:

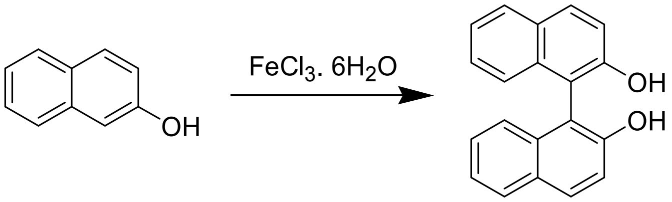
The synthesis of chalcones illustrates the reaction that proceeds with high atom economy and is relatively easy to perform in teaching labs. Chalcones are important compounds with applications in medicine and physics.

In 2004, ***Palleros*** was found that the reactions proceed rapidly and afford very good yields of product. Most of the chalcones can be obtained in a matter of minutes by mixing the corresponding benzaldehyde and acetophenone in the presence of solid NaOH in a mortar with pestle; the yields of crude product were in the range 81-94%.



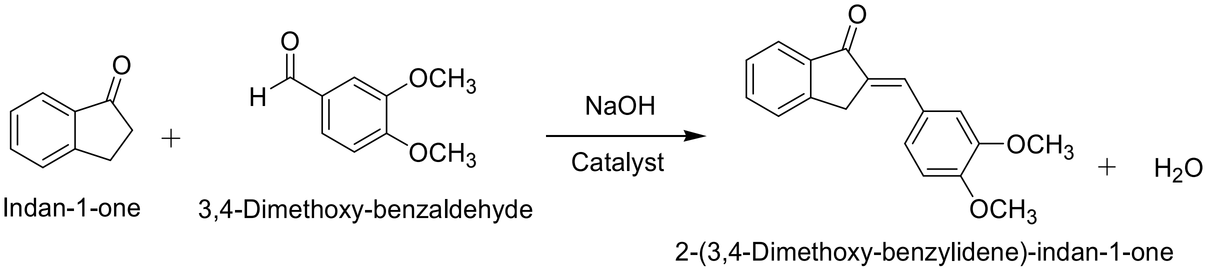
Oxidative coupling Reaction of phenols with $FeCl_3$:

Oxidative couplings of phenols are usually carried out by treatment of phenols in solution with more than equimolar amount of metal salts such as $FeCl_3$ or manganese tris(acetylacetonate), although the latter one is too expensive to use in a large quantity. The coupling reaction of phenols with $FeCl_3$, some times quinines as byproducts.



In 1989, Toda have reported that some oxidative coupling reactions of phenols with $FeCl_3$ are faster and more efficient in the solid state than in solution. Some coupling reactions in the solid state were accelerated by irradiation with ultrasound. Some coupling reactions are achieved by using a catalytic amount of $FeCl_3$.

The Crossed-Aldol Condensation



Limitations of solvent free reactions

- Not all reactions will work in the absence of solvent.
- Function of catalysts.
- Exothermic reactions are potentially dangerous.
- Specialized equipment needed for some procedures.
- If aqueous quench and organic extraction are performed, this reduces green benefits.

Use of non-organic solvents

- Liquid and supercritical CO2
- Ionic liquids
- Fluorous Phase Chemistry
- Water

Green chemistry in ecofriendly safe reaction follows the solvent-free or solid state reaction carried out using the reactants alone or incorporating them in clays, zeolites, silica, alumina or other matrices to achieve high degree of stereoselectivity in the products, to reduce byproducts, to maximize rate of reaction.

Non-Covalent Derivatization:

A non-covalent derivative (NCD) is formed when one (or more) coformer molecule(s) is incorporated into the matrix of the target molecule by way of non-covalent forces. The non-covalent forces are

(i) Ionic forces

(ii) Van der Waals forces

(iii) Hydrogen bonding

(vi) Lipophilic-lipophilic interactions and

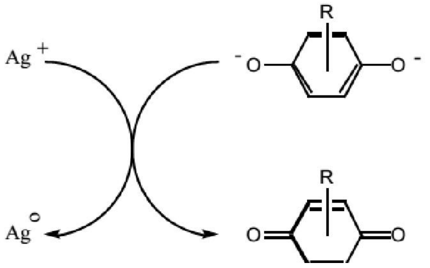
(v) pi-pi interactions.

The NCDs self-assemble according to mutual molecular recognition based on the co-formers' cooperative topography. NCDs often show significant differences when compared to their parent molecules. These differences can include dramatic changes in solubility, melting point, optical properties, bioavailability, or stability. In light of this powerful utility and the fact that NCDs can be formed by way of economic and environmentally-friendly means, NCD-based strategies can have significant value in the development of greener chemistries.

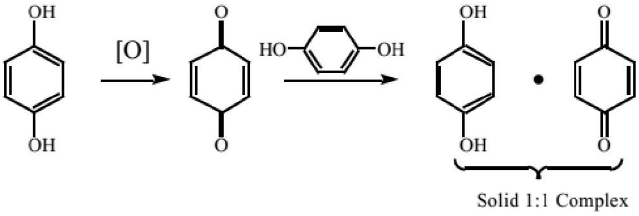
Preparation of NCDs

Compared to traditional synthetic modifications, the preparation of NCDs is an alternative that can be less toxic, produce less waste, and be less labor-intensive and more economical when used to affect the same types of property changes. A variety of solvent methods can be used to prepare NCDs. Co crystal preparation has been reported using traditional methods of precipitation, cooling crystallization and slurry formation. Evaporation has emerged as the most common solvent-based method for the preparation of co crystals. The preparation of eutectics has also been reported using solvent evaporation. Solvent-based preparation methods for NCDs have significant limitations. All the NCD partners are required to have a solubility relationship with the solvent that allows for effective dissolution followed by concurrent precipitation as the solution cools or evaporates.

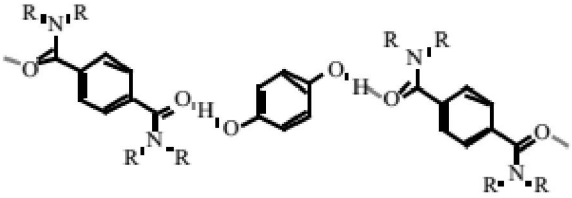
(i) Ionic forces



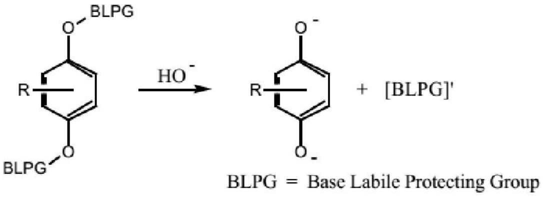
(ii) Van der Waals forces



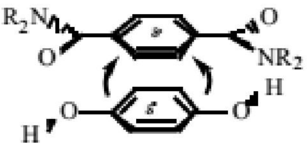
(iii) Hydrogen bonding


Hydrogen Bonds

(iv) Lipophilic-lipophilic interactions



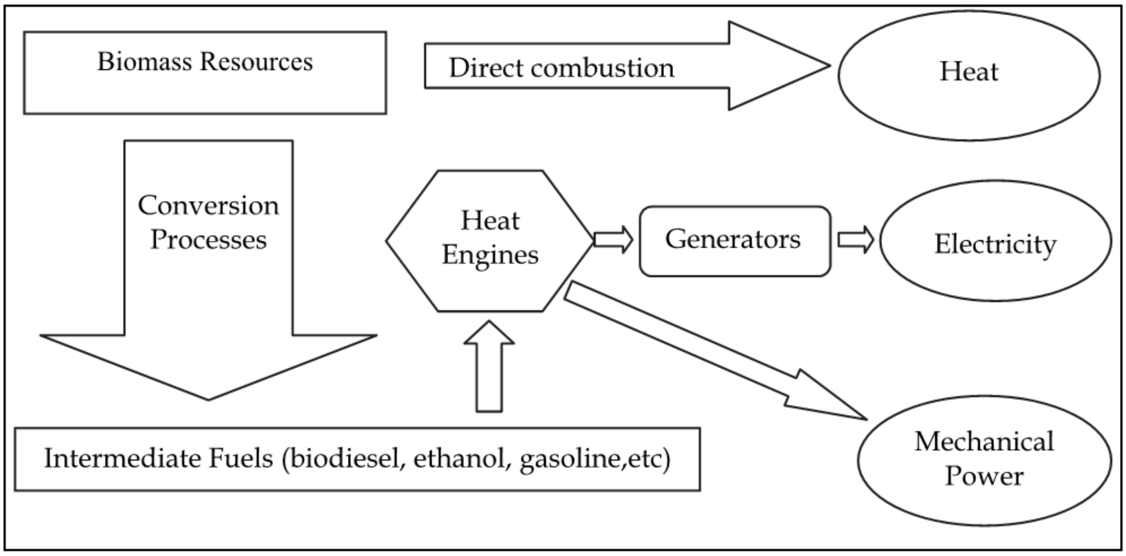
(v) pi-pi interactions


Charge Transfer

NCDs, encompassing both cocrystal and eutectic forms, possess properties that are unique to their supramolecular matrix. These properties include critical product performance factors such as solubility, stability and bioavailability. NCDs have been used to tailor materials for a variety of applications and have the potential to be valuable in an even broader range of materials and processes. NCDs can be prepared using little or no solvent and none of the reagents typical to synthetic modifications. Thus, non-covalent derivatization is a powerfully versatile, environmentally-friendly and cost-effective tool

Biomass Conversion

In general, biomass-to-energy conversion technologies have to deal with a feedstock which can be highly variable in mass and energy density, size, moisture content, and intermittent supply. Therefore, modern industrial technologies are often hybrid fossil - fuel/biomass technologies which use the fossil fuel for drying, preheating and maintaining fuel supply when the biomass supply is interrupted.



Thermochemical Processes

These processes do not necessarily produce useful energy directly, but under controlled temperature and oxygen conditions are used to convert the original biomass feedstock into more convenient forms of energy carriers, such as producer gas, oils or methanol. These carriers are either more energy dense and therefore reduce transport costs, or have more predictable and convenient combustion characteristics allowing them to be used in internal combustion engines and gas turbines and these are:

a) Pyrolysis.

b) Carbonisation.
c) Gasification.
d) Catalytic Liquefaction.

a). Pyrolysis

Pyrolysis is the application of heat to a feedstock in the absence of oxygen to break down the long chain molecules into short chain molecules. Typically the feedstock is biomass or waste, and the process is used to produce a syngas (a mixture of hydrogen, volatile organic compounds, and carbon monoxide). Varying the process conditions allows the production of fluids similar to diesel, and a variety of other products.

A more detailed understanding of the physical and chemical properties governing the pyrolytic reactions has allowed the optimisation of reactor conditions necessary for these types of pyrolysis. Further work is now concentrating on the use of high pressure reactor conditions to produce hydrogen and on low pressure catalytic techniques (requiring zeolites) for alcohol production from the pyrolytic oil. The advantage of pyrolysis and gasification are that they convert solid material into gases and vapours which are less costly to handle, transport and store. The gases will burn in boilers, gas turbines and reciprocating engines increasing fuel flexibility and security. Capturing and combusting the methane and carbon monoxide in syngas makes use of the energy in the gas and produces carbon dioxide which is a less potent greenhouse gas than methane and offsets fossil fuel energy production. The disadvantages of pyrolysis and gasification are that they require heat input to drive the chemical reactions that produce a syngas. Thus some fuel must be used to generate the syngas.

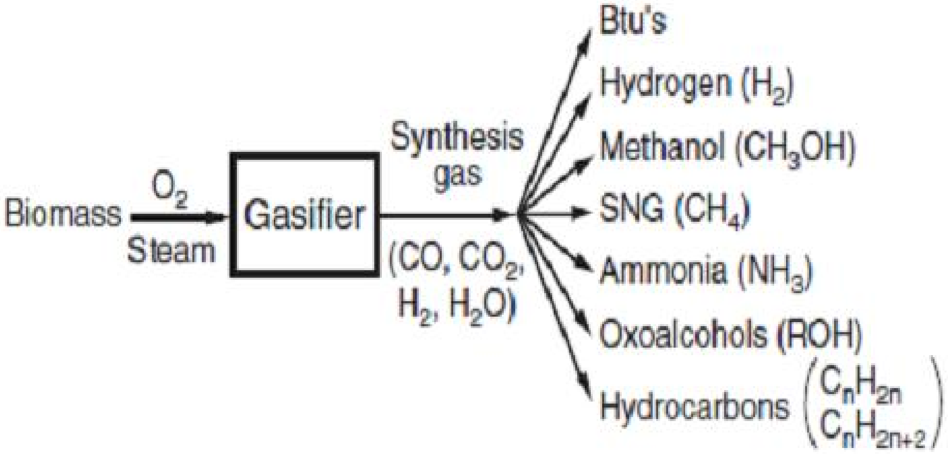
b). Carbonisation

This is an age old pyrolytic process optimised for the production of charcoal. Traditional methods of charcoal production have centred on the use of earth mounds or covered pits into which the wood is piled. Control of the reaction conditions is often crude and relies heavily on experience. The conversion efficiency using these traditional techniques is believed to be very low; on a weight basis estimates that the wood to charcoal conversion rate for such techniques ranges from 6 to 12 tonnes of wood per tonne of charcoal. During carbonisation most of the volatile components of the wood are eliminated; this process is also called "dry wood distillation." Carbon accumulates mainly due to a reduction in the levels of hydrogen and oxygen in the wood. The wood undergoes a number of physico -chemical changes as the temperature rises. Between 100°C and 170°C most of the water is evaporated; between 170°C and 270°C gases develop containing condensible vapours, CO and CO_2. These condensible vapours (long chain carbon molecules) form pyrolysis oil, which can then be used for the production of chemicals or as a fuel after cooling and scrubbing. Between 270°C and 280°C an exothermic reaction develops which can be detected by the spontaneous generation of heat. The modernisation of charcoal production has lead to large increases in production efficiencies with large-scale industrial production in Brazil now achieving efficiencies of over 30% (by weight). There are three basic types of charcoal-making: a) internally heated (by controlled combustion of the raw material), b) externally heated (using fuelwood or fossil fuels), and c) hot circulating gas (retort or convert er gas, used for the production of chemicals). Internally heated charcoal kilns are the most common form of charcoal kiln. It is estimated that 10 to 20% of the wood (by weight) is sacrificed, a further 60% (by weight) is lost through the conversion to, and release of, gases to the atmosphere from these kilns. Externally heated reactors allow oxygen to be completely excluded, and thus provide better quality charcoal on a larger scale. They do, however, require the use of an external fuel source, which may be provided from the "producer gas" once pyrolysis is initiated. Re-circulating heated gas systems offer the potential to generate large quantities of charcoal and associated by-products, but are presently limited by high investment costs for large scale plant.

c). Gasification

Gasification is the partial oxidation of an organic feedstock to produce a syngas (a mixture of hydrogen, volatile short chain organic compounds, and carbon monoxide). Typically the feedstock is biomass or waste, and varying the process conditions allows control over proportions of the compounds in the syngas. In this approach to the development of fixed carbon supplies from renewable carbon resources is to convert CO_2 outside the biomass species to synthetic fuels and organic intermediates. The ambient air, which contains about 360 ppm by volume of CO_2, the dissolved CO_2 and carbonates in the oceans, and the earth's large carbonate deposits, could serve as renewable carbon resources. But since CO_2 is the final oxidation state of fixed carbon, it contains no chemical energy. Energy must be supplied in a chemical reduction step. A convenient method of supplying the required energy and of simultaneously reducing the oxidation state is to reduce CO_2 with hydrogen. The end product, for example, can be methane (CH_4), the dominant component in natural gas and the simplest hydrocarbon known, or other organic compounds. With all components in the ideal gas state, the standard enthalpy of the process is exothermic by 165 EJ (39.4 kcal) per gram mole of methane formed

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$$



d). Catalytic Liquefaction

This technology has the potential to produce higher quality products of greater energy density. These products should also require less processing to produce marketable products. Catalytic liquefaction is a low temperature, high pressure thermochemical conversion process carried out in the liquid phase. It requires either a catalyst or a high hydrogen partial pressure. Technical problems have so far limited the opportunities of this technology.

Biochemical Processes

The use of micro-organisms for the production of ethanol is an ancient art. However, in more recent times such organisms have become regarded as biochemical "factories" for the treatment and conversion of most forms of human generated organic waste. Microbial engineering has encour aged the use of fermentation technologies (aerobic and anaerobic) for use in the production of energy (biogas) and fertiliser, and for the use in the removal of unwanted products from water and waste streams.

i) Anaerobic Fermentation.
ii) Methane Production in Landfills.
iii) Ethanol Fermentation.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{Catalyst}]{\text{Invertase}} \underset{\text{Fructose}}{C_6H_{12}O_6} + \underset{\text{Glucose}}{C_6H_{12}O_6}$$

$$\underset{\text{Fructose (OR) Glucose}}{C_6H_{12}O_6} \xrightarrow[\text{Catalyst}]{\text{Zymase}} \underset{\text{Ethanol}}{2C_2H_5OH} + 2CO_2$$

i). Anaerobic Fermentation

Anaerobic digestion is the microbial digestion of feedstock releasing heat, methane, hydrogen sulphide, carbon dioxide and under specific conditions hydrogen gas. This process takes place over several days in large tanks where the ideal conditions are maintained. After the process the remaining solid digestate is suitable for use as fertiliser and the gases released are collectively referred to as biogas. This gas can be used as a fuel in a CHP scheme once the gas has been cleaned to remove acidic compounds by condensation. Anaerobic reactors are generally used for the production of methane rich biogas from manure (human and animal) and crop residues. They utilise mixed methanogenic bacterial cultures which are characterised by defined optimal temperature ranges for growth. These mixed cultures allow digesters to be operated over a wide temperature range i.e. above 0°C up to 60°C. When functioning well, the bacteria convert about 90% of the feedstock energy content into biogas (containing about 55% methane), which is a readily useable energy source for cooking and lighting. The sludge produced after the manure has passed through the digester is non-toxic and odourless. Also, it has lost relatively little of its nitrogen or other nutrients during the digestion process thus, making a good fertiliser. In fact, compared to cattle manure left to dry in the field the digester sludge has a higher nitrogen content; many of the nitrogen compounds in fresh manure become volatised whilst drying in the sun. The advantage of anaerobic digestion is that it naturally occurs to organic material and would release methane, a potent greenhouse gas, into the atmosphere. Capturing and combusting the methane makes use of the energy in the gas and produces carbon dioxide which is a less potent greenhouse gas than methane and offsets fossil fuel energy production.

The disadvantages of anaerobic digestion are that the microbes required pose a health threat to people and livestock. The microbes are sensitive to changes in the feedstock, especially the presence of anti -microbial compounds, and changes in the reactor conditions: they require constant circulation of the reactor fluid, and a constant operating temperature and pH. Anaerobic digesters of various types were widely distributed throughout India and China. Extension programmes promote biogas plants as ideal candidates for rural village use due to their energy and fertiliser production potential along with their improved health benefits. Health benefits primarily arise from the cleaner combustion products of biogas as opposed to other biomass or fossil fuels which may be used in the domestic environment. Reliability problems have arisen from a number of problems i.e. construction defects, the mixed nature of the bacterial population, the digesters requirements for water & maintenance of optimum nitrogen ratio of the medium. Another problem is the digester's demand for dung, which may have alternative uses.

ii). Methane Production in Landfills

Methane is a powerful greenhouse gas, with substantial amounts being derived from unutilized methane production from landfill sites. Its recovery therefore, not only results in the stabilisation of the landfill site, allowing faster reuse of the land, but also serves to lessen the impact of biospheric methane emissions on global warming. Anaerobic digestion in landfills is brought about by the microbial decomposition of the organic matter in refuse. The levels of organic matter produced per capita vary considerably from developed to developing countries e.g. the percentage of Municipal Solid Waste (MSW) which is putrescible in Sierra Leone is about 90% compared to about 60% for US MSW. Commercial production of land -gas can also aid with the leaching problems now increasingly associated with landfill sites. Local communities neighbouring land fill sites are becoming more aware of the potential for heavy metals and nutrients to leach into aquifers. Landfill processing reduces the volume of sludge to be disposed of, and the nutrient content, thus facilitating proper disposal.

iii). Fermentation

Ethanol is mainly used as a substitute for imported oil in order to reduce their dependence on imported energy supplies. The substantial gains made in fermentation technologies now make the production of ethanol for use as a petroleum substitute and fuel enhancer, both economically competitive (given certain assumptions) and environmentally beneficial. The most commonly used feedstock in developing countries is sugarcane, due to its high productivity when supplied with sufficient water. Where water availability is limited, sweet sorghum or cassava may become the preferred feed stocks. Other advantages of sugarcane feedstock include the high residue energy potential and modern management practices which make sustainable and environmentally benign production possible whilst at the same time allowing continued production of sugar. Other feed stocks include saccharide-rich sugar beet, and carbohydrate rich potatoes, wheat and maize. Recent advances in the use of cellulosic feedstock, may allow the competitive production of alcohol from woody agricultural residues and trees to become economically competitive in the medium term.

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Emission control

"Emission control means employed to limit the discharge of noxious gases from the internal-combustion engine and other components. There are three main sources of these gases: the engine exhaust, the crankcase, and the fuel tank and carburettor".

The following engine parameters have large influence on emissions and hence have undergone substantial modifications since the pre-emission control era.

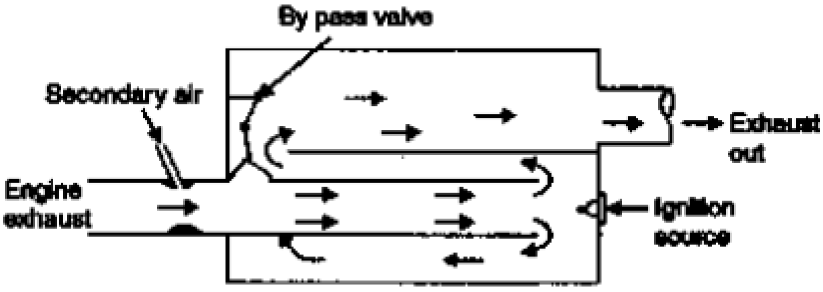
- Modification in the engine design and operating parameters
- Treatment of exhaust products of combustion
- Modification of the fuels

Modification in the Engine Design and Operating Parameters

- Modification of combustion chamber involves avoiding flame quenching zones where combustion might otherwise be incomplete and resulting in high HC emission. This includes: Reduction of surface to volume (SAT) ratio, Reduction of surface to volume (SAT) ratio, Reduction of surface to volume (SAT) ratio, Reduced space around piston ring.
- Lower compression ratio: Lower compression ratio reduces the quenching effect by reducing the quenching area, thus reducing HC. Lower compression ratio also reduces NO emissions due to lower maximum temperature. Lower compression, however, reduces thermal efficiency and increases fuel consumption.

Treatment of exhaust products of combustion

The exhaust gas coming out of exhaust ma The exhaust gas coming out of exhaust manifold is treated to reduce CO emissions. The devices used to accomplish are after burner , exhaust manifold reactor and catalytic converter.



Direct flame-after burner

After burner is a burner where air is supplied to the exhaust gases and mixture is burnt with the help of ignition system. The HC and CO which are formed in the engine combustion because of inadequate O_2 and inadequate time to burn are further brunt by providing air in a separate box, known as after burner.

Exhaust manifold reactor is a further development of after-burner where the design is changed so as to minimize the heat loss and to provide sufficient time for mixing of exhaust and secondary air.

A catalytic converter is a device which is placed in the vehicle exhaust system to reduce HC and CO by oxidizing catalyst and NO by reducing catalyst.

Modification of the fuels

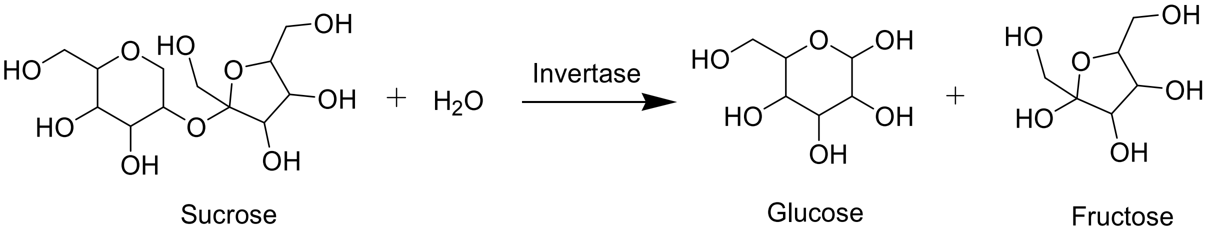
The ability of a fuel to burn in mixtures leaner than stoichiometric ratio is a rough indication of its potential emission reducing characteristics and reduced fuel consumption. If gasoline is changed to propane as engine fuel CO emission can substantially be reduced with reduced HC and NO and in changing from propane to methane the CO as well HC emission touch zero level and only the NO remains as a significant factor. From pollution point of view both methane and steam reformed hexane are very attractive fuels but we are unable to use at present for want of technological progress.

Biocatalysis

Biocatalysis has many attractive features in the context of green chemistry: mild reaction conditions (physiological pH and temperature), an environmentally compatible catalyst (an enzyme) and solvent (often water) combined with high activities and chemo-, regio- and stereoselectivities in multifunctional molecules. Furthermore, the use of enzymes generally circumvents the need for functional group activation and avoids protection and deprotection steps required in traditional organic syntheses. This affords processes which are shorter, generate less waste and are, therefore, both environmentally and economically more attractive than conventional routes.

The time is ripe for the widespread application of biocatalysis in industrial organic synthesis and according to a recent estimate more than 130 processes have been commercialised. Advances in recombinant DNA techniques have made it, in principle, possible to produce virtually any enzyme for a commercially acceptable price. Advances in protein engineering have made it possible, using techniques such as site directed mutagenesis and *in vitro* evolution, to manipulate enzymes such that they exhibit the desired substrate specificity, activity, stability, pH profile, etc. Furthermore, the development of effective immobilisation techniques has paved the way for optimising the performance and recovery and recycling of enzymes.

Enzymes are an important class of proteins that catalyze virtually all biochemical reactions. One such reaction and the one that we will study in this experiment, is the inversion of sucrose, catalyzed by the enzyme invertase that is derived from yeast:



DuPont has developed a process for the manufacture of glyoxylic acid, a large volume fine chemical, by aerobic oxidation of glycolic acid, mediated by resting whole cells of recombinant methylotrophic yeast. The glycolic acid is readily available from acid-catalysed carbonylation of formaldehyde. Traditionally, glyoxylic acid was produced by nitric acid oxidation of acetaldehyde or glyoxal, processes with high E factors, and more recently by ozonolysis of maleic anhydride.

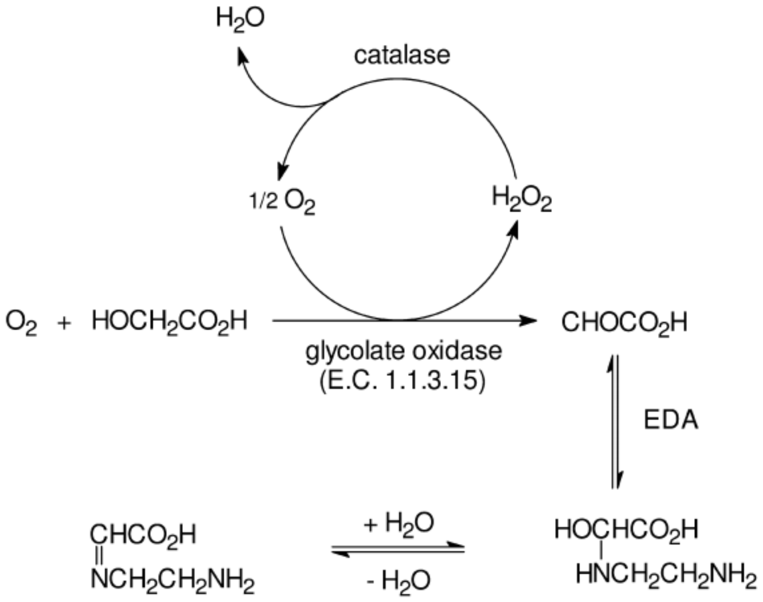
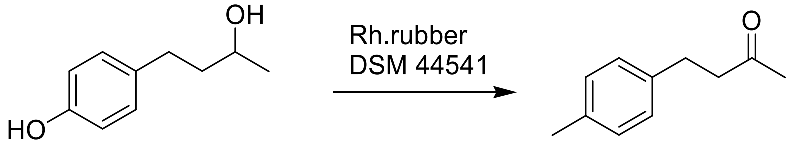


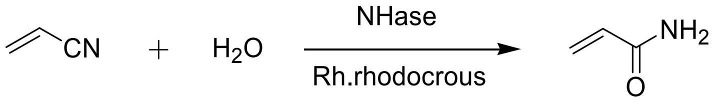
Fig. Glyoxylic acid by microbial oxidation

The key enzyme in the above process is an oxidase which utilises dioxygen as the oxidant, producing one equivalent of hydrogen peroxide, without the need for cofactor regeneration. Another class of enzymes which catalyse the oxidation of alcohols comprises the alcohol dehydrogenases. However, in this case cofactor regeneration is required, which is an impediment to commercialisation. Re-cently, a highly enantioselective alcohol dehydrogenase, showing broad substrate specificity and exceptionally high tolerance for organic solvents, was isolated from *Rhodococcus ruber* DSM 4451.

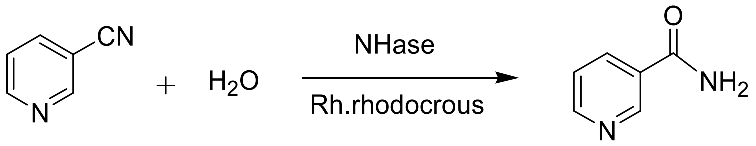
The enzyme, conveniently as whole microbial cells as a catalyst for (enantioselective) Oppenauer oxidation of a broad range of alcohols.



Another example in which a biocatalytic transformation has replaced a chemocatalytic one, in a very simple reaction, is the **Mitsubishi Rayon process** for the production of acrylamide by hydration of acrylonitrile. Whole cells of *Rhodococcus rhodocrous*, containing a nitrile hydratase, produced acrylamide in >99.9% purity at >99.9% conversion, and in high volumetric and space time yields.



Acrylamide



Nicotinamide
(Vitamin B6)

Advantages of biocatalysts and enzymes

a) Very high enantioselectivity

b) Very highr egioselectivity

c) Transformation under mild conditions

d) 'Green chemistry' e.g. solvent often water

Disadvantages of biocatalysts and enzymes

a) Often low specificactivity

b) In stability at extreme temperatures and pH values

c) Availability for selected reactions only

d) Long development time for new enzymes

UNIT V

Possible Questions

PART A – Objective type questions (Each carry 1 mark)

1. A biocatalyst works under

   a. **Physiological pH** b. High temperature reaction condition

   c. High pressure d. High pressure and high temperature

2. One of the raw materials used in the preparation of Nylon-6,6 is

   a. **Adipic acid** b. succinic acid c. tartaric acid d. lactic acid

3. In conventional method for the preparation of Adipic acid, the raw material used is

   a. ethanol b. **Non renewable source** c. propanol d. Plant feedstock

4. The first listed of the 12 Principles of Green Chemistry is?

   a. Prevent waste b. Catalysis c. Atom economy d. Benign solvents

5. D-glucose is used to prepare

   a. Ethanoic acid b. **adipic acid** c. citric acid d. crotonic acid

6. Liquids with a wide temperature range and no vapour pressure

   a. Solid supports b. organic catalysts c. organic solvents d. **Ionic liquids**

7. Organic salts with melting points under 100^0C are called

   a. **Ionic liquids** b. super critical liquids c. supercritical gas d. tertiary salts

8. Heart of green chemistry is

   a. to maximize the waste products formation b. **to minimize the waste products** formation c. to increase the toxic materials d. to increase toxic materials and waste products formation

9. Triple point is a point where

   a. **Three different phases of a substance coexist**

   b. Three different substances ofsame phase coexist

   c. Two different phases of a substance coexist

   d. Four different phases of a substance coexist

10. The purpose of Anhy. $AlCl_3$ in Friedel Crafts reaction is

    a.To provide the electrophile b. To provide the nuycleophile

    c. To provide the free radicals d. To provide the carbanions

PART B (Each carry 6 marks)

1. Write notes on proliferation of solvent less reactions.
2. Write the catalytic reaction in green chemistry.
3. Give the significance of biocatalysis.
4. What is emission control? Explain.
5. What are the multifunctional reagents? Give the suitable reactions?
6. Illustrate the seventh principle of green chemistry.
7. Describe the oxidation-reduction reagents in green chemistry.
8. Write notes on noncovalent derivatization.
9. What is combinatorial chemistry? Explain.

PART C (Each carry 10 marks)

1. Give the detailed account on biomass conversion.
2. Consider the reaction of ethyl propionate with methyl amine.

$CH_3CH_2COC_2H_5 + H_3CNH_2 \longrightarrow CH_3CH_2CONHCH_3 + CH_3CH_2OH$

Calculate % yield, % of atom economy and % of atom utilization.

UNIT V (Objective type questions)

	Option A	Option B	Option C	Option D	Answer
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 vessel block?	1000	12	312	96	96
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 compound	The core structure of a molecule that is common to a series of compounds	The pharmacophore	The core structure of a molecule that is 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 benzene is	15ppm	20ppm	25ppm	30ppm	25ppm
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 reactions?	phosphorylases	isomerases	hydrolases	dehydrogenases	dehydrogenases
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 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
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 energy through	Collision among the molecules	Interaction among the molecules	No interaction among the molecules	Vibration Collision among the molecules	Collision among the molecules

[17CHP105A] Reg. No------------------------

Karpagam University

(Deemed University Established Under Section 3 of UGC Act 1956)
Combatore-21
(For the candidates admitted from 2017 onwards)
M.Sc. Degree Examination, November 2017
I M.Sc. Chemistry
Elective – I Greenchemistry
Internal-I

Date Maximum: 50 marks
Time: 2 hrs

Part A

Answer all the questions (20 x 1 = 20 marks)

1. Green chemistry aims to?
a. Design chemical products and process that maximise profits
b. Design safer chemical products and processes that reduce or eliminate the uso and generation of hazardous substances
c. Design chemical products and processes that work most efficiently
d. Utilize non-renewable energy

2. The first listed of the 12 principles of green chemistry is?
a. Prevent waste b. Catalysis c. Atom economy d. Benign solvents

3. An example for green chemistry is?
a. Recycled carpet b. A product made on earth day
c. A sublimation reaction **d. Bio plastics**

4. Which is fulfilling the needs of the present generation without compromising the ability of future generations to meet their needs?
a. Sustainability b. Green chemistry c. Life cycle assessment d. Recycling

5. Branch of chemistry dealing with plantation and overcoming greenhouse effect is
a. Biochemistry b. Organic chemistry
c. Environmental chemistry d. Inorganic chemistry

6. Maximum amount of ozone (O3) is present in
a. Troposphere **b. Stratosphere** c. Mesosphere d. Thermosphere

7. Biodiesel is an example of which of the 12 Principles of Green Chemistry?

2

a. Waste prevention **b. Use of renewable feedstocks**
c. Use of catalysis d. Safer solvents

8. The formation of ethene from the dehydration of ethanol can best be described as
a. an addition reaction **b. an elimination reaction**
c. an oxidation reaction d. a substitution reaction

9. Upset caused in natural balance of concentration of greenhouse gases is called
a. Pollution **b. Global warming** c. Atmospheric poisoning d. Earth heating

10. Which of the following gases is not a green house gas?
a. CO b. O_3 c. CH_4 d. H_2O vapour

11. Microwave radiation is selectively absorbed by the
a. Non polar molecules **b. Polar Molecules**
c. Asymmetric molecules d. Crystalline substances

12. The safer reagent for methylation is
a. Methyl iodide b. Dimethyl sulphate **c. Dimethyl carbonate** d. Methyl bromide

13. The Neat reaction takes place
a. In the absence of solvent b. In the absence of a solid support
c. In the absence of a catalyst d. In presence of a solvent

14. Fog is a solution of
a. Water vapors in air b. Air in water vapour c. Air in air d. Vapors in vapors

15. Among them which is green solvent
a. Benzene b. Dichloro methane **c. Super critical water** d. Ducirated water

16. Which of the following reaction gives 100% atom economy
a. Clemmenson reduction b. Elimination reaction
c. Diels alder reaction d. Aldol condensation

17. When gas liquefies, molecules lose kinetic energy and experience increase
a. Forces of attraction b. Volume c. Density d. Pressure

18. which one is an excellent 'green' solvent as well as a greenhouse gas?
a. Methanol b. CFCs c. Carbon monoxide **d. Carbon dioxide**

19. Solvents used for cleaning electronic circuit boards are
a. Chlorofluorocarbons b. Carbons c. Fluorides d. Grease

20. Ionic bonding is very strong hence it needs a
a. High temperatures b. Low temperatures c. Constant temperature d. High pressure

Part B

Answer all the questions (3 x 2 = 6 marks)

21. What do you mean by "Green Chemistry"?

22. Why catalytic reagents are superior to stoichiometric reagents?

22. What do you mean by the concept of atom economy?

Part C

Answer all the questions (3 x 8 = 24 marks)

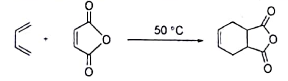
24. a. Give the twelve principles of Green Chemistry.

Or

b. How do you prepare adipic acid from renewable and non-renewable sources? Illustrate with suitable example.

25. a Calculate the atom economy of the following reactions

i)



ii) $(CH_3)_3C\text{-}Br \xrightarrow{EtONa} (CH_3)_3C{=}CH_2 + C_2H_5OH + NaOH$

Or

b. Explain the term water as solvent by giving suitable examples.

26. a. Illustrate the solvent less reactions with the suitable examples.

Or

b. What are ionic liquids? Explain advantage of ionic liquids in synthesis? Write the synthesis of some the common ionic liquids by giving specific example.

[17CHP105A] **Batch: 2017-2019**

KARPAGAM ACADEMY OF HIGHER EDUCATION
(Deemed to be University Under Section 3 of UGC Act 1956)
COIMBATORE-641 021

DEPARTMENT OF CHEMISTRY
I M.Sc., CHEMISTRY
Elective – I Green chemistry

Internal Test I- Answer Key

Part A

1. b. Design safer chemical products and processes that reduce or eliminate the use and generation of hazardous substances
2. a. Prevent waste
3. d. Bio plastics
4. a. Sustainability
5. c. Environmental chemistry
6. b. Stratosphere
7. b. Use of renewable feedstocks
8. b. an elimination reaction
9. b. Global warming
10. a. CO
11. b. Polar Molecules
12. c. Dimethyl carbonate
13. a. In the absence of solvent
14. a. Water vapours in air
15. c. Super critical water
16. c. Diels alder reaction
17. a. Forces of attraction
18. d. Carbon dioxide
19. a. Chlorofluorocarbons
20. a. High temperatures

Part B

21. Green chemistry, also called sustainable chemistry, 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.

22. Catalysts are selective in their action in that the degree of reaction that takes place is controlled

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

Part C

24. Twelve principles of Green Chemistry.

- It is better to prevent waste than to treat or clean up waste after it is formed.
- Synthetic methods should be designed to maximize the incorporation of all the materials used in the process into the final product.
- 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.
- Chemical products should be designed to preserve efficiency of function while reducing toxicity
- The use auxiliary substances (e.g. solvents, separating agents) should be made unnecessary wherever possible and innocuous when used.
- Energy requirements should be recognized for their environmental and economic impacts and should be minimized.
- A raw material or feedstock should be renewable rather than depleting, whenever technically and economically practicable.
- Unnecessary derivatization (blocking group, protection, deportation, temporary modification of physical/chemical processes) should be avoided whenever possible.
- Catalytic reagents (as selective as possible are superior to stoichiometric reagents.
- 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.

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

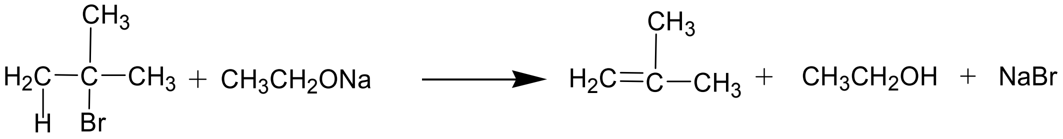
Or

b. How do you prepare adipic acid from renewable and non-renewable sources? Illustrate with suitable example.

25. a.

$$(CH_3)_3C\text{-}Br \xrightarrow{EtONa} (CH_3)_3C{=}CH_2 + C_2H_5OH + NaOH$$

Equation



$$H_2C(H)\text{—}C(CH_3)(Br)\text{—}CH_3 + CH_3CH_2ONa \longrightarrow H_2C{=}C(CH_3)\text{—}CH_3 + CH_3CH_2OH + NaBr$$

(**7**) (**8**) (**9**) (**10**) (**2**)

Table 6 Atom Economy Equation 5

Reagents Formula	Reagents FW	Utilized Atoms	Weight of Utilized Atoms	Unutilized Atoms	Weight of Unutilized Atoms
(7) C_4H_9Br	137	4C,8H	56	HBr	81
(8) C_2H_5ONa	68	—	0	2C,5H,O,Na	68
Total 6C,14H,O,Br,Na	205	4C,8H	56	2C,6H,O,Br,Na	149

% Atom Economy = (FW of atoms utilized/FW of all reactants) X 100

= (56/205) X 100 = 27%

economy is a result not only of the loss of the HBr but also because this is a base promoted reaction and all of the atoms of the sodium ethoxide base are found in unwanted side products.

Or

b.

Water as a solvent for organic reactions

Despite the fact that it is the cheapest, safest and most non toxic **solvent** in the world, its presence is generally avoided through the dehydrative drying of substrates and **solvents**. The use of **water** as a medium for **organic reactions** is therefore one of the latest challenges for modern **organic** chemists.

Organic Synthesis in Water

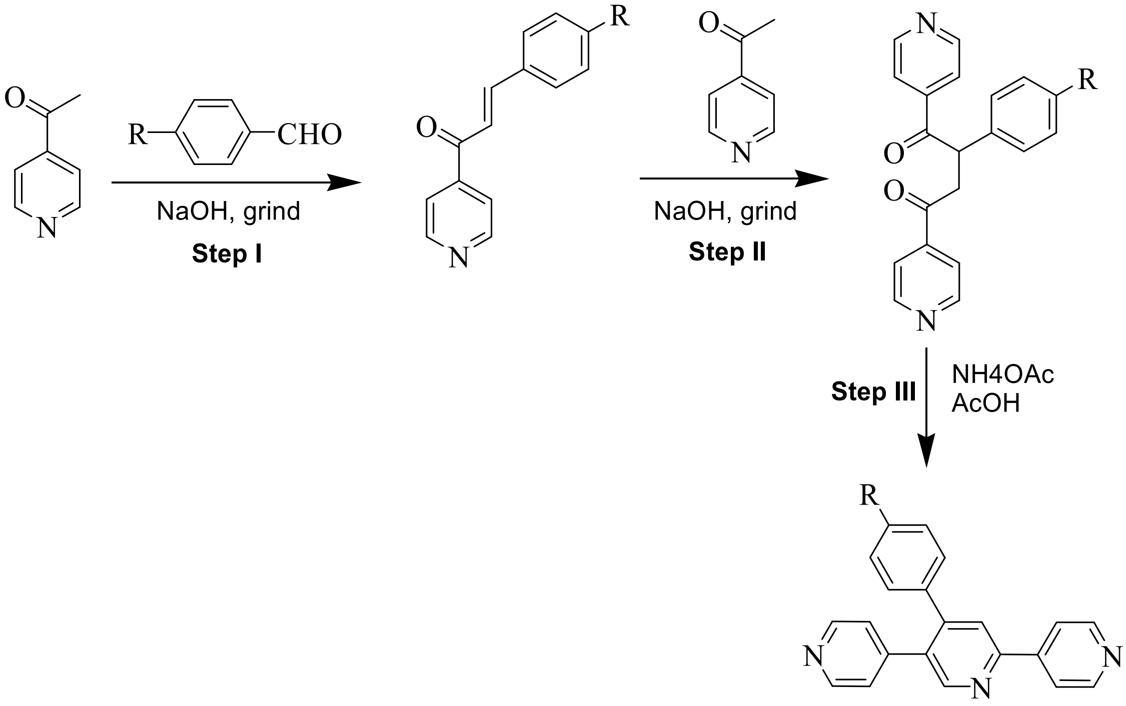
Although water is considered a problem for organic synthesis and the purification processes and drying in final products is very cumbersome, in recent years water is considered a good solvent for organic reactions. A good example is the synthetic routes of the Diels-Alder reactions in which the hydrophobic properties of some reagents makes water an ideal solvent. Water as a solvent accelerates some reactions because some reagents are not soluble and provides selectivity. The low solubility of Oxygen is also an advantage for some reactions where metal catalysts are used. In the last years water is used in many methods for organic reactions Water plays an essential role in life processes; however its use as a solvent has been limited in organic synthesis. Despite the fact that it is the cheapest, safest and most non toxic solvent in the world, its presence is generally avoided through the dehydrative drying of substrates and solvents.

1 Dehydrogenation, Hydrogenation, Halogenation and Dehalogenation
2 Allylations
3 Coupling of Acyl Chlorides and Alkynes
4 Heck Reaction
5 Wittig Reaction
6 Mannich-type Reactions
7 Intramolecular Diels-Alder Reaction
8 Deprotection of Functional Groups
9 Acetates, Alkyl Ethers and Acetals

26. a.

Solvent less process

The toxicity and volatile nature of many organic solvents, particularly chlorinated hydrocarbons that are widely used in huge amounts for organic reactions have posed a serious threat to the environment. Thus, design of solvent less catalytic reaction has received tremendous attention in recent times in the area of green synthesis. 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 to achieve high degree of stereo selectivity in the products, to reduce by-products, to maximize rate of reaction.



Step 1: Aldol condensation reaction - no solvent required

Step 2: Michael Addition reaction - no solvent required

Step 3: The only stage that requires solvent, but no purification of the dione precursor is required

❖ Both steps 1 and 2 are fast and quantitative, (in EtOH, yields of both steps are 50%)

Advantages

➢ Energy-efficient because Process reduces primary energy consumption by over 75%, compared with conventional Process

- Environmentally friendly because it eliminates the need to use hazardous organic solvents
- Likely to result in new tackifier products made with a mixture of resins having different melting points and different solubility properties
- Cost-effective because it allows adhesives to be made in a single step
- Adaptable because process can be used with commercially available equipment, yielding further cost savings
- Could open new markets for manufacturers of tackifiers or resins because dry, pulverized resins can be shipped instead of emulsions
- Faster than conventional processes

Disadvantages of solvent-free syntheses:

- Solvents are often still required during work-up (e.g. extraction)
- Poor heat transfer in the solid state (although this may be overcome using microwaves)

Or

b. **IONIC LIQUIDS**

An ionic liquid (IL) is a salt in the liquid state. In some contexts, the term has been restricted to salts whose melting point is below some arbitrary temperature, such as 100 °C (212 °F). While ordinary liquids such as water and gasoline are predominantly made of electrically neutral molecules, ionic liquids are largely made of ions and short-lived ion pairs. These substances are variously called liquid electrolytes, ionic melts, ionic fluids, fused salts, liquid salts, or ionic glasses. They are known as "solvents of the future" as well as "designer solvents".

Ionic liquids are described as having many potential applications. They are powerful solvents and electrically conducting fluids (electrolytes). Salts that are liquid at near-ambient temperature are important for electric battery applications, and have been considered as sealants due to their very low vapor pressure.

Any salt that melts without decomposing or vaporizing usually yields an ionic liquid. Sodium chloride (NaCl), for example, melts at 801 °C (1,474 °F) into a liquid that consists largely of sodium cations ($Na+$) and chloride anions ($Cl−$). Conversely, when an ionic liquid is cooled, it often forms an ionic solid-which may be either crystalline or glassy.

The ionic bond is usually stronger than the Van der Waals forces between the molecules of ordinary liquids. For that reason, common salts tend to melt at higher temperatures than other solid molecules. Some salts are liquid at or below room temperature. Examples include compounds based on the 1-Ethyl-3-methylimidazolium (EMIM) cation and include: EMIM:Cl, EMIM dicyanamide, $(C_2H_5)(CH_3)C_3H_3N+2 \cdot N(CN)-2$, that melts at −21 °C (−6 °F);[4] and 1-butyl-3,5-dimethylpyridinium bromide which becomes a glass below −24 °C (−11 °F).

Low-temperature ionic liquids can be compared to ionic solutions, liquids that contain both ions and neutral molecules, and in particular to the so-called deep eutectic solvents, mixtures of ionic and non-ionic solid substances which have much lower melting points than the pure compounds. Certain mixtures of nitrate salts can have melting points below 100 °C.

75 copies

[17CHP105A] Reg. No-------------------

Karpagam University

Karpagam Academy Of Higher Education

(Deemed University Established Under Section 3 of UGC Act 1956)
Coimbatore-21
(For the candidates admitted from 2017 onwards)
M.Sc. Degree Examination, November 2017
I M.Sc. Chemistry
Elective – I Green chemistry
Internal-II

Date: Maximum: 50 marks
Time: 2hrs

Part A

Answer all the questions (20 x 1 = 20 marks)

1. Which of the following reaction gives 100% atom economy
   a. Clemmenson reduction b. Elimination reaction
   c. Diels alder reaction d. Aldol condensation
2. Microwave reactions are faster than thermal reaction
   a. True b. False c. Not applicable d. None of above
3. Which of the following is the greenest solvent?
   a. Formaldehyde b. Benzene c. Ethanol d. Water
4. Diels alder reaction is a
   a. [3+1] cycloaddition b. [4+2] cycloaddition
   c. [2+2] cycloaddition d. [2+2] cycloaddition
5. Which is a chemical reaction that removes a carboxyl group and releases carbon dioxide?
   a. Decarboxylation b. Demethylation c. Dehydration d. Dehydrogenation
6. Which is an organic cheletropic reaction?
   a. Hofmann elimination b. Hetero diels alder reaction
   c. Retro-Diels–Alder reaction d. Simmons–Smith reaction
7. Ultrasound energy is a type of
   a. Electrical energy b. Chemical energy c. Mechanical energy d. Kinetic energy
8. Primary alcohols can be oxidized to form
   a. Aldehydes and hydrocarbons b. Carboxylic acid and hydrocarbons
   c. Aldehyde and carboxylic acids d. Ketones and carboxylic acids
9. Adipic acid is otherwise called as
   a. Hexanedioic acid b. Pentadioic acid c. Propadioic acid d. Butadioic acid
10. One of the raw materials used in the preparation of Nylon-6,6 is
    a. Adipic acid b. Succinic acid c. Tartaric acid d. Lactic acid
11. Which is used in the Strecker synthesis?
    a. Formaldehyde b. Diethanol amine c. DMC d. Potassium carbonate
12. In the conventional method for the preparation of ibuprofen, the atom economy is
    a. 10% b. 77% c. 50% d. 40%
13. Disodium iminodiacetate is an essential reactant in manufacturing of
    a. Pesticides b. Fertilizers c. Insecticides d. Herbicides
14. The critical temperature of super critical carbon dioxide
    a. 304.25 K b. 309.25 K c. 292.95 K d. 404.25 K
15. Using a biocatalyst in a reaction makes it
    a. Environmentally friendly b. Unattractive
    c. Economically unviable d. Environmentally unviable
16. Example for green oxidants
    a. Oxygen b. Chromates c. Permanganates d. Iodides
17. Example for a biocatalyst
    a. Enzymes b. Raney Nickel c. Zeolites d. Aluminium chloride
18. An example for a renewable resource
    a. Crude oil b. Petroleum c. Diesel d. Biomass
19. D-glucose is used to prepare adipic acid is manufactured from
    a. Agricultural wastes b. Animal protein c. Petroleum d. Animal fats
20. Which of the following is an extracellular enzyme?
    a. Catalase b. DNA polymerase c. Keratin d. Trypsin

Part B

Answer all the questions (3 x 2 = 6 marks)

21. What are the advantages of ultrasound synthesis?
22. What is meant by green solvents? Give an example.
23. Give the significance of biocatalysis.

Part C

Answer all the questions (3 x 8 = 24 marks)

24. a. Give the detailed account on Diels-Alder reactions under microwave and ultra sonification methods.

(OR)

b. Explain the following reactions

i) Hoffmann elimination reaction   ii) Simmons-Smith reaction

25. a. Outline the conventional route of synthesis of Ibuprofen. Give the greener synthesis of this drug? What are the major advantages in this greener synthesis?

(OR)

b. Discuss the following green synthesis reactions

i) Adipic acid   ii) Disodium iminodiacetate.

26. a. Give the detailed account on biomass conversion.

(OR)

b. Write notes on proliferation of solvent less reactions.

……

[17CHP105A] **Batch: 2017-2019**

KARPAGAM ACADEMY OF HIGHER EDUCATION
(Deemed to be University Under Section 3 of UGC Act 1956)
COIMBATORE-641 021

DEPARTMENT OF CHEMISTRY
I M.Sc., CHEMISTRY
Elective – I Green chemistry

Internal Test II- Answer Key

1. c. Diels alder reaction
2. a. True
3. d. Water
4. b. [4+2] cycloaddition
5. a. Decarboxylation
6. d. Simmons–Smith reaction
7. c. Mechanical energy
8. c. aldehyde and carboxylic acids
9. a. hexanedioic acid
10. a. Adipic acid
11. a. Formaldehyde
12. d. 40%
13. d. herbicides
14. a. 304.25 K
15. a. Eco friendly
16. a. oxygen
17. a. Enzymes
18. d. biomass
19. a. Agricultural wastes
20. d. trypsin

Part B

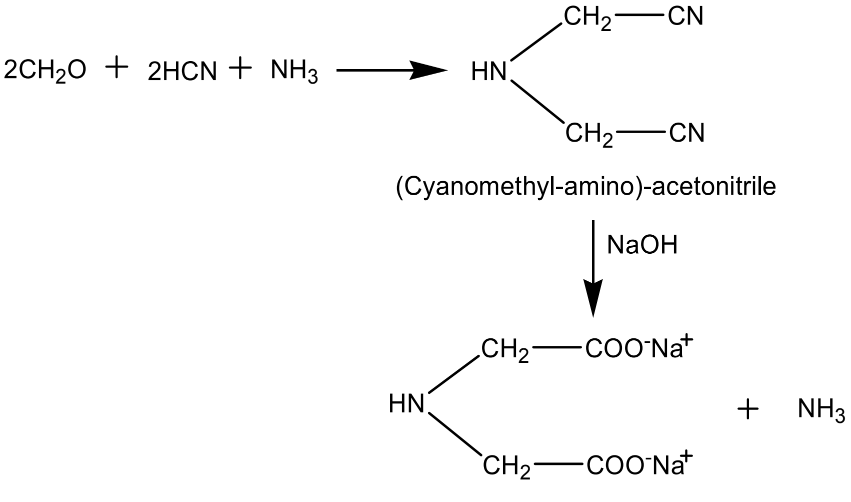
21.

- The increasing requirement for environmentally clean technology that minimizes the production of waste at source.
- Ultrasound may offer cleaner reactions by improving product yields and selectivities, enhancing product recovery and quality through application to crystallization and other product recovery and purification processes.
- Ultrasound enhances the rates of reactions.
- Sonicatiion allows the use of non-activated and crude reagents as well as an aqueous solvent system, therefore it is friendly and non-toxic.

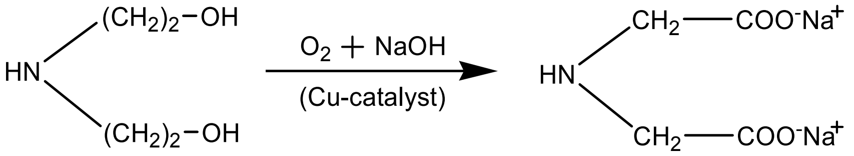
22. Disodium iminodiacetate (Na_2ida):

Disodium iminodiacetate is an essential reactant in manufacturing an herbicide. Conventional route uses the hazardous chemicals like formaldehyde and HCN while the green synthesis (developed by Monsanto) does not use any much hazardous substances.

Strecker Synthesis:



Green Synthesis of Disodium iminodiacetate:
(Alternative to Strecker synthesis)



Dsodium iminodiacetate

22.

a) Very high enantioselectivity

b) Very highr egioselectivity

c) Transformation under mild conditions

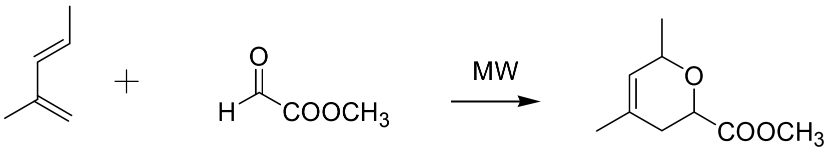
d) 'Green chemistry' e.g. solvent often water

Part C

24. a.

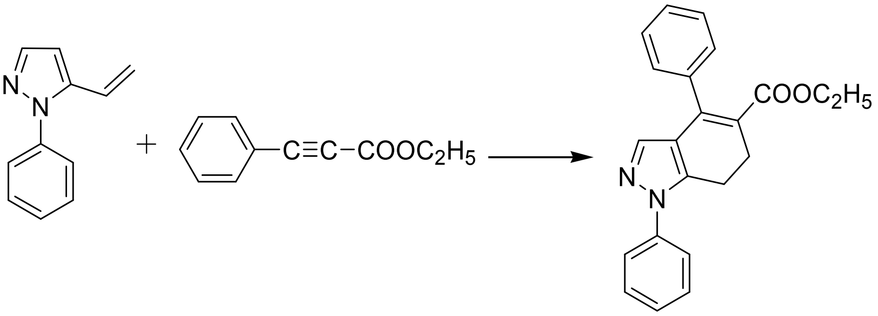
Microwave assisted Diels-Alder reaction

Diels-Alder reactions were carried out methylgloxylate in water at 140ºC gives 82% adduct product obtained after 3 hours. Whereas, microwave irradiation reactions reduce the reactions time to 8 minutes.



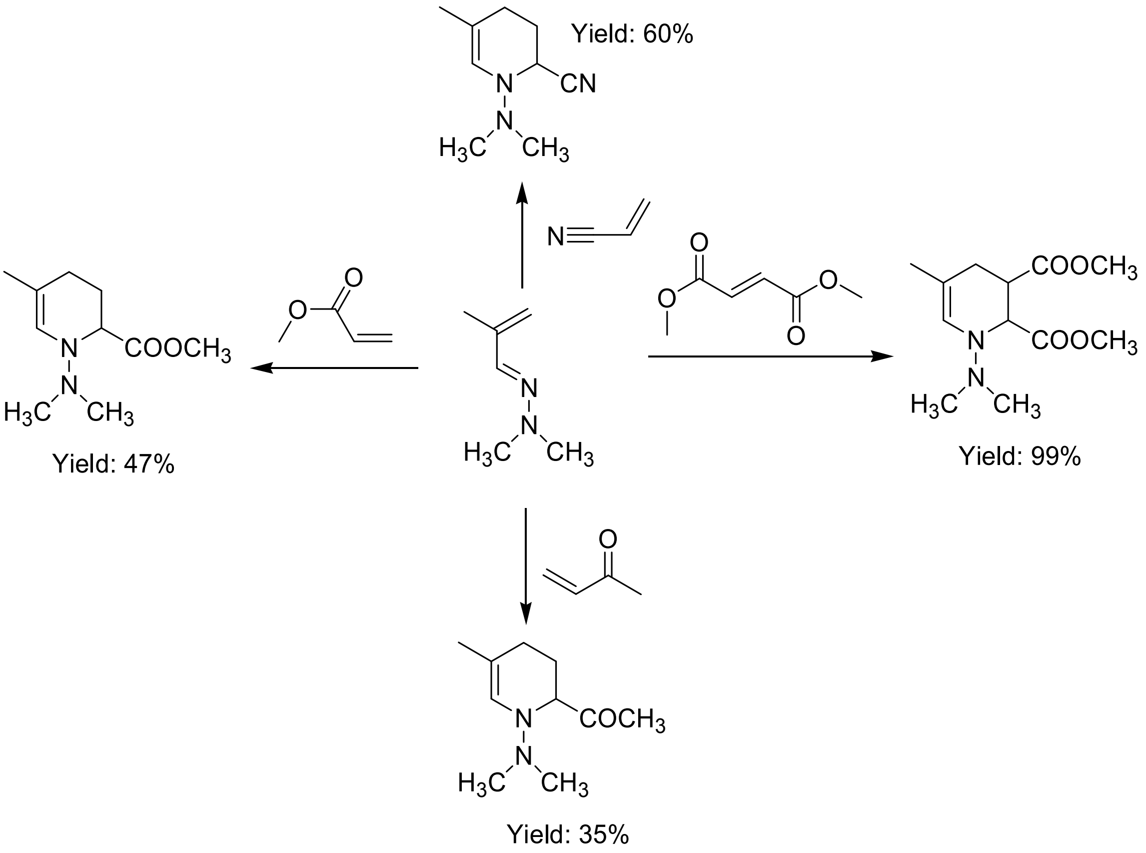
Solvent: H_2O, Time: 8 min, Yield: 80
Solvent: No Solvent, Time: 10 min, Yield: 96

The microwave assisted cycloaddition of pyrazole with the poorly reactive dienophile ethylphenyl-propiolate is significant, under the classical thermal reaction conditions (140˚C, 6 days) only polymerization or decomposition product were obtained.



Ultrasound-Assisted Diels-alder reactions

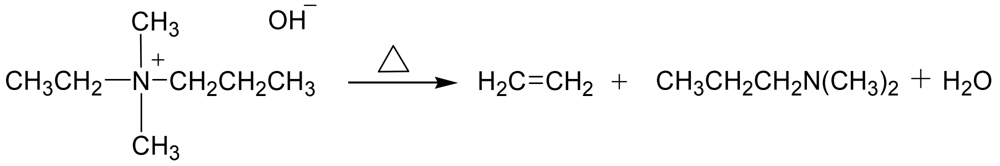
Sonication of Diels-Alder reactions of 1-dimethylamino-3-methyl-azadiene with electron-deficient dienohiles by using diene as solvent or in acetonitrile. Ultrasound irradiation which allows mild reaction condition gave good yields.



(OR)

b. Hofmann elimination

Hofmann elimination reaction used to synthesis the olefins from quaternary ammonium hydroxides.

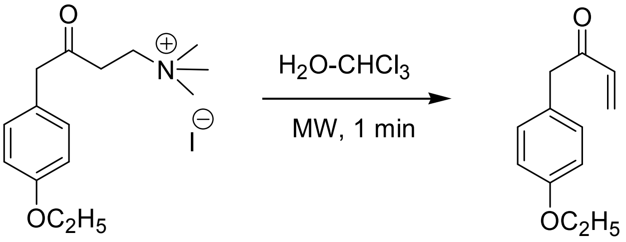


$$CH_3CH_2-\overset{+}{N}(CH_3)_2-CH_2CH_2CH_3\ \ OH^- \xrightarrow{\triangle} H_2C{=}CH_2 + CH_3CH_2CH_2N(CH_3)_2 + H_2O$$

This reaction results in the formation of a double bond between α-carbon and β-carbon atom.

Hofmann elimination under Microwave Irradiation

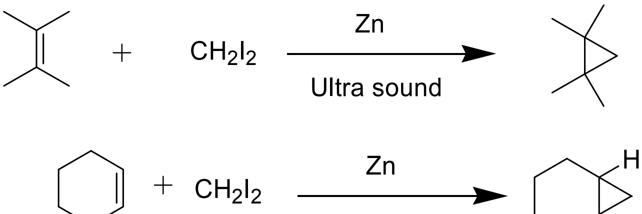
On microwave irradiation reactions carried out in water-chloroform mixture solvent, the quaternary ammonium salts converted into an olefin compound.

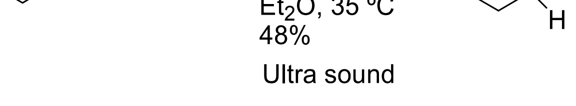


From the microwave irradiation reaction, the yields are twice than those obtained by traditional methods.

ii) Simmons-Smith reaction

This reaction affords the cyclopropanation of olefins.

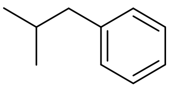




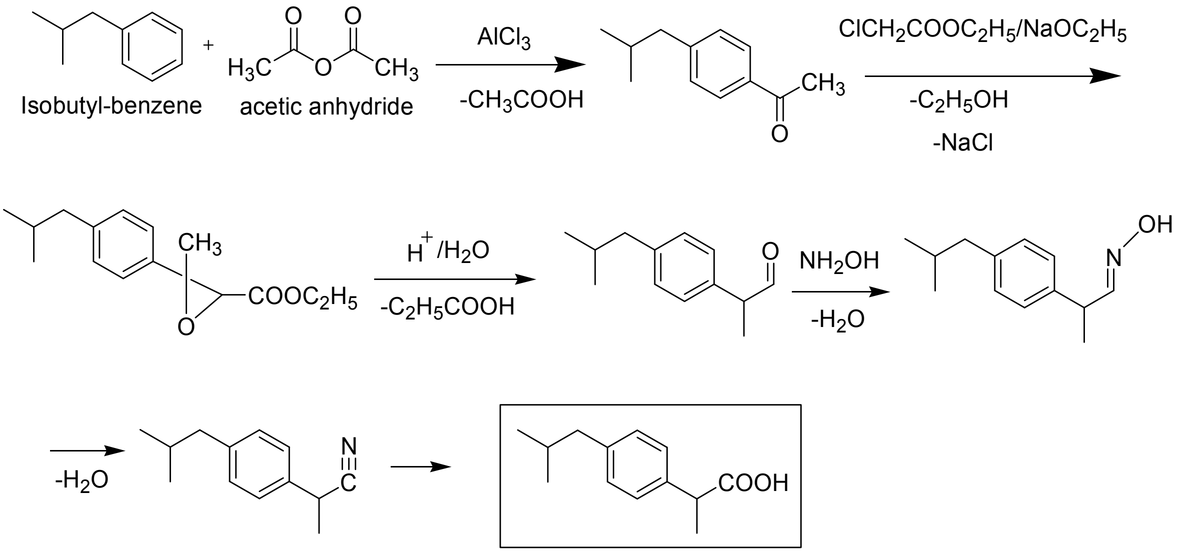
25. a.

Boots' synthesis of ibuprofen

Boots' method of making ibuprofen described in their patent starts from the compound 2-methylpropylbenzene that can be made from compounds separated from crude oil. This compound has a similar carbon skeleton to that of ibuprofen



2-methypropyl benzene



2-(4-Isobutyl-phenyl)-propionic acid

(Ibuprofen)

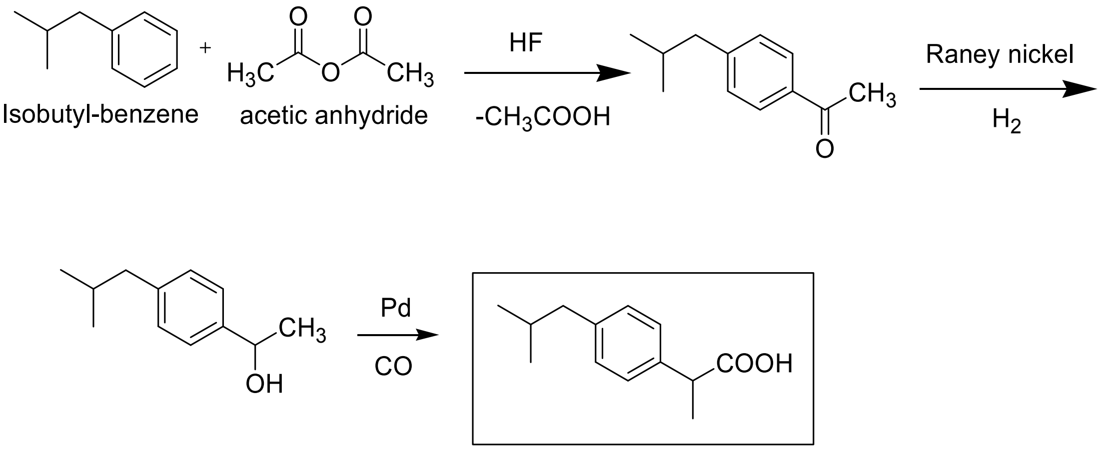
Atom economy = 40%

The overall figure is 40%. This means that more than half the materials used in the synthesis are wasted. Since the UK market for ibuprofen is about 3000 tonnes (3000 000 kg) per year this is an awful lot of waste

Green synthesis of ibuprofen

The ibuprofen patent ran out in the mid-1980s. Prior to that, only Boots had the right to make and sell the drug. The patent system protects the interests of companies that develop drugs, and allows them to sell patented drugs exclusively, normally for 20 years (although by the time the drug gets to the market, there is usually only about ten years left to run).

This allows them to recoup the money spent on a drug’ s development and also make a profit, some of which will go on investment in new drugs. After the patent ran out, any company could make and sell the drug. A new company, called BHC, was formed to develop a new ‘green’ synthesis of ibuprofen and to sell the pain-killer. This consortium developed an alternative synthesis of ibuprofen from the same starting material in just three steps. The calculation of the overall atom economy; it is 77% - almost double that of the Boots’ synthesis.



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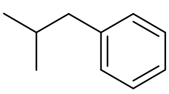
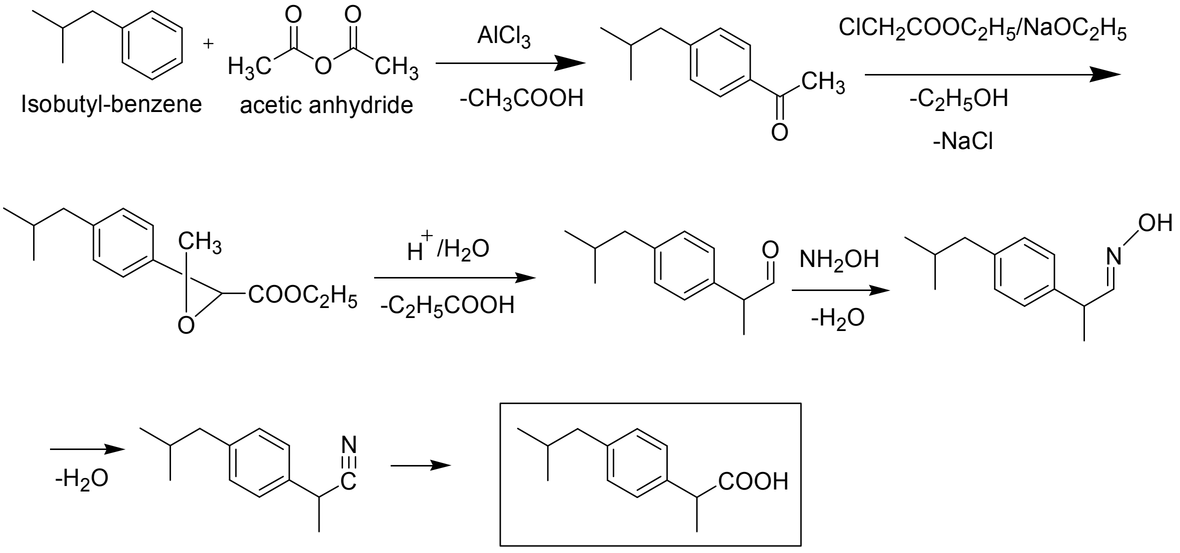


2-methypropyl benzene



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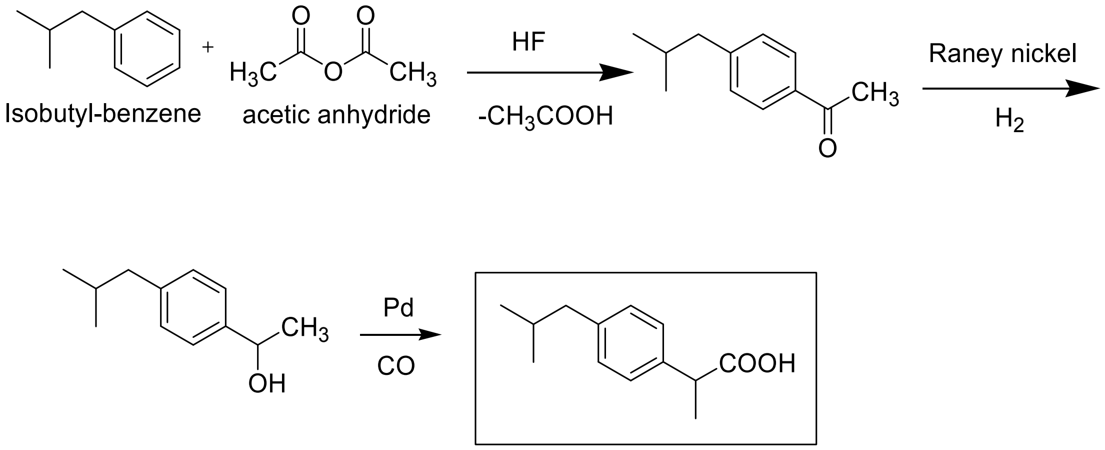


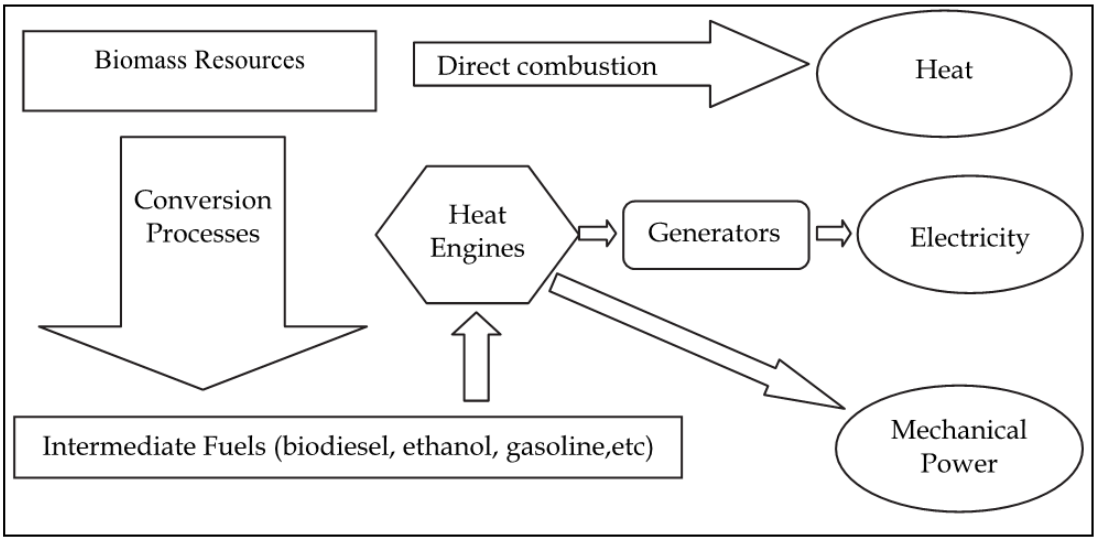
(Ibuprofen)

Atom economy = 77%

26. a.

Biomass Conversion

In general, biomass-to-energy conversion technologies have to deal with a feedstock which can be highly variable in mass and energy density, size, moisture content, and intermittent supply. Therefore, modern industrial technologies are often hybrid fossil - fuel/biomass technologies which use the fossil fuel for drying, preheating and maintaining fuel supply when the biomass supply is interrupted.



Thermochemical Processes

These processes do not necessarily produce useful energy directly, but under controlled temperature and oxygen conditions are used to convert the original biomass feedstock into more convenient forms of energy carriers, such as producer gas, oils or methanol. These carriers are either more energy dense and therefore reduce transport costs, or have more predictable and convenient combustion characteristics allowing them to be used in internal combustion engines and gas turbines and these are:

a) Pyrolysis.
b) Carbonisation.
c) Gasification.
d) Catalytic Liquefaction.

a). Pyrolysis

Pyrolysis is the application of heat to a feedstock in the absence of oxygen to break down the long chain molecules into short chain molecules. Typically the feedstock is biomass or waste, and the process is used to produce a syngas (a mixture of hydrogen, volatile organic compounds, and carbon monoxide). Varying the process conditions allows the production of fluids similar to diesel, and a variety of other products.

A more detailed understanding of the physical and chemical properties governing the pyrolytic reactions has allowed the optimisation of reactor conditions necessary for these types of pyrolysis. Further work is now concentrating on the use of high pressure reactor conditions to produce hydrogen and on low pressure catalytic techniques (requiring zeolites) for alcohol production from the pyrolytic oil. The advantage of pyrolysis and gasification are that they convert solid material into gases and vapours which are less costly to handle, transport and store. The gases will burn in boilers, gas turbines and reciprocating engines increasing fuel flexibility and security. Capturing and combusting the methane and carbon monoxide in syngas makes use of the energy in the gas and produces carbon dioxide which is a less potent greenhouse gas than methane and offsets fossil fuel energy production. The disadvantages of pyrolysis and gasification are that they require heat input to drive the chemical reactions that produce a syngas. Thus some fuel must be used to generate the syngas.

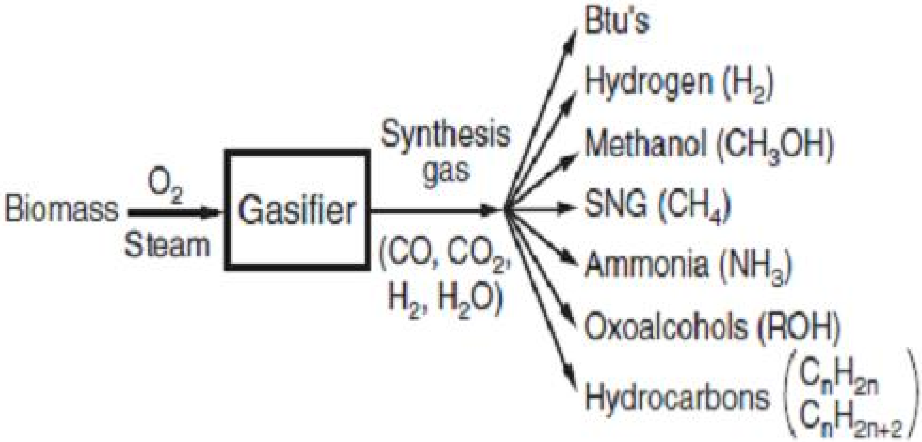
b). Carbonisation

This is an age old pyrolytic process optimised for the production of charcoal. Traditional methods of charcoal production have centred on the use of earth mounds or covered pits into which the wood is piled. Control of the reaction conditions is often crude and relies heavily on experience. The conversion efficiency using these traditional techniques is believed to be very low; on a weight basis estimates that the wood to charcoal conversion rate for such techniques ranges from 6 to 12 tonnes of wood per tonne of charcoal. During carbonisation most of the volatile components of the wood are eliminated; this process is also called "dry wood distillation." Carbon accumulates mainly due to a reduction in the levels of hydrogen and oxygen in the wood. The wood undergoes a number of physico -chemical changes as the temperature rises. Between 100°C and 170°C most of the water is evaporated; between 170°C and 270°C gases develop containing condensible vapours, CO and CO_2. These condensible vapours (long chain carbon molecules) form pyrolysis oil, which can then be used for the production of chemicals or as a fuel after cooling and scrubbing. Between 270°C and 280°C an exothermic reaction develops which can be detected by the spontaneous generation of heat. The modernisation of charcoal production has lead to large increases in production efficiencies with large-scale industrial production in Brazil now achieving efficiencies of over 30% (by weight). There are three basic types of charcoal-making: a) internally heated (by controlled combustion of the raw material), b) externally heated (using fuelwood or fossil fuels), and c) hot circulating gas (retort or convert er gas, used for the production of chemicals). Internally heated charcoal kilns are the most common form of charcoal kiln. It is estimated that 10 to 20% of the wood (by weight) is sacrificed, a further 60% (by weight) is lost through the conversion to, and release of, gases to the atmosphere from these kilns. Externally heated reactors allow oxygen to be completely excluded, and thus provide better quality charcoal on a larger scale. They do, however, require the use of an external fuel source, which may be provided from the "producer gas" once pyrolysis is initiated. Re-circulating heated gas systems offer the potential to generate large quantities of charcoal and associated by-products, but are presently limited by high investment costs for large scale plant.

c). Gasification

Gasification is the partial oxidation of an organic feedstock to produce a syngas (a mixture of hydrogen, volatile short chain organic compounds, and carbon monoxide). Typically the feedstock is biomass or waste, and varying the process conditions allows control over proportions of the compounds in the syngas. In this approach to the development of fixed carbon supplies from renewable carbon resources is to convert CO_2 outside the biomass species to synthetic fuels and organic intermediates. The ambient air, which contains about 360 ppm by volume of CO_2, the dissolved CO_2 and carbonates in the oceans, and the earth's large carbonate deposits, could serve as renewable carbon resources. But since CO_2 is the final oxidation state of fixed carbon, it contains no chemical energy. Energy must be supplied in a chemical reduction step. A convenient method of supplying the required energy and of simultaneously reducing the oxidation state is to reduce CO_2 with hydrogen. The end product, for example, can be methane (CH_4), the dominant component in natural gas and the simplest hydrocarbon known, or other organic compounds. With all components in the ideal gas state, the standard enthalpy of the process is exothermic by 165 EJ (39.4 kcal) per gram mole of methane formed

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$$



d). Catalytic Liquefaction

This technology has the potential to produce higher quality products of greater energy density. These products should also require less processing to produce marketable products. Catalytic liquefaction is a low temperature, high pressure thermochemical conversion process carried out in the liquid phase. It requires either a catalyst or a high hydrogen partial pressure. Technical problems have so far limited the opportunities of this technology.

Biochemical Processes

The use of micro-organisms for the production of ethanol is an ancient art. However, in more recent times such organisms have become regarded as biochemical "factories" for the treatment and conversion of most forms of human generated organic waste. Microbial engineering has encour aged the use of fermentation technologies (aerobic and anaerobic) for use in the production of energy (biogas) and fertiliser, and for the use in the removal of unwanted products from water and waste streams.

i) Anaerobic Fermentation.

ii) Methane Production in Landfills.

iii) Ethanol Fermentation.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{Catalyst}]{\text{Invertase}} \underset{\text{Fructose}}{C_6H_{12}O_6} + \underset{\text{Glucose}}{C_6H_{12}O_6}$$

$$\underset{\text{Fructose (OR) Glucose}}{C_6H_{12}O_6} \xrightarrow[\text{Catalyst}]{\text{Zymase}} \underset{\text{Ethanol}}{2C_2H_5OH} + 2CO_2$$

i). Anaerobic Fermentation

Anaerobic digestion is the microbial digestion of feedstock releasing heat, methane, hydrogen sulphide, carbon dioxide and under specific conditions hydrogen gas. This process takes place over several days in large tanks where the ideal conditions are maintained. After the process the remaining solid digestate is suitable for use as fertiliser and the gases released are collectively referred to as biogas. This gas can be used as a fuel in a CHP scheme once the gas has been cleaned to remove acidic compounds by condensation. Anaerobic reactors are generally used for the production of methane rich biogas from manure (human and animal) and crop residues. They utilise mixed methanogenic bacterial cultures which are characterised by defined optimal temperature ranges for growth. These mixed cultures allow digesters to be operated over a wide temperature range i.e. above 0°C up to 60°C. When functioning well, the bacteria convert about 90% of the feedstock energy content into biogas (containing about 55% methane), which is a readily useable energy source for cooking and lighting. The sludge produced after the manure has passed through the digester is non-toxic and odourless. Also, it has lost relatively little of its nitrogen or other nutrients during the digestion process thus, making a good fertiliser. In fact, compared to cattle manure left to dry in the field the digester sludge has a higher nitrogen content; many of the nitrogen compounds in fresh manure become volatised whilst drying in the sun. The advantage of anaerobic digestion is that it naturally occurs to organic material and would release methane, a potent greenhouse gas, into the atmosphere. Capturing and combusting the methane makes use of the energy in the gas and produces carbon dioxide which is a less potent greenhouse gas than methane and offsets fossil fuel energy production.

The disadvantages of anaerobic digestion are that the microbes required pose a health threat to people and livestock. The microbes are sensitive to changes in the feedstock, especially the presence of anti -microbial compounds, and changes in the reactor conditions: they require constant circulation of the reactor fluid, and a constant operating temperature and pH. Anaerobic digesters of various types were widely distributed throughout India and China. Extension programmes promote biogas plants as ideal candidates for rural village use due to their energy and fertiliser production potential along with their improved health benefits. Health benefits primarily arise from the cleaner combustion products of biogas as opposed to other biomass or fossil fuels which may be used in the domestic environment. Reliability problems have arisen from a number of problems i.e. construction defects, the mixed nature of the bacterial population, the digesters requirements for water & maintenance of optimum nitrogen ratio of the medium. Another problem is the digester's demand for dung, which may have alternative uses.

ii). Methane Production in Landfills

Methane is a powerful greenhouse gas, with substantial amounts being derived from unutilized methane production from landfill sites. Its recovery therefore, not only results in the stabilisation of the landfill site, allowing faster reuse of the land, but also serves to lessen the impact of biospheric methane emissions on global warming. Anaerobic digestion in landfills is brought about by the microbial decomposition of the organic matter in refuse. The levels of organic matter produced per capita vary considerably from developed to developing countries e.g. the percentage of Municipal Solid Waste (MSW) which is putrescible in Sierra Leone is about 90% compared to about 60% for US MSW. Commercial production of land -gas can also aid with the leaching problems now increasingly associated with landfill sites. Local communities neighbouring land fill sites are becoming more aware of the potential for heavy metals and nutrients to leach into aquifers. Landfill processing reduces the volume of sludge to be disposed of, and the nutrient content, thus facilitating proper disposal.

iii). Fermentation

Ethanol is mainly used as a substitute for imported oil in order to reduce their dependence on imported energy supplies. The substantial gains made in fermentation technologies now make the production of ethanol for use as a petroleum substitute and fuel enhancer, both economically competitive (given certain assumptions) and environmentally beneficial. The most commonly used feedstock in developing countries is sugarcane, due to its high productivity when supplied with sufficient water. Where water availability is limited, sweet sorghum or cassava may become the preferred feed stocks. Other advantages of sugarcane feedstock include the high residue energy potential and modern management practices which make sustainable and environmentally benign production possible whilst at the same time allowing continued production of sugar. Other feed stocks include saccharide-rich sugar beet, and carbohydrate rich potatoes, wheat and maize. Recent advances in the use of cellulosic feedstock, may allow the competitive production of alcohol from woody agricultural residues and trees to become economically competitive in the medium term.

(b).

Emission control

“Emission control means employed to limit the discharge of noxious gases from the internal-combustion engine and other components. There are three main sources of these gases: the engine exhaust, the crankcase, and the fuel tank and carburettor”.

The following engine parameters have large influence on emissions and hence have undergone substantial modifications since the pre-emission control era.

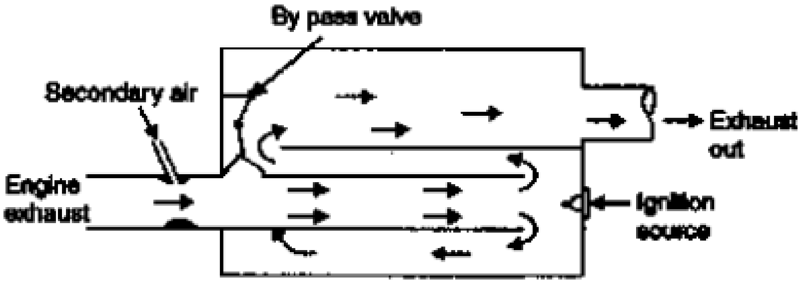
- Modification in the engine design and operating parameters
- Treatment of exhaust products of combustion
- Modification of the fuels

Modification in the Engine Design and Operating Parameters

- Modification of combustion chamber involves avoiding flame quenching zones where combustion might otherwise be incomplete and resulting in high HC emission. This includes: Reduction of surface to volume (SAT) ratio, Reduction of surface to volume (SAT) ratio, Reduction of surface to volume (SAT) ratio, Reduced space around piston ring.
- Lower compression ratio: Lower compression ratio reduces the quenching effect by reducing the quenching area, thus reducing HC. Lower compression ratio also reduces NO emissions due to lower maximum temperature. Lower compression, however, reduces thermal efficiency and increases fuel consumption.

Treatment of exhaust products of combustion

The exhaust gas coming out of exhaust ma The exhaust gas coming out of exhaust manifold is treated to reduce CO emissions. The devices used to accomplish are after burner , exhaust manifold reactor and catalytic converter.



Direct flame-after burner

After burner is a burner where air is supplied to the exhaust gases and mixture is burnt with the help of ignition system. The HC and CO which are formed in the engine combustion because of inadequate O_2 and inadequate time to burn are further brunt by providing air in a separate box, known as after burner.

Exhaust manifold reactor is a further development of after-burner where the design is changed so as to minimize the heat loss and to provide sufficient time for mixing of exhaust and secondary air.

A catalytic converter is a device which is placed in the vehicle exhaust system to reduce HC and CO by oxidizing catalyst and NO by reducing catalyst.

Modification of the fuels

The ability of a fuel to burn in mixtures leaner than stoichiometric ratio is a rough indication of its potential emission reducing characteristics and reduced fuel consumption. If gasoline is changed to propane as engine fuel CO emission can substantially be reduced with reduced HC and NO and in changing from propane to methane the CO as well HC emission touch zero level and only the NO remains as a significant factor. From pollution point of view both methane and steam reformed hexane are very attractive fuels but we are unable to use at present for want of technological progress.

(OR)

b. Write notes on proliferation of solvent less reactions.

Proliferation of solventless reactions:

Aristotle believed that "***No reaction occurs in the absence of solvent***."

(This is not true!)

Introduction

The earlier belief that no reaction is possible without the use of a solvent is no more valid. It has been found that a large number of reactions occur in solid state without the solvent. Infact in a number of cases, such reactions occur more efficiently and with more selectivity compared to reactions carried out in solvents. Such reactions are simple to handle, reduce pollution, comparatively cheaper to operate and are especially important in industry. It is believed that solvent free organic synthesis and transformations are industrially useful and largely green. Green chemistry, also called sustainable chemistry, is a chemical philosophy encouraging the design of products and processes that reduce or eliminate the use and generation of hazardous substances.

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.

Need of solvents in chemical reactions:

- 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 in reactions:

- 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:

- Use of solventless reactions
- Use of "non-organic" solvents
- Processing technology

Advantages to Solventless 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.

Solvent-Free synthesis

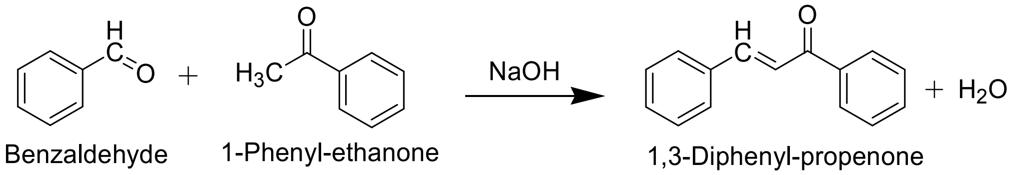
- Neat – reagents react together in the liquid phase in the absence of a solvent.
- Solid-state synthesis– two macroscopic solids interact directly and form a third, solid product without the intervention of a liquid or vapour phase.

➢ Generally solventless reactions are atom efficient reaction:

Solvent free synthesis of chalcones:

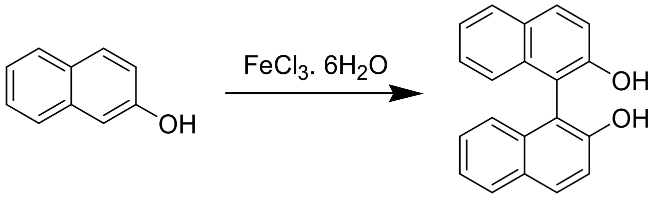
The synthesis of chalcones illustrates the reaction that proceeds with high atom economy and is relatively easy to perform in teaching labs. Chalcones are important compounds with applications in medicine and physics.

In 2004, ***Palleros*** was found that the reactions proceed rapidly and afford very good yields of product. Most of the chalcones can be obtained in a matter of minutes by mixing the corresponding benzaldehyde and acetophenone in the presence of solid NaOH in a mortar with pestle; the yields of crude product were in the range 81-94%.



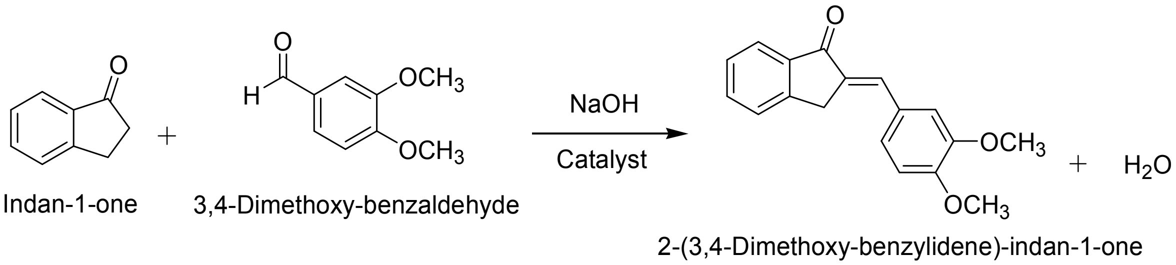
Oxidative coupling Reaction of phenols with FeCl$_3$:

Oxidative couplings of phenols are usually carried out by treatment of phenols in solution with more than equimolar amount of metal salts such as FeCl$_3$ or manganese tris(acetylacetonate), although the latter one is too expensive to use in a large quantity. The coupling reaction of phenols with FeCl$_3$, some times quinines as byproducts.



In 1989, Toda have reported that some oxidative coupling reactions of phenols with FeCl$_3$ are faster and more efficient in the solid state than in solution. Some coupling reactions in the solid state were accelerated by irradiation with ultrasound. Some coupling reactions are achieved by using a catalytic amount of FeCl$_3$.

The Crossed-Aldol Condensation



Limitations of solvent free reactions

- Not all reactions will work in the absence of solvent.
- Function of catalysts.
- Exothermic reactions are potentially dangerous.
- Specialized equipment needed for some procedures.
- If aqueous quench and organic extraction are performed, this reduces green benefits.

Use of non-organic solvents

- Liquid and supercritical CO2
- Ionic liquids
- Fluorous Phase Chemistry
- Water

Green chemistry in ecofriendly safe reaction follows the solvent-free or solid state reaction carried out using the reactants alone or incorporating them in clays, zeolites, silica, alumina or other matrices to achieve high degree of stereoselectivity in the products, to reduce byproducts, to maximize rate of reaction.