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5.1 Introduction

[May 2008 !]

- The *knowledge of chemistry* and all the developments in different branches of chemistry during last few decades have given many useful products to mankind, e.g. *medicines, fabrics, insecticides, drugs, dyes,rubber ,petrol, etc are few to mention.*

- The *dependence of humans* on all these formulations/products is *increasing* day by day and hence with growing populations *more* number of *industries* are established to produce *these products in large quantity.*

- The *chemical reactions* involved are always associated with certain *by-products* which are *harmful for the environment* and cause severe pollution problems.

- In fact all the *chemicals are toxic in varying extent.* Hence, to *minimize* the problems of *environmental pollution and hazardous waste* it became necessary to *review and modify* all the chemical processes used for manufacture .

- Thus design of harmless processes to produce various products has emerged as a new branch commonly known as "clean chemistry" or *"Green Chemistry" or "Environmentally benign chemistry".*

- *Green Chemistry* came into existence more than a decade back is now *becoming very popular.*

- It includes any chemical process or technology that improves the environment and thus our quality of life.

- Green chemistry is a highly *effective approach* to pollution prevention because it applies innovative scientific solutions to real-world environmental situations.

5.2 Goals /Objectives of Green Chemistry

[May 2008, Dec. 2008 !]

- The primary mission of the Green Chemistry and Engineering is the dissemination of current and pertinent information to professionals in chemistry and chemical engineering.

- The goals of the green chemistry and engineering target the professional both from industry and academia.

- Those who are actively involved in the future of our planet understand the importance of *using science to* further a flourishing and *sustainable chemical industry.*

- The *objective* of green chemistry is to *minimize* the environmental *pollution* caused due to chemical processes. Hence it aims to design harmless chemical processes with respect to

  1. chemicals used
  2. products formed
  3. byproducts generated
  4. waste generated from the process
  5. energy requirement

- The green chemistry utilizes a *set of principles* that reduces or eliminates the use or generation of hazardous substances in the manufacture and facilitates the formation of product which is safe for the use.

- The set of these principles is known as *"12 principles of Green Chemistry"*.

- The 12 Principles of Green Chemistry, originally suggested by *Paul Anastas and John Warner, are well accepted* by the chemists *all over the world.*
- As a chemical philosophy, green chemistry derives from organic chemistry, inorganic chemistry, biochemistry, analytical chemistry, even physical chemistry.
- The philosophy of green chemistry tends to focus on industrial applications.
- *It is distinct from environmental chemistry* which focuses on chemical phenomena in the environment.

The principles cover such concepts as :

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

5.3 The Twelve Principles of Green Chemistry

1. Prevention of waste
2. Maximise Atom economy
3. Non-hazardous chemical
4. Safer chemical
5. Auxiliary Substances

6. Energy efficiency

7. Renewable feedstocks

8. Derivatisation

9. Catalysts

10. Degradable products

11. New Analytical methods

12. Accident prevention

We will discuss each of these principles in brief,

1. Prevention of waste

- It is better to prevent waste than to treat and clean up waste after it is formed.
- It has been a common practice to *dump* waste on land or in water or released in air. This resulted in soil, water and air pollution.
- This made the legislation to be stringent on industries and hence there was compulsion to have waste treatment and disposal units attached to the manufacturing plants. Thus the cost of process increased considerably.
- Thus green chemistry involved to design chemical syntheses in such a way that the process involves pathway to give products, leaving no waste to treat or clean up. "Prevention is better than the cure"

2. Maximize atom economy

- The design of the synthesis of the product should be such that all the chemicals/materials used in the process converted into the products to the maximum extent.
- It is common observation that most of the *organic reactions release undesired products* along with the useful products of the reaction.
- The unutilized material is considered as waste which causes trouble and the process becomes uneconomical.
- Green chemistry requires that new processes should be designed such that the most of the starting material gets converted into product. This is called as *Maximising atom economy.* This is explained further as ;

Atom Economy

The theoretical yield for every reaction can be calculated as,

$$\text{Theoretical yield} = \text{Stoichiometric ratio} \times \left[\frac{\text{Molecular weight of the desired product}}{\text{Molecular weight of limiting reagent}}\right] \times \text{weight of limiting reagent}$$

On conducting the reaction the experimental or actual yield of the process is obtained. From this percentage yield is calculated.

$$\text{Percentage yield} = \left[\frac{\text{Actual yield}}{\text{Theoretical yield}}\right] \times 100$$

e.g. Preparation of n-propyl bromide from n-propyl alcohol (0.6 g)

$$CH_3CH_2CH_2\text{-}OH + NaBr + H_2SO_4 \longrightarrow CH_3CH_2CH_2Br + NaHSO_4 + H_2O$$

Mol Wt = 60 103 98 Mol Wt. 123 120 18

Thus 1 mole of reactant gives one mole of product

Hence

$$\text{Theoretical yield} = \text{Stoichiometric ratio} \times \left[\frac{\text{Molecular weight of the desired product}}{\text{Molecular weight of limiting reagent}}\right] \times \text{Weight of limiting reagent}$$

$$= \frac{1}{1} \times \left[\frac{123}{60}\right] \times 0.6$$

$$= 1.23 \text{ gms}$$

But actually yield of the above reaction is found to be 0.99 gms

$$\text{Hence percentage yield} = \frac{0.99}{1.23} \times 100$$

$$= 80.49\ \%$$

Atom economy can be calculated by using following formula,

$$\%\ \text{Atom economy} = \frac{\text{Molecular weight of product}}{\text{Total molecular weight of reactants}} \times 100$$

$\therefore$ In above reaction, % atom economy can be calculated as,

$$\%\ \text{Atom economy} = \frac{\text{Molecular weight of n-propyl bromide}}{\text{Molecular weight of (n-propanol + NaBr)}} \times 100$$

$$= \frac{123}{60 + 103} \times 100$$

$$= \frac{123}{163} \times 100$$

$$= 75.5\%$$

Other examples for understanding the efficiency of reaction is given here,

Preparation (synthesis) of Maleic Anhydride

Maleic Anhydride can be prepared by oxidation of

a) Benzene

b) Butene

c) Butane

I)

I) + $4.5\,O_2$ $\xrightarrow{V_2O_5}$ + $2CO_2 + 2H_2O$

Benzene

Mol.wt. 78 $\quad 4.5 \times 32 = 144$ $\quad$ 98

$$\% \text{ Atom economy} = \frac{98}{78 + 144} \times 100$$

$$= \frac{98}{222} \times 100$$

$$\boxed{\therefore \% \text{ Atom economy} = 44.1\%}$$

II)

$$C_4H_8 + 3O_2 \longrightarrow C_4H_2O_3 + 3H_2O$$

Butene

Mol. Wt. = 56 $\quad 3 \times 32 = 96$ $\quad$ 98

$$\% \text{ Atom economy} = \frac{98}{56 + 96} \times 100$$

$$= \frac{98}{152} \times 100$$

$$\boxed{\therefore \% \text{ Atom economy} = 64.5\ \%}$$

III)

$$C_4H_{10} + 2.5\,O_2 \longrightarrow C_4H_2O_3 + 4H_2O$$

Butane

Mol. wt. = 58 $\quad 2.5 \times 32 = 80$ $\quad$ 98

$$\% \text{ Atom economy} = \frac{98}{58 + 80} \times 100$$

$$= \frac{98}{138} \times 100$$

$$\boxed{\therefore \% \text{ Atom economy} = 71.0\ \%}$$

Thus for different reaction atom economy can be calculated and thus the process giving maximum atom economy can be selected.

The processes with *90 % yield* and *higher atom* economy are considered as *excellent* and those with *20 % yield* and *lower atom economy* are *poor*.

Thus it becomes essential to design synthesis so that the final product contains the maximum proportion of the starting materials thereby increasing the atom economy. There should be few, if any, wasted atoms.

3. Non -hazardous chemical synthesis

- The synthetic method should be designed wherever practicable to use and generate substances having little or no toxicity to human health and the environment.

- The starting material selected should be least toxic. Thus e.g. pyridine, or β-naphthyl amine being known to be carcinogenic should be avoided as starting materials.

- The reactions in which intermediates or reagents or products are toxic, should not be followed. In stead alternative pathways should be used for synthesis.

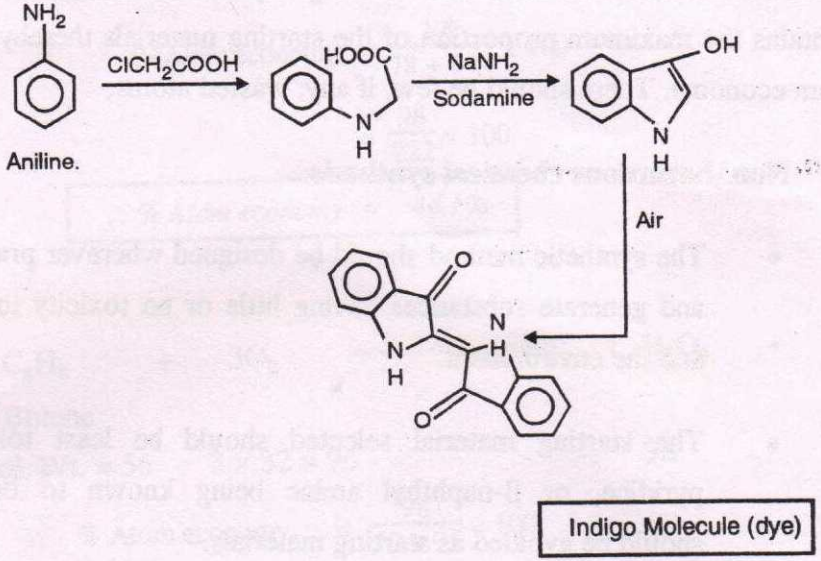
- For example : In 1984, due to leakage of MIC at Bhopal there was major casualty and the after effects of the same are still suffered by many. This compound MIC is an intermediate in manufacture of agricultural pesticides and was known to be highly poisonous.

- Hence green chemistry recommends the design of synthesis to use and generate substances with little or no toxicity to humans and the environment.

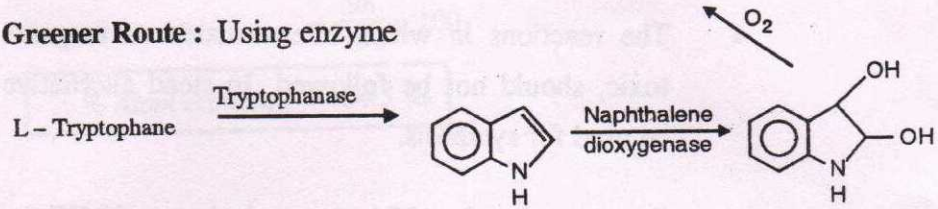
- Other example is of synthesis of indigo as given below

Synthesis of Indigo

(A) Conventional Route using hazardous Aniline



(B) Greener Route : Using enzyme



4. Design safer chemicals and products

- The chemical products should be designed to preserve the efficiency of desired function while reducing toxicity.

- When any medicinal formulations are to be put in market , they are put first on trials to check their toxic effects on humans.

- If found to be toxic then alternatives are prepared keeping in mind the function of the medicine but only toxicity reduced.

- Similarly in many insecticides like *DDT, gamaxane, aldrin* etc which are found to be *toxic to humans*, the use of these is *curtailed* and alternatively *biological pesticides* are more in use.

- *Thus green chemistry emphasizes to design chemical products to be fully effective, yet have little or no toxicity.*

5. Auxiliary substances (Use safer solvents and reaction conditions)

- The use of auxiliary substances like solvents, separating agents etc. should be made unnecessary wherever possible and innocuous when used.

- Avoid using carcinogenic solvents, separation agents, or other auxiliary chemicals. If these chemicals are necessary, use innocuous chemicals.

- The solvents such as **acetone, benzene, ether** being highly inflammable should be *avoided.*

- Other chemicals such as CCl_4, $CHCl_3$, carry health risk hence should be *avoided.*

- If a solvent is necessary, *water is a good medium* as well as certain *eco-friendly solvents* that do not contribute to smog formation or destroy the ozone.

- For example : For *drycleaning* the fabrics, the toxic solvent like *perchloroethylene* was used, which is *replaced* during recent years by *liquid* CO_2.

6. Energy efficiency

- The energy requirements of chemical processes should be minimized considering their environmental and economic impacts. The synthetic methods should be carried out at ambient temperature and pressure wherever possible.

- The aim of green chemistry is to increase energy efficiency.

- This can be achieved by use of catalysts, and by stopping the use of fossil / gaseous fuels which release solid or gaseous pollutants.

- The recently found substitutes are microwave radiations and ultra sound, which are used in the processes requiring very less energy.

- The energy efficiency of process can be increased by

  a) *proper heat transfer and*

  b) *minimal wastage of energy during the process.*

- Many chemical are produced by *fermentation* process where energy requirement is low and also the products are less harmful

7. Use renewable feedstock

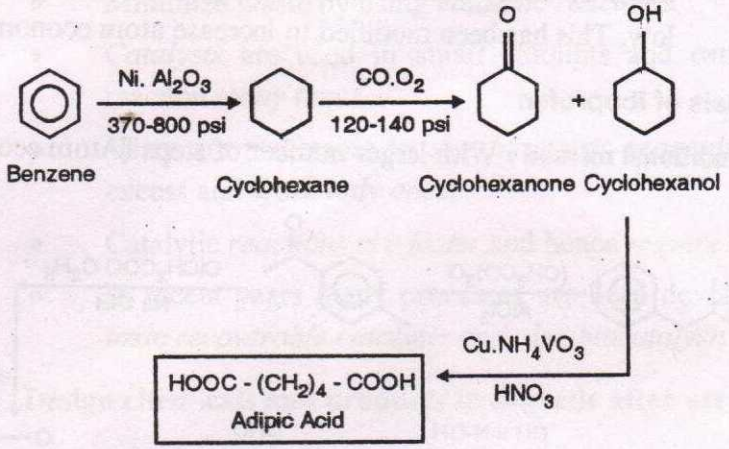
- The raw materials should be renewable rather than depleting, wherever technically and economically feasible.

- Renewable feedstock are often made from agricultural products or are the wastes of other processes; depleting feedstock are made from fossil fuels (petroleum, natural gas, or coal) or are mined.

- For example : A new method is developed to prepare adipic acid from glucose obtained from corn starch or cellulose. This is green process because it *replaces benzene* as starting material for production of same product. *Benzene* is a known *carcinogen.*

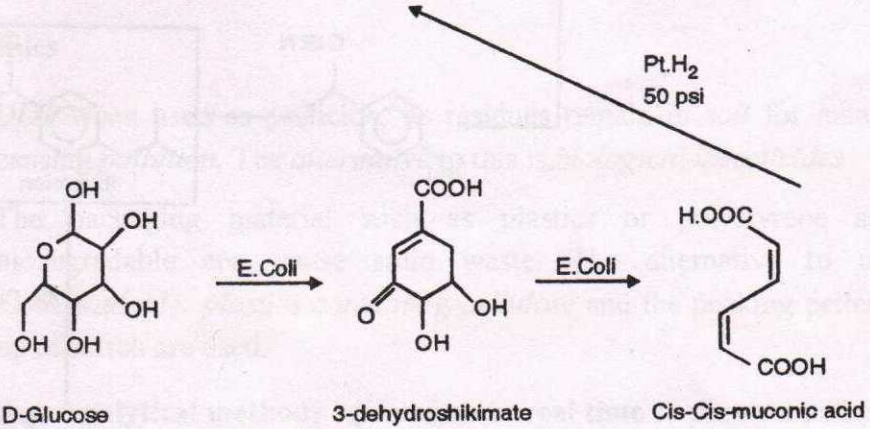
Synthesis of Adipic Acid

(A) Traditional pathway : Using Benzene (Carcinogenic solvent)



(B) Greener pathway

Using glucose (absolutely safe)



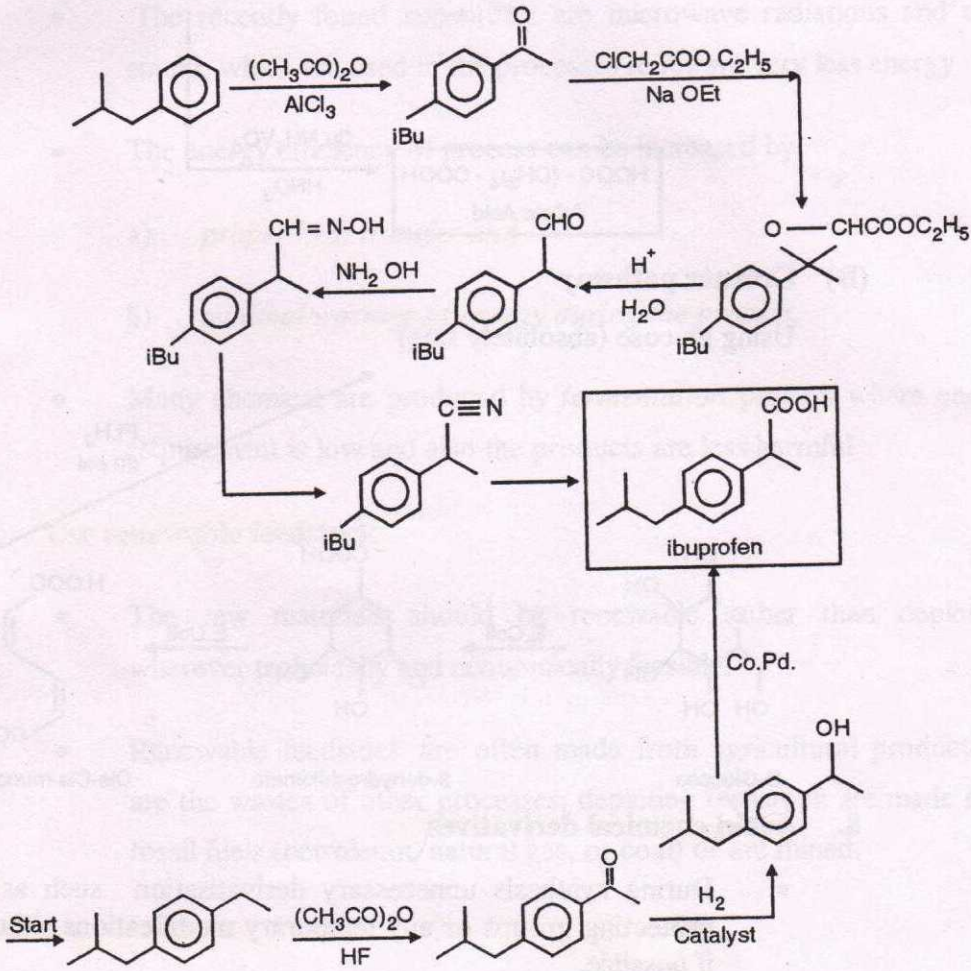
8. Avoid chemical derivatives

- During synthesis unnecessary derivatisation such as blocking or protecting groups or any temporary modifications should be avoided if possible.

- The use of derivatives *increases the steps* of the process
- The additional reagents are required
- It generates more waste products
- To avoid these effects, alternative reagents are to be used which are more *selective*.
- Example : *Synthesis of Ibuprofen* is given below where in traditional pathway larger number of steps are involved, and atom economy is low. This has been modified to increase atom economy.

Synthesis of Ibuprofen

(A) **Traditional method :** With larger number of steps (Atom economy = 40 %)



(B) Alternative Synthesis

With the atom economy = 77 %

and recoverable catalyst.

9. Use catalysts, not stoichiometric reagents

- The catalytic reagents which are selective are preferred over stoichiometric reagents.
- Minimize waste by using *catalytic reactions.*
- *Catalysts* are used in small amounts and can carry out a single reaction *many times.*
- They are preferable to *stoichiometric reagents,* which are used in excess and work *only once.*
- Catalytic *reactions are faster* and hence *require less energy.*
- In recent years many processes are been developed which use *non toxic recoverable catalysts and also biocatalysis.*

10. Design chemicals and products to degrade after use

Chemical products should be designed such that they break down to innocuous substances after use so that they do not accumulate in the environment.

Examples

1. *DDT* when used as pesticide, its residues remain in *soil* for many years causing *pollution.* The *alternative* to this is *biological insecticides.*
2. The packaging material such as plastics or polystyrene are non biodegradable and cause solid waste. The alternative to this the *biodegradable plastics containing cellulose* and the packing pellets made up of starch are used.

11. New Analytical methods : (Analyze in real time to prevent pollution)

- New analytical processes have to be developed to allow on-line monitoring and control prior to the formation of hazardous substances.

- **Example :** *Preparation of ethylene glycol*, in which if reaction conditions are not monitored perfectly, toxic substances are produced at higher temperature.

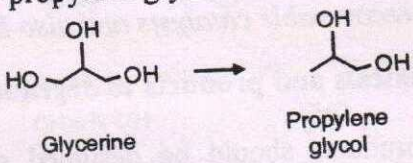
12. Minimize the potential for accidents

- The substances and its forms used in chemical process should be chosen to minimize the potential for the chemical releases, accidents, explosions and fire.
- The use of safer chemicals, minimizing temperature, pressure and using catalysts helps in minimizing the potential of accidents which is desirable.

5.4 Examples of Green Chemistry

I) Biodiesel Application

Glycerine to propylene glycol



- In 2006, Professor Galen J. Suppes, from the University of Missouri–Columbia, was awarded the Academic Award for his system of converting *waste glycerine from biodiesel* production to *propylene glycol.*
- Through the use of *a copper-chromite catalyst*, Professor Suppes was able to lower the required temperature of conversion while raising the efficiency of the distillation reaction.
- Propylene glycol produced in this way will be cheap enough to replace the more toxic ethylene glycol that is the primary ingredient in automobile antifreeze.

II) Supercritical Fluid Extraction

Introduction

- Supercritical fluids combine properties of gases and liquids in an intriguing manner, which could offer a range of applications possibilities in both synthetic and analytical chemistry.

- Supercritical carbon dioxide has found to be an energy conserving, selective and waste reducing alternatives to organic solvents and therefore is viewed as promising environmentally benign solvents. In addition, supercritical fluids can lead to reaction, which are difficult or even impossible to achieve in conventional solvents.
- Supercritical extraction is relatively new technology with a large potential for application in industry.
- The technology has been popularly preferred over conventional solvent extraction process because of environmental concerns, such as the need to eliminate organic solvents and to find appropriate technologies for their disposal.

Principle

- The basic principle of Supercritical Fluid Extraction (SFE) technology is that when the *feed material is contacted* with a *supercritical fluid* then the *volatile substances* will *partition* into the *supercritical phase.*
- After the dissolution of soluble material the supercritical fluid containing the dissolved substances is removed from the feed material.
- The extracted component is then completely separated from the supercritical fluids (SCF) by means of a temperature and/or pressure change. The SCF may then be recompressed to the extraction conditions and recycled.

Choice of Solvents of Supercritical fluid Extraction

The choice of the SFE solvents is similar to a regular extraction. Principal considerations are as follow :

- Good solvent property
- Inert to the product
- Easy separation from the product
- Low cost

Carbon dioxide is the most commonly used *SCF*, primarily due to its low critical parameters (31.1°C, 73.8 bar), low cost and non-toxicity. However, several other SCF's have also been used in industrial processes.

5.5 Industrial Applications of Green Chemistry

The green chemistry is finding wider applications in the industrial processes due to its advantages such as,

- The technology is prominently applied in the extraction and fractionation of fats, oils, essence, pigments, functional or bioactive compounds, pharmaceuticals, hop extracts, caffeine, and cholesterol.
- Applications have also been extended to many other areas such as: chemical synthesis, polymer processing, petrochemicals processing, environmental protection (Cleaning solvents, removal of pollutants from waste water, soil remediation), biotechnology etc.

5.5.1 Green Chemicals : Prospects and Future in Designing New Drugs

Introduction

The biodiversity of plants and microbes is an unending resource for newer chemical templets. It provides information on the synergy of molecular tools like *genomics, proteomics* and *advanced bioanalytical technique* for development of new drugs or new molecules.

5.5.2 Plants as a Sources of New Drugs/Biomolecules

- Plants have been playing an important role in the field of pharmacy, not only in ancient times but also in the arena of modern drug discovery.
- The chemical diversity of plants gives the important clew for synthesis of different efficient pharmacophores in pharmaceutical drug design.
- Examples like Mepridine (Demerol), Pentazocine (Darvon), are totally synthetic drugs for which opiates such as morphine and codeine were the models.
- Japanese research group has recently isolated Stilbene derivative from the bark of a *Shorea hemsleyana* (dipterocarpeaceae) and roots of Cyphostemma bainessi (Vitaceae).
- The active compound identified is Hemsleyanol-D is a potent antibacterial agent Methicillin resistant staphylococcus aureus (MRSA) responsible for variety of human diseases.

5.5.3 Dimethyl Carbonate (Green Reagent)

The salient features of DMC can be summarised as follows :

- *Dimethylcarbonate (DMC)* is a valuable methylating reagent which can replace methyl halides and dimethylsulphate in the methylation of a variety of compounds.
- It possesses adequate reactivity andvery good selectivity towards mono-*C*- and mono-*N*-methylation in the reactions of acidic CH_2 and primary aromatic amines, respectively.
- In addition, it is a prototype example of a *green reagent*, since it is
  - (i) Nontoxic,
  - (ii) Made by a clean process,
  - (iii) Biodegradable, and
  - (iv) It reacts in the presence of a catalytic amount of base
  - (v) It helps avoiding the formation of undesirable inorganic salts as by-products.
- Other remarkable reactions are those where DMC behaves as an oxidant: are cyclic ketones are transformed into dimethylesters with a reaction of atom efficiency of 1.0.

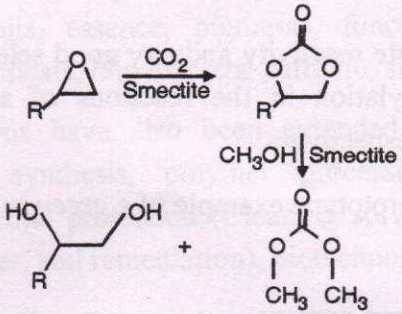
DMC can be synthesised by various processes. Two of such known methods are as follows:

Synthesis of DMC

Method 1

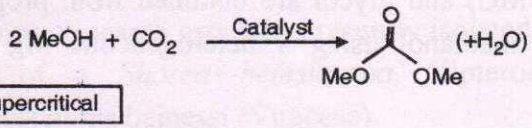
- The DMC can be obtained by two-step synthesis in which dimethyl carbonate (DMC) and glycol are obtained from propylene oxide, carbon dioxide and methanol using a heterogeneous Mg containing smectite catalyst.
- The first step, *the reaction of propylene oxide with* CO_2 to form propylene carbonate, and the

- The second step, *the trans-esterification reaction* of the cyclic carbonate such as ethylene carbonate with methanol to DMC and ethylene glycol, have been studied.
- The catalyst was found to be effective for one step synthesis of DMC, *i.e.* the sequential reaction of the epoxide, CO_2 and methanol.

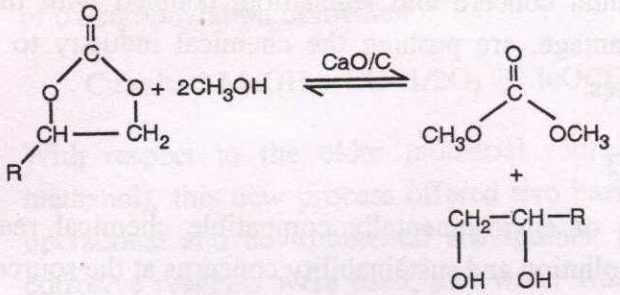


Method 2

- Supercritical carbon dioxide is efficiently converted to dimethyl carbonate (DMC) by the reaction with methanol in the presence of a catalytic amount of dialkyltin oxide or its derivatives.
- The removal of water is the key step to be accomplished for the high conversion which is done by shifting the equilibrium to dimethyl carbonate.
- Dehydration is successfully carried out by circulating the reaction mixture through a dehydrating tube packed with molecular sieve 3A.
- Under the effective dehydration conditions, the DMC yield is almost linearly dependent on the reaction time, catalyst amount, methanol concentration, and CO_2 pressure.



- Other catalysts, CaO/C composite, *a new solid base catalyst*, was prepared and served as a convenient and efficient heterogeneous for synthesis of DMC from methanol and propylene carbonate.
- Compared with pure CaO, the CaO/C shows the same basic properties and a high performance.
- In addition, the CaO/C catalyst, which is easily recovered, can be reused with little deactivation, if a suitable particle size is chosen.



Advantages of Dimethyl carbonate (DMC)

- It is a versatile compound that represents an attractive eco-friendly alternative to both methyl halides (or dimethyl sulphate) and phosgene for methylation and carbonylation processes, respectively.
- In fact, the reactivity of DMC is tunable: at T = 90°C, methoxycarbonylations take place, whereas at higher reaction temperatures, methylation reactions are observed with a variety of nucleophiles.
- In the particular case of substrates susceptible to multiple alkylations (e.g. CH_2-active compounds and primary amines), DMC allows unprecedented selectivity toward mono-C- and mono-N-methylation reactions.
- Nowadays produced by a clean process, DMC possesses properties of nontoxicity and biodegradability which makes it a true *green reagent* to use in synthesis that prevent pollution at the source.

- Moreover, DMC-mediated methylations are catalytic reactions that use safe solids (alkaline carbonates or zeolites), thereby avoiding the formation of undesirable inorganic salts as byproducts.
- The reactivity of other carbonates is reported as well, higher homologues of DMC (i.e., diethyl and dibenzyl carbonate), are excellent mono-C- and mono-N-alkylating agents,

5.6 Significance of Green Chemistry

Environmental concern and legislation, coupled with the prospect of a competitive advantage, are pushing the chemical industry to develop cleaner chemical processes.

Green chemistry

1) The design of environmentally compatible chemical reactions, helps to approach pollution and sustainability concerns at the source.

   In order to be eco-friendly, or *green, organic syntheses must meet*, if not all, at least some of the following requirements:

   - Avoid waste
   - Be atom efficient
   - *Avoid* use and production of *toxic and dangerous chemicals*, produce compounds which perform better or equal to existing ones and are biodegradable,
   - Avoid auxiliary substances (e.g., solvents),
   - Reduce energy requirements,
   - Use renewable materials,
   - Use catalysts rather than stoichiometric reagents

2) In particular, an underdeveloped area of chemistry is in the replacement of reagents which are toxic, dangerous, produced by eco-unfriendly processes, not selective, and which produce expensive-to-dispose-of inorganic salts, in short: not green.

- Examples of undesirable reagents used for methylation and carboxymethylation are

  a) methyl halides (CH_3X),

  b) dimethylsulphate (DMS), and

  c) phosgene($COCl_2$).

- For example production of dimethyl carbonate, based on the reaction of oxicarbonylation of methanol.

$$\text{Cu salts } 2\ MeOH + CO + 1/2O_2 \ |||\ MeOCO_2Me + H_2O$$

- With respect to the older industrial route (the phosgenation of methanol), this new process offered two basic advantages from the operational and environmental standpoints: it was much safer (no corrosive reagents were used, and water was the only co-product), and it allowed obtaining DMC in a high purity as a nontoxic compound.

5.7 Solved University Examples :

(3 Marks)

Ex. 5.7.1 :

Calculate the percentage atom economy for the following reaction with respect to Allyl chloride.

$$CH_3 - CH = CH_2 + CI_2 \longrightarrow CI - CH_2 - CH = CH_2 + HCI$$

Allyl chloride

Solution :

Reaction given :

$$CH_3 - CH = CH_2 + Cl_2 \longrightarrow Cl - CH_2 - CH = CH_2 + HCI\ 36.5$$

42 71 Allyl chloride (76.5)

$$\%\ \text{Atom economy} = \frac{\text{Molecular weight of product}}{\text{Total molecular wt. of reactants}} \times 100$$

$$= \frac{76.5}{42 + 71} \times 100$$

$$= \frac{76.5}{113} \times 100$$

$$= 67.7\ \%$$

Ans. : % Atom economy = 67.7%

Important Terms and Definitions

- The design of harmless processes to produce various products has emerged as a new branch commonly known as "clean chemistry" or *"Green Chemistry" or "Environmentally benign chemistry"*.
- Atom economy can be calculated by using following formula,

$$\% \text{ Atom economy} = \frac{\text{Molecular weight of product}}{\text{Total molecular weight of reactants}} \times 100$$