GREEN CHEMISTRY

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What is Green Chemistry?

Green chemistry can also be described as

- Sustainable chemistry.
- Chemistry that is benign by design.
- Pollution prevention at the molecular level.
- All of the above.

- Focus on processes and products that reduce or eliminate the use of polluting substances

- Any synthesis, whether performed in teaching, laboratories or industries should create none or minimum by-products which pollute the atmosphere

The Benefits of Green Chemistry

- Economical
- Energy efficient
- Lowers cost of production and regulation
- Less wastes
- Fewer accidents
- Safer products
- Healthier workplaces and communities
- Protects human health and the environment

WHY DO WE NEED GREEN CHEMISTRY?

- Chemistry is undeniably a very prominent part of our daily lives.
- Chemical developments bring new environmental problems and harmful unexpected side effects, which result in the need for **'greener' chemical products. Eg.** DDT.
- **Green chemistry looks at pollution prevention on the molecular scale**

It is an extremely important area of Chemistry due to the importance of Chemistry in our world today and the implications it can show on our environment.

- The **Green Chemistry program supports the invention of more environmentally friendly chemical processes which reduce or even eliminate the generation of hazardous substances.**

This program works very closely with the twelve principles of **Green Chemistry.**

12 Principles of Green Chemistry

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

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

3. **Less Hazardous Chemical Synthesis.** Whenever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. **Designing Safer Chemicals.** Chemical products should be designed to preserve efficacy of the function while reducing toxicity.

5. **Safer Solvents and Auxiliaries.** The use of auxiliary substances (solvents, separation agents, etc.) should be made unnecessary whenever possible and, when used, innocuous (harmless)

.

6. **Design for Energy Efficiency.** Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.

7. **Use of Renewable Feedstocks.** A raw material or feedstock should be renewable rather than depleting whenever technically and economically practical.

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

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

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

11. **Real-time Analysis for Pollution Prevention.** Analytical methodologies need to be further developed to allow for real-time in-process monitoring and control prior to the formation of hazardous substances.

12. **Inherently Safer Chemistry for Accident Prevention.** Substance 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.

1 . . Prevention of Waste/By-Products

- It is better to prevent waste/**By-Products** than to treat or clean up waste after it is formed
- carry out a synthesis in such a way so that formation of waste (by-roducts) is minimum or absent
- cost involved in the treatment and disposal of waste adds to the overall production cost.
- the unreacted starting materials also form part of the waste.
- if discharged causes pollution and requires expenditure for cleaning-up

2. Maximum Incorporation of the Reactants into the Final Product/ Atom economy

Synthetic methods should be designed to maximize the incorporation of all materials (**Starting materials and reagents**)used in the process into the final product.

chemists globally consider that if the yield of a reaction is above 90%, the reaction is good.

$$\text{percentage yield} = \frac{\text{actual mass of product}}{\text{theoretical mass of product}} \times 100\%$$

$$C_6H_6 + H_2SO_4 + 2NaOH \longrightarrow C_6H_5OH + Na_2SO_3 + 2H_2O$$

(12x6)
+(1x6)
=78

(12x6)
+(1x6)
+16
=88

The equation indicates that 1 mole of benzene (78g) should yield 1 mole of phenol (88g).
But other reactions take place and the actual mass of phenol will be in the region of 77g, giving a yield of about 88%.

$$\text{percentage yield} = \frac{\text{actual mass of product}}{\text{theoretical mass of product}} \times 100\%$$

$$= \frac{77}{88} \times 100\%$$

$$= 87.5\ \%$$

calculating percentage yield for phenol production

100% yield synthesis -perfectly efficient
But, it generate significant amount of waste (or byproducts) - not green synthesis.

- Green synthesis maximum incorporation of the starting materials and reagents in the final product

Atom Economy

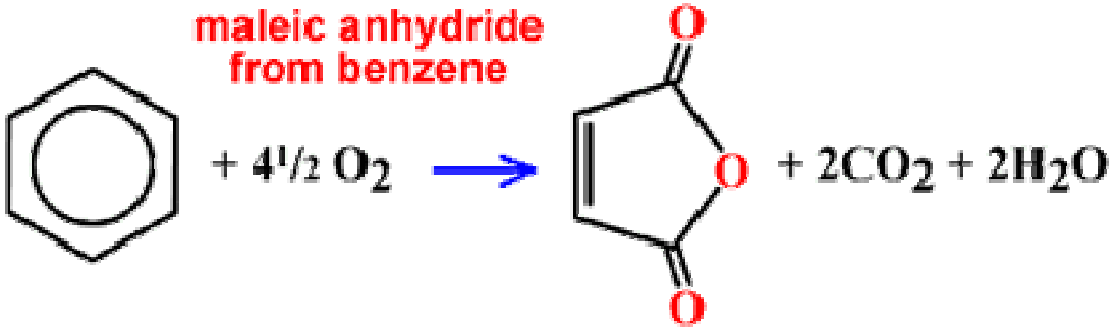
It is a method of expressing how efficiently a particular reaction makes use of the reactant atoms.

Calculation of Atom Economy

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

This approach does not take yield into account

Benzene can be oxidised to make maleic anhydride, an important intermediate chemical.



benzene	oxygen	maleic anhydride
(6 x 12)	4.5 x (2 x 16)	(4 x 12)
+(6 x 1)		+(3 x 16)
=78	=144	=96

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

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

$$= 43\%$$

The Atom Economy of this reaction is 43%, calculated using the relative formula masses. This means that 43% of the mass of the reactants ends up in the desired product.

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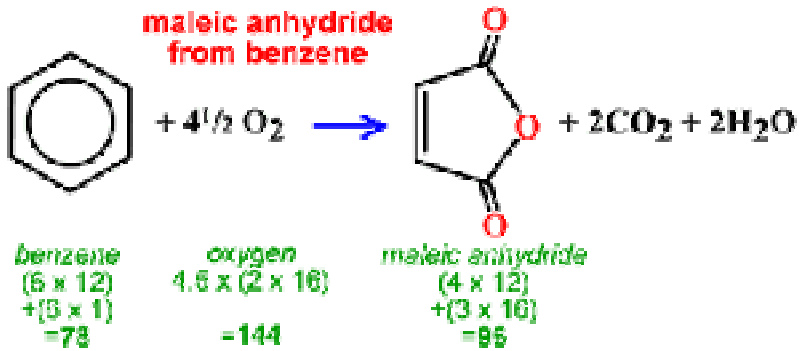

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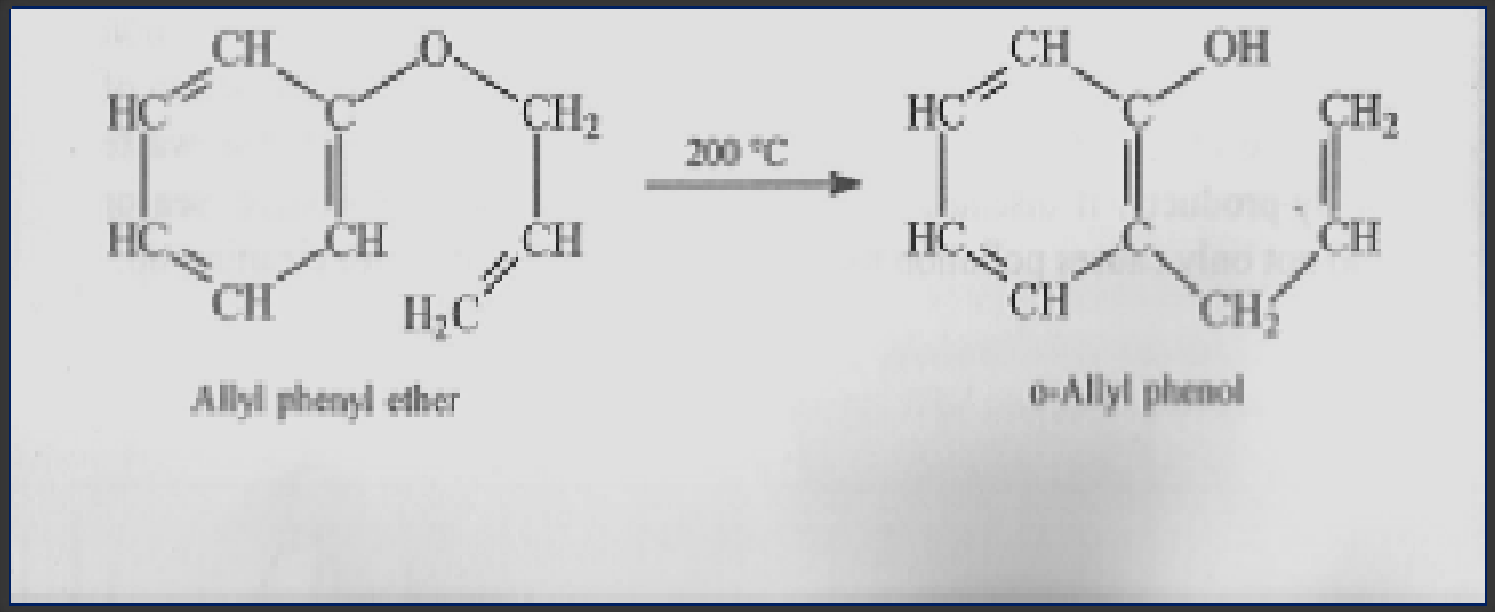
1.Rearrangement Reactions

These reactions involve rearrangement of the atoms that make up a molecule.

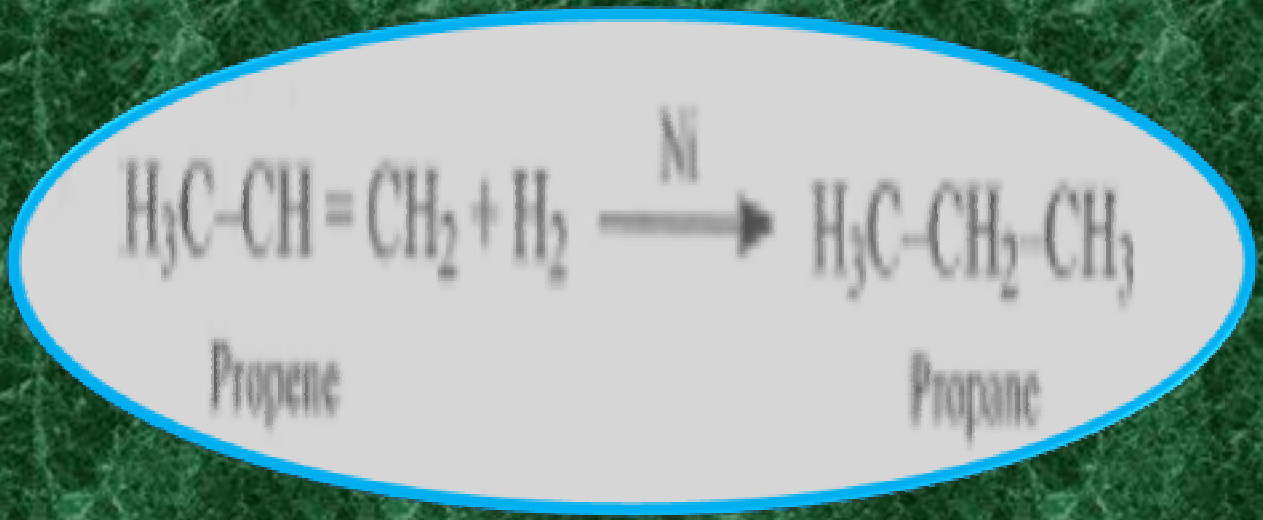
For example, allyl phenyl ether on heating at 200°C gives o-allyl phenol.

100% ATOM ECONMICAL



2 Addition Reactions

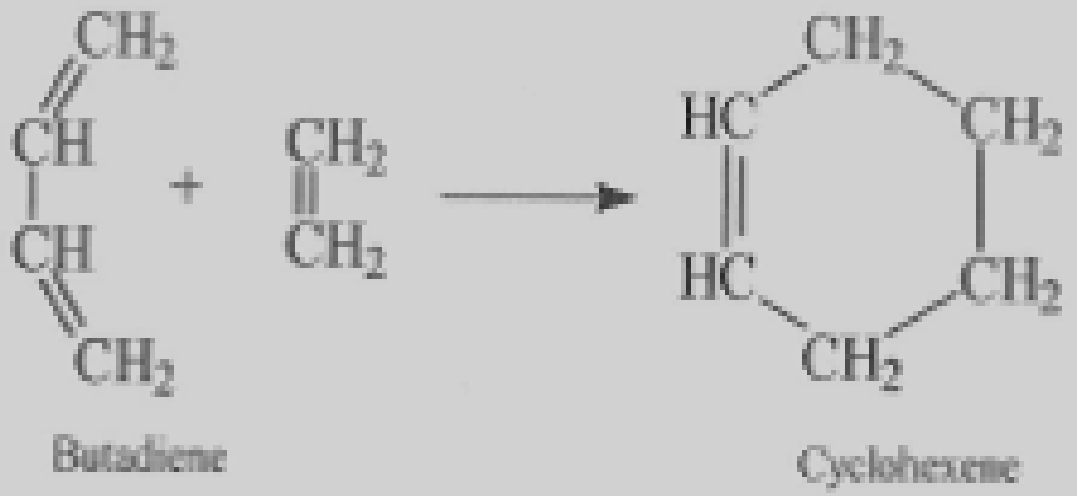
a. addition of hydrogen to an olefin



100% ATOM ECONMICAL

3. cycloaddition reactions and bromination of olefins

100% ATOM ECONMICAL

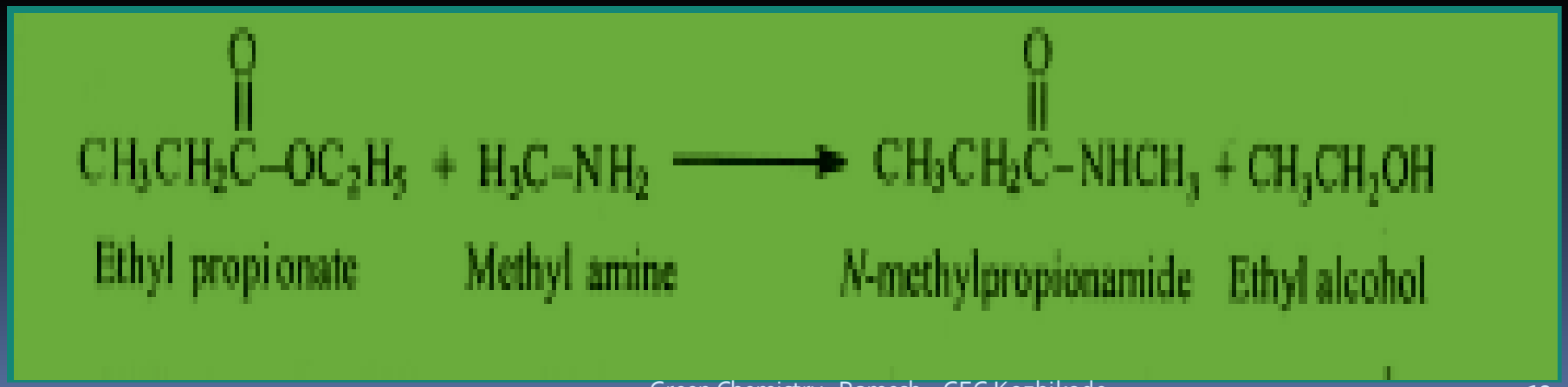


3.2.3 Substitution Reactions

4. substitution reactions

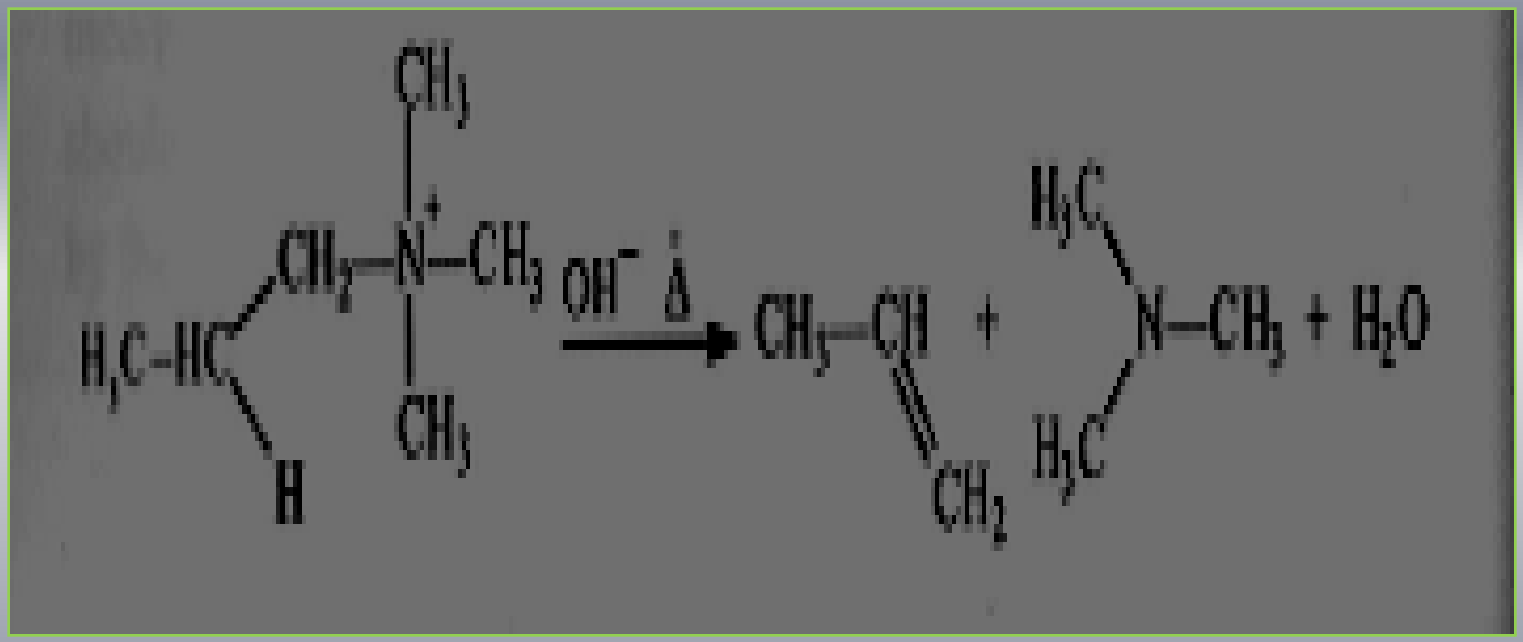
one atom (or group of atoms) is replaced by another atom (or group of atoms).
The atom or group that is replaced is not utilised in the final product.

In this reaction, the leaving group (OC2H5) & one hydrogen atom of the amine is not utilised.
less atom-economical than rearrangement



5. Elimination Reactions

In an elimination reaction, two atoms or group of atoms are lost from the reactant to form a pi bond

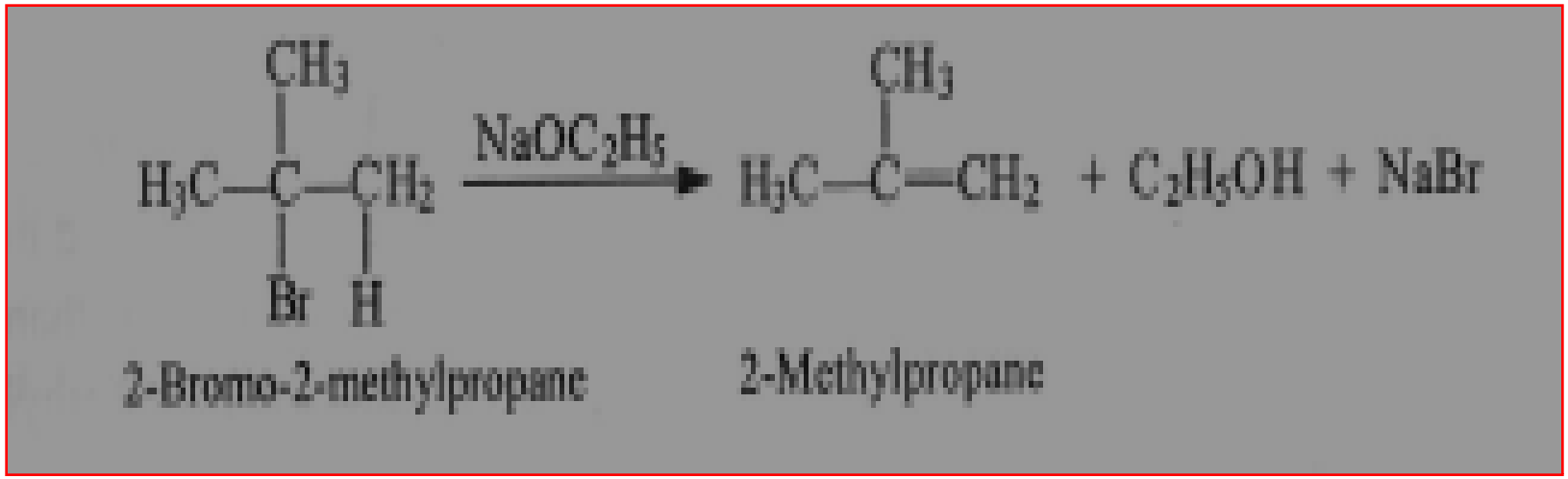


Hofmann elimination

economy is 35.30%.

least atom-economical of all the above reactions.

Dehydrohalogenation



not very atom economical.
atom economy is 27%
even less atom-economical than the Hofmann elimination reaction.

3. Less Hazardous Chemical Synthesis

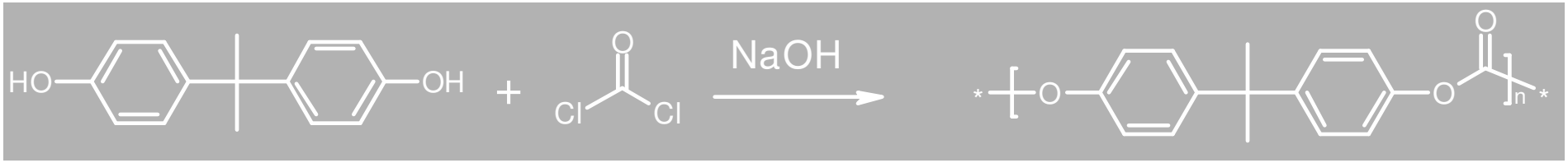
Whenever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

Risk=f(HAZARD, Exposure)

Eliminate the hazard, no need to worry about the exposure!

- the chemicals synthesised (dyes, paints) should be safe to use.
- thalidomide was used for lessening the effects of nausea and vomiting during pregnancy
- The children born to women taking the drug suffered birth defects (including missing or deformed limbs).
- Thus the use of thalidomide was banned
- the drug withdrawn
- With the advancement of technology, the designing and production of safer chemicals has become possible

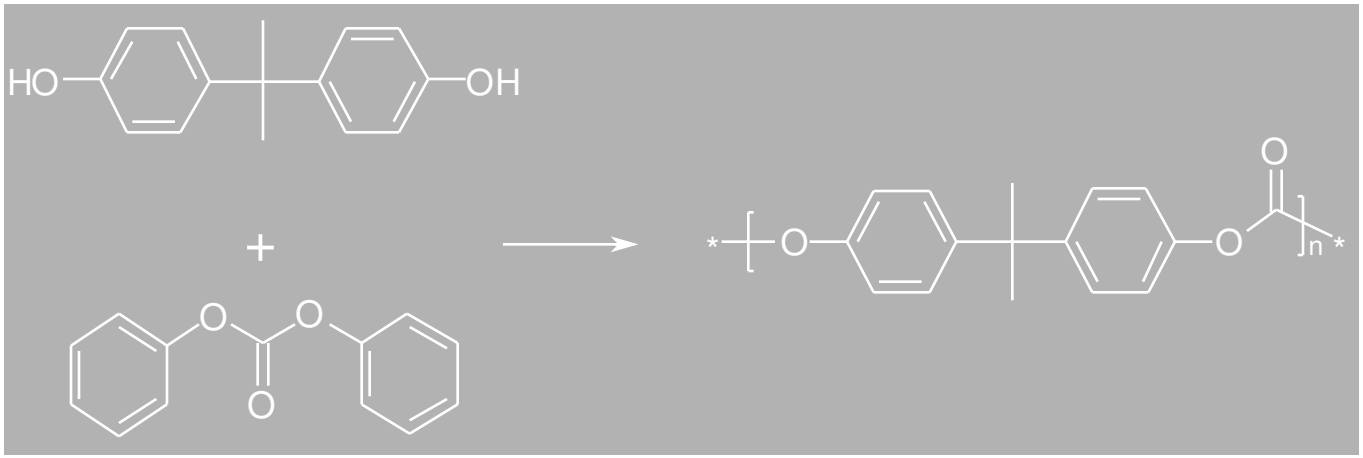
Polycarbonate Synthesis: Phosgene Process



- Disadvantages
  - phosgene is highly toxic, corrosive
  - requires large amount of $COCl_2$
  - polycarbonate contaminated with Cl impurities

Less Hazardous Chemical Synthesis

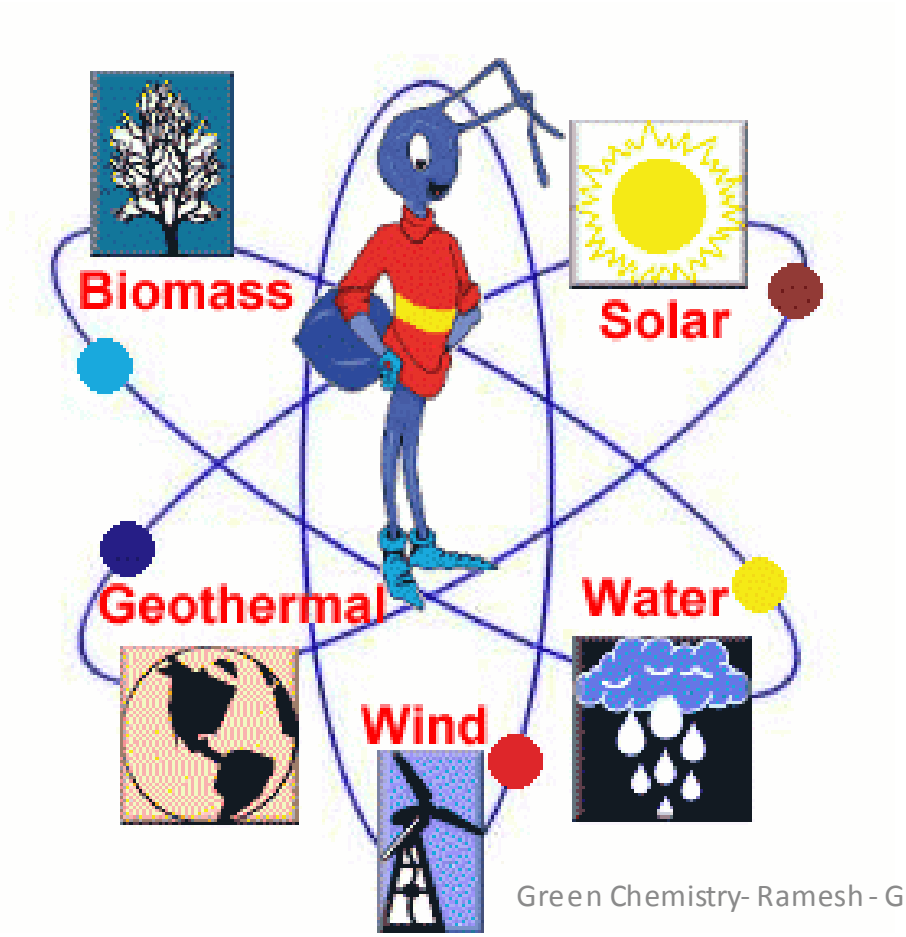
Polycarbonate Synthesis: Solid-State Process

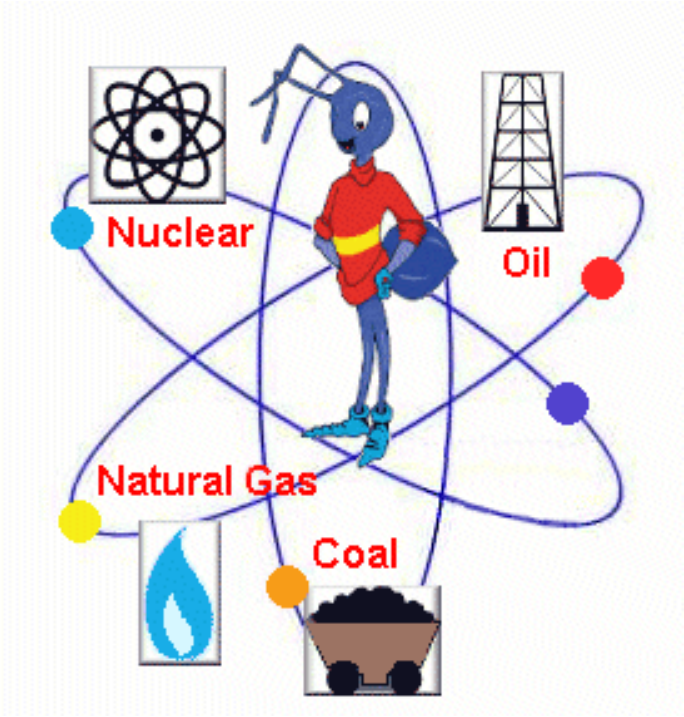


- Advantages
  - diphenylcarbonate synthesized without phosgene
  - eliminates use of CH_2Cl_2
  - higher-quality polycarbonates

4. Design for Energy Efficiency

Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.





- During chemical synthesis, the energy requirements should be kept to a minimum.

- if the starting material and the reagents in reaction mixture has to be heated to reflux for a required time, time required has to be kept minimum for the minimum usage of energy.

- Use of a catalyst has the great advantage of lowering the energy requirement of a reaction.

- In case the reaction is exothermic, sometimes extensive cooling is required- adds to the overall cost.

- If the final product is impure, it has to be purified by distillation, recrystallisation or ultrafiltration -All these steps involves energy.

- By designing the process such that there is no need for separation or purification, the final energy requirements can be kept at minimum.

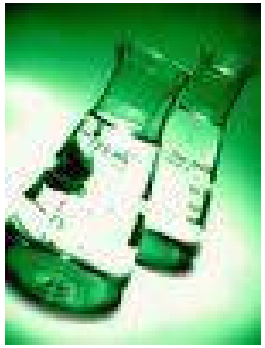
- Energy to a reaction can be supplied by photochemical means, microwave or sonication

5. Safer Solvents and Auxiliaries.

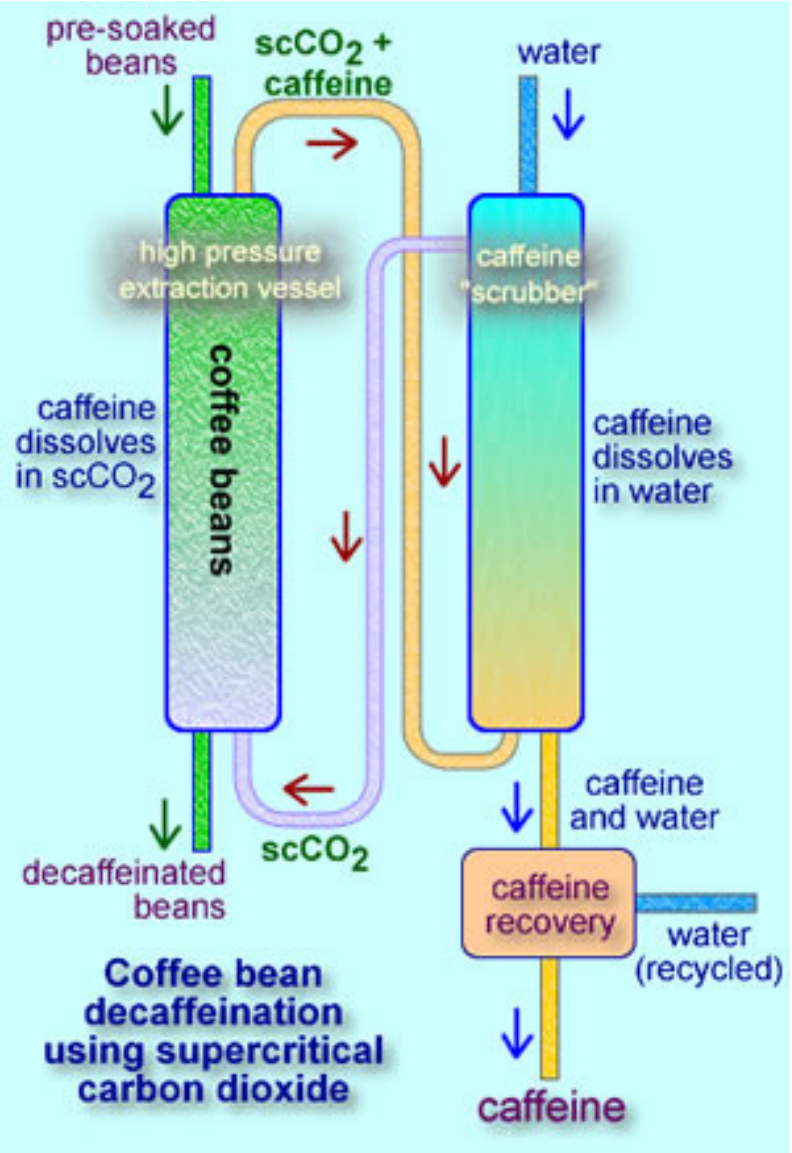
The use of auxiliary substances (solvents, separation agents, etc.) should be made unnecessary whenever possible and, when used, innocuous.

Green methods

- solvent selected not cause any environmental pollution and health hazard.
- the reaction should be carried out in aqueous phase
- the reaction should be carried out without the use a of solvent (solventless reactions).
- The use of liquid or supercritical liquid CO2 should be explored.
- A better method is to carry out reactions in the solid phase
- immobilised solvents can be used



- The immobilised solvent maintains the solvency of the material, but it is non-volatile and does not expose humans or the environment to the hazards of that substance.



http://www.uyseg.org/greener_industry/pages/superCO2/3superCO2_coffee.htm

Solvent Selection

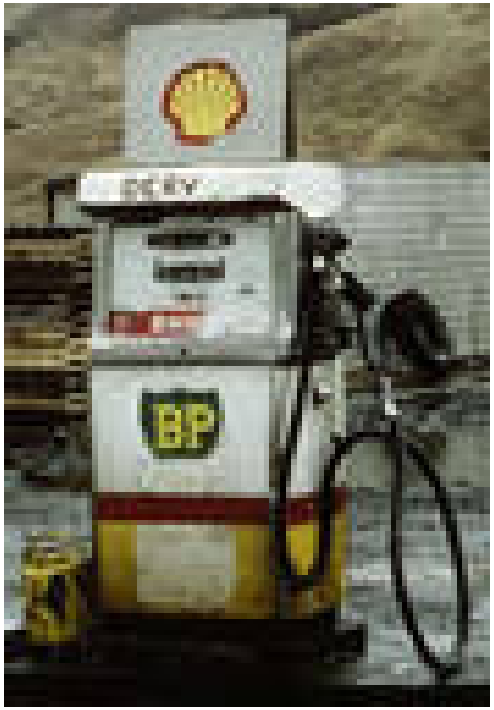
Preferred	Useable	Undesirable
Water	Cyclohexane	Pentane
Acetone	Heptane	Hexane(s)
Ethanol	Toluene	Di-isopropyl ether
2-Propanol	Methylcyclohexane	Diethyl ether
1-Propanol	Methyl t-butyl ether	Dichloromethane
Ethyl acetate	Isooctane	Dichloroethane
Isopropyl acetate	Acetonitrile	Chloroform
Methanol	2-MethylTHF	Dimethyl formamide
Methyl ethyl ketone	Tetrahydrofuran	N-Methylpyrrolidinone
1-Butanol	Xylenes	Pyridine
t-Butanol	Dimethyl sulfoxide	Dimethyl acetate
	Acetic acid	Dioxane
	Ethylene glycol	Dimethoxyethane
		Benzene
		Carbon tetrachloride

"Green chemistry tools to influence a medicinal chemistry and research chemistry based organization"
Dunn and Perry, et. al., Green Chem., 2008, 10, 31-36

6.Use of Renewable Feedstocks. A raw material or feedstock should be renewable rather than depleting whenever technically and economically practical.

Starting materials are those obtained from renewable or non-renewable material.

- non-renewable Source
- Petrochemicals obtained from petroleum,



Green

- The starting materials which can be obtained from agricultural or biological products are referred to as renewable starting materials
- But, cannot be obtained in continuous supply due to factors like cropfailure etc.
- Substances like carbon dioxide and methane gas
- are available in abundance. These are considered as renewable starting materials

Raw Materials from Renewable Resources: The BioFine Process

Paper mill sludge

Agricultural residues, Waste wood

Municipal solid waste and waste paper

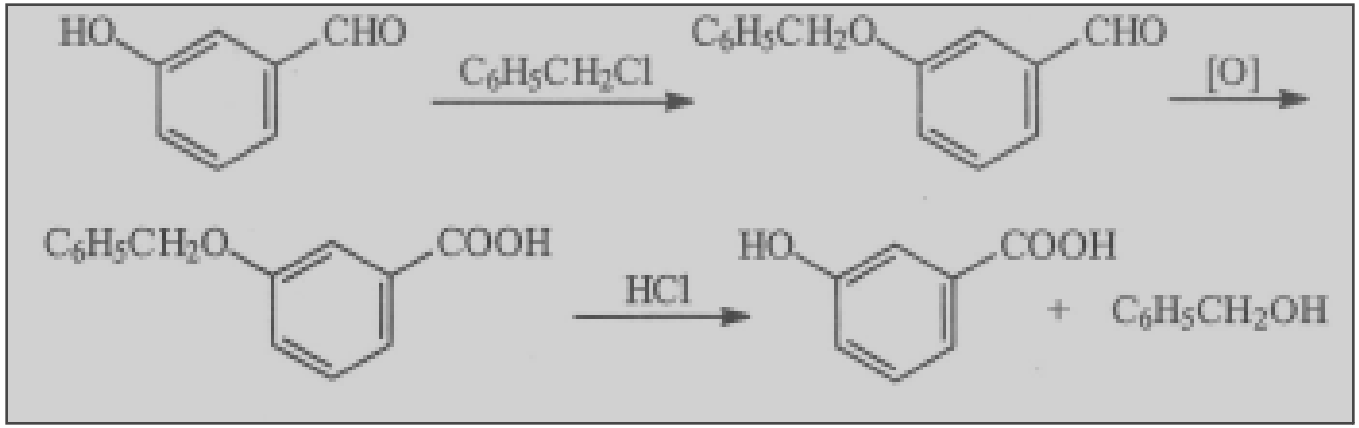
Levulinic acid

Green Chemistry Challenge Award
1999 Small Business Award

7 Use of Protecting **Groups/Reduce Derivatives.**

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

If an organic molecule contains two reactive groups and you want to use only one of these groups, the other group has to be protected, the desired reaction completed and the protecting group removed.



benzyl chloride (a known hazard) and the waste generated after deprotection should be handled carefully.

- Protecting gps are added in stoichiometric amounts
- Should be removed once the reaction is complete
- Not included in the product.
- Less atom economical

8. Catalysis

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

Catalysts performs transformation without consumed in the reaction and without being incorporated in the final product hence is preferred whenever possible.

ADVATAGES

- Better yield
- Reaction becomes feasible
- Selectivity
- Advantage in energy requirement
- better utilisation of starting materials and minimum waste product formation.

9. Design for Degradation

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

➢Products Designed Should be Biodegradable

Eg. insecticides and polymers are non biodegradable Insecticides

(DDT) bioaccumulate in many plant and animal species and. Incorporate into the food chain.

Some of the insecticides are also responsible for population decline" of beneficial insects

✓insecticides must be biodegradable

✓. during degradation the products themselves should not possess any toxic effects or be harmful to human health.

✓It is possible to have a molecule which may possess functional groups that facilitate it.for biodegradation.

✓ The functional groups should be susceptible to hydrolysis, photolysis or other cleavage.

Degradation of Polymers: Polylactic Acid

- Manufactured from renewable resources
  - Corn or wheat; agricultural waste in future
- Uses 20-50% fewer fossil fuels than conventional plastics
- PLA products can be recycled or composted

11. Real-time Analysis for Pollution Prevention.

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

- Analytical methodologies should be so designed so that they require minimum usage chemical , like recyling of some unreacted chemicals , for the completion of the reaction.
- Placement of sensors to monitor the generation of hazardous products during chemical reaction is also advatageous

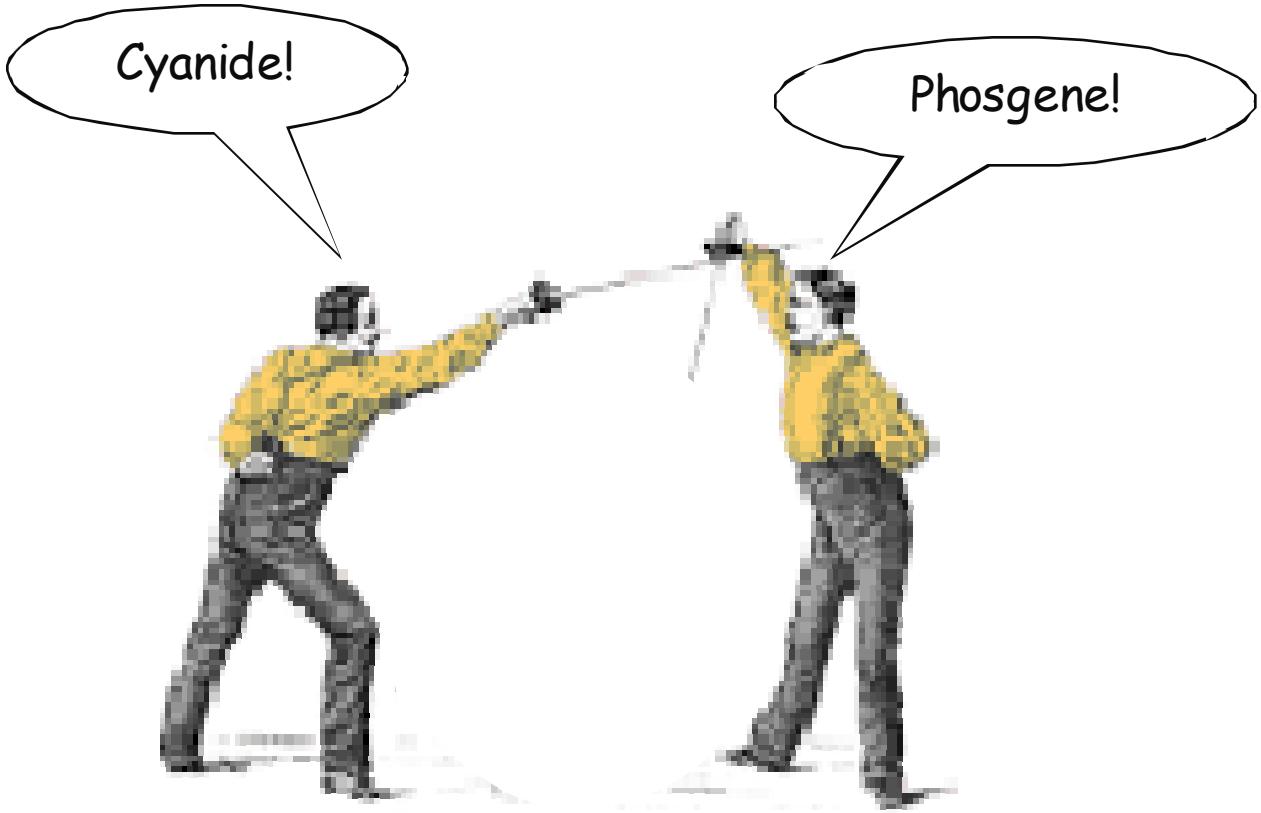
Real time analysis for a chemist is the process of “checking the progress of chemical reactions as it happens.”

Knowing when your product is “done” can save a lot of waste, time and energy!

12. Inherently Safer Chemistry for Accident Prevention

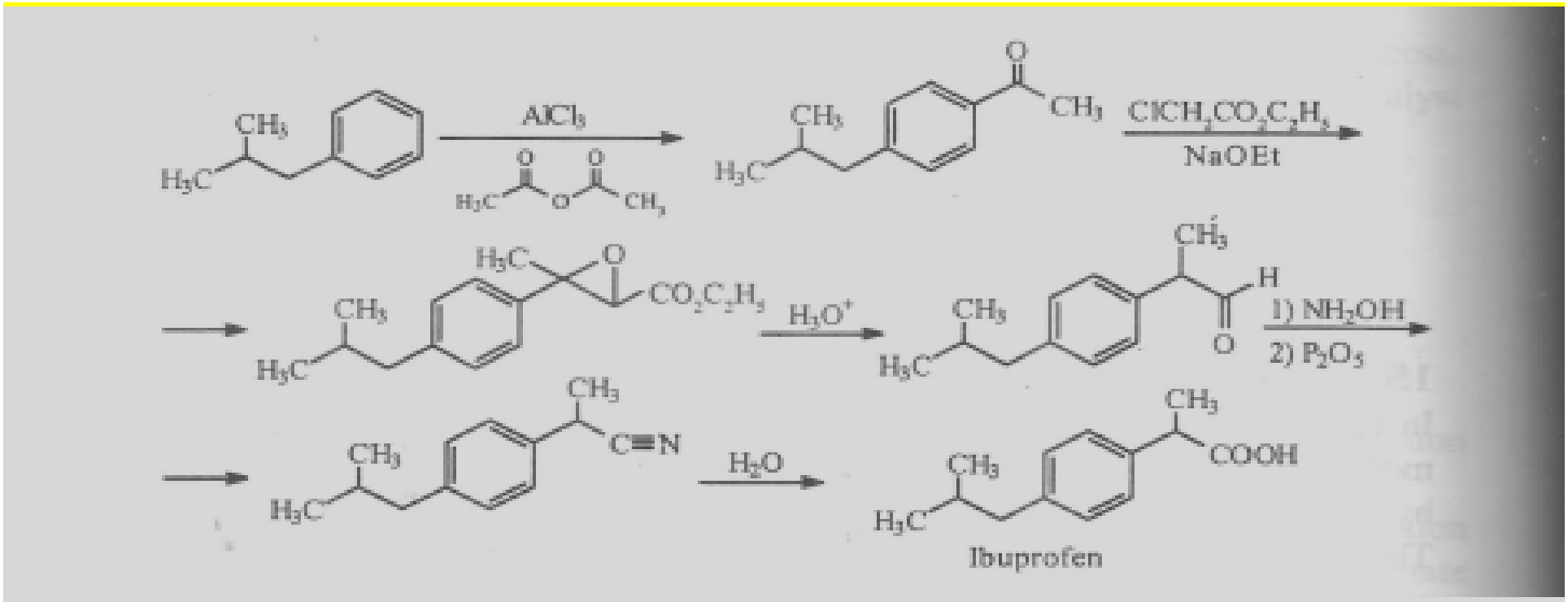
Substance and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires. .

The hazards posed by toxicity, explosion , fire etc might be looked into and manufacturing plants should be so designed to eliminate the possibility of accidents

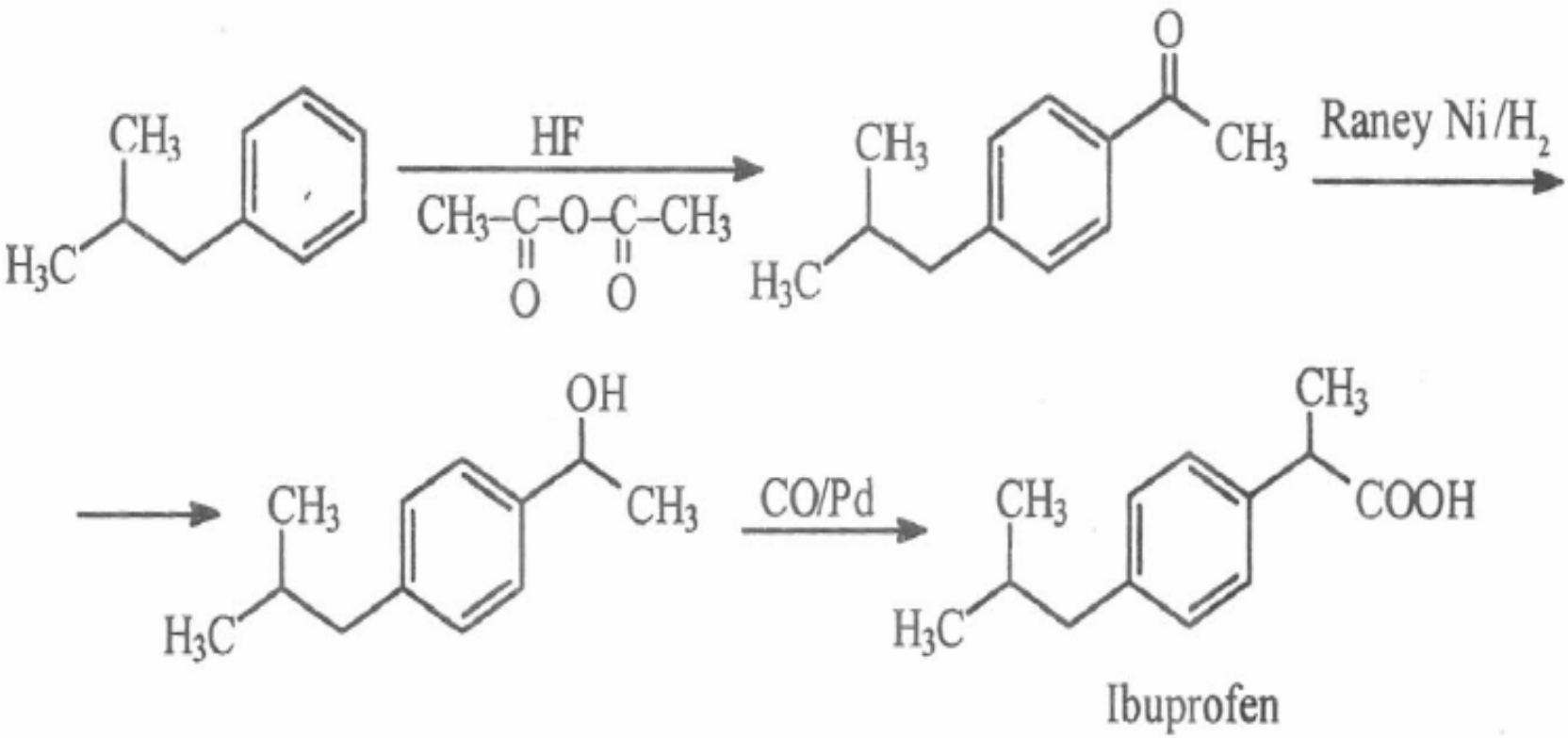


Synthesis of Ibuprofen

Used for making pharmaceutical drugs-analgesics (pain killers).
developed by the Boots Company of England
6 step process
Atom economy 40%
60% waste of atoms



Economic Advantages of BHC Synthesis of Ibuprofen



Microwave Induced Green Synthesis

Microwave frequencies 30 GHz to 300 Hz
Home appliances frequency of 2.45 GHz.
used for heating purposes

mechanism

microwave reactions involve selective absorption of electromagnetic waves by polar molecules. When molecules with a permanent dipole are submitted to an electric field, they become aligned as the field oscillates their orientation changes, this rapid reorientation produces intense internal heating.

Microwave Assisted Reactions **in Water**

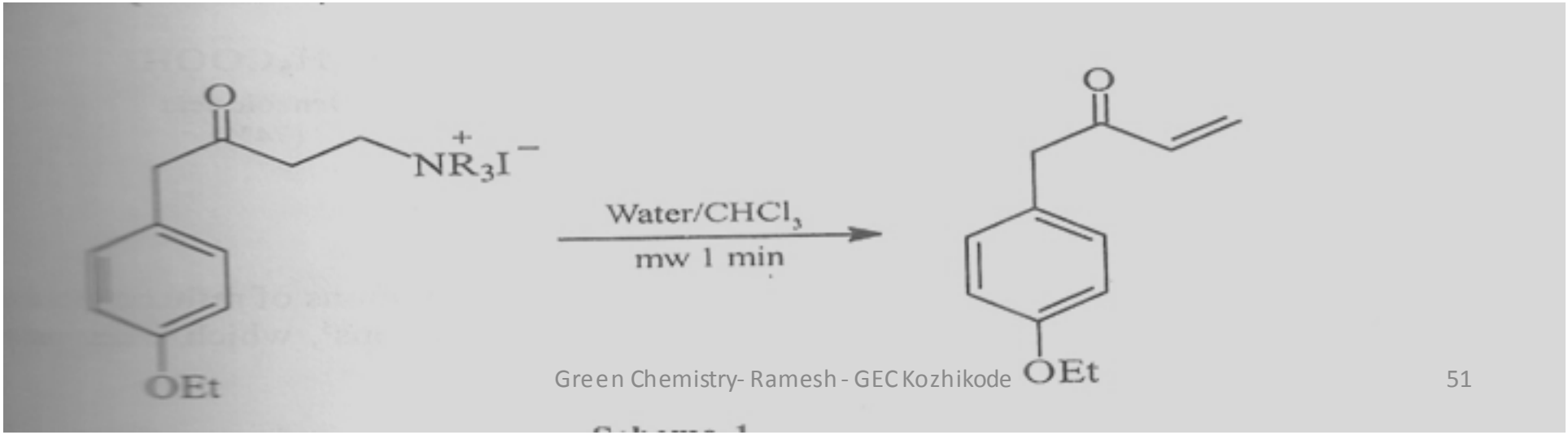
Hofmann Elimination

➢normally quaternary ammonium salts are heated at high temperature and the yield is low.

Use of microwave irradiation

high-yielding synthesis

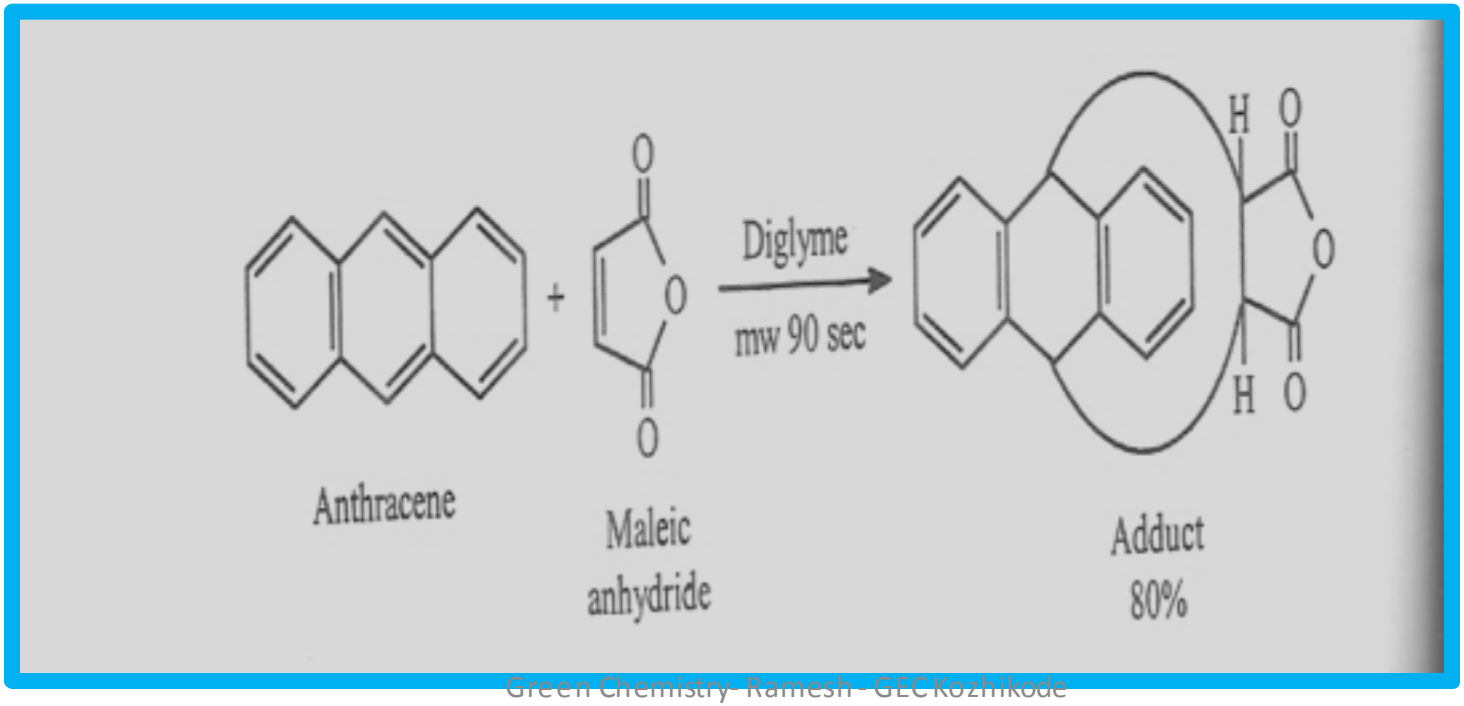
water-chloroform system is used



Diels Alder Reaction

l,4-addition of an alkene (e.g., maleic anhydride) to a conjugated diene (e.g. anthracene) to form an adduct of six membered ring.

usual conditions- reflux period of 90 min. in xylene using oil bath
microwave conditions
diglyme is used as a solvent and
80% yield of the adduct is obtained in one minute`



Ultrasound Assisted Green Synthesis

Ultrasound refers to sound waves having frequencies higher than those to which the human ear can respond.

When a sound wave, propagated by a series of compression and refraction cycles pass through a liquid medium, it causes the molecules to oscillate around their mean position. During the compression cycle, the average distance between the molecules is reduced and during refraction, the average distance between the molecules is increased.

In the refraction cycle, under appropriate conditions, the attractive forces of the molecules of the liquid may be overcome, causing formation of bubbles. In case the internal forces are great enough to ensure collapse of these bubbles, very high local temperature (around 5000°C) *and pressure (over1000 bar) may be created. It is this very high temperature. This very high temperature and pressure initiate chemical reactions*

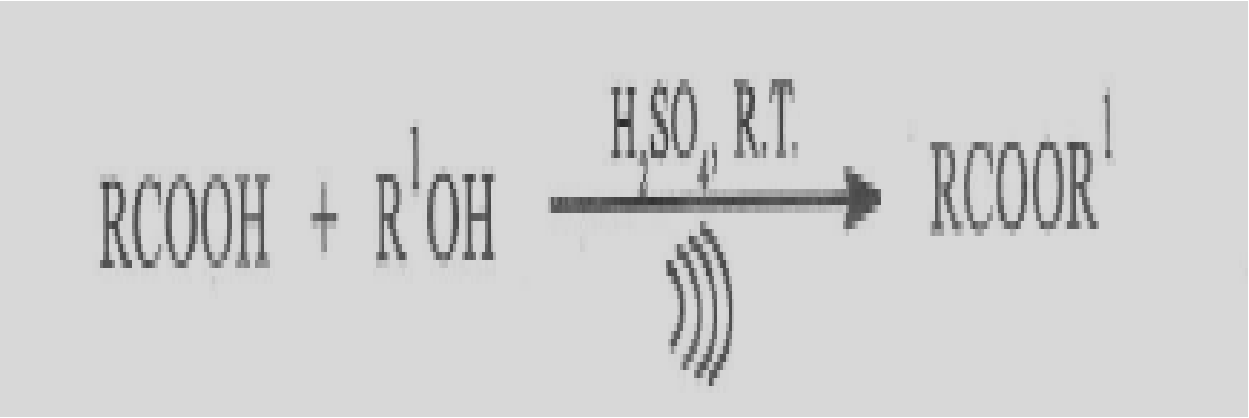
1 Esterification

generally carried out in presence of a catalyst like sulphuric acid, p-toluenesulphonic acid, tosylchloride, polyphosphoric acid, dicyclo-hexylcarbodiimide etc.

longer time

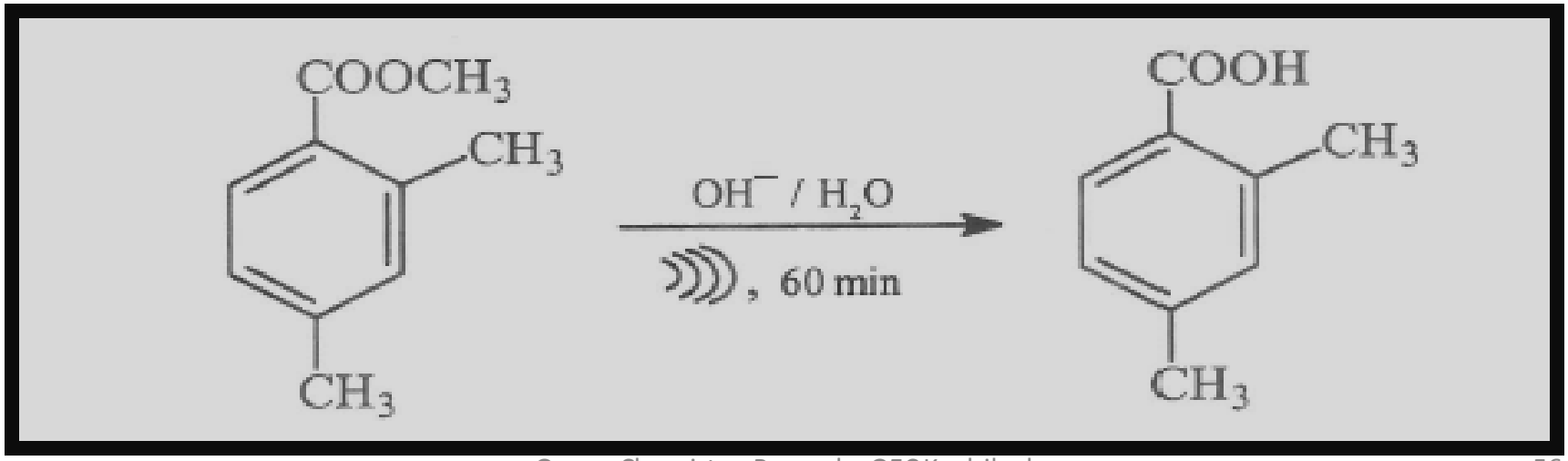
yields are low.

A simple procedure for the esterification of a variety of carboxylic acids with different alcohols at ambient temperature using ultrasound has been



2 Saponification

15% yield by the usual process of heating with aqueous alkali (90 min).
Saponification can be carried out under milder conditions.
Thus, methyl 2,4-dimethylbenzoate on saponification (20 KHz) gives the
corresponding acid in 94% yield



Examples of Green Chemistry

- New syntheses of Ibuprofen and Zoloft.
- Integrated circuit production.
- Removing Arsenic and Chromate from pressure treated wood.
- Many new pesticides.
- New oxidants for bleaching paper and disinfecting water.
- Getting the lead out of automobile paints.
- Recyclable carpeting.
- Replacing VOCs and chlorinated solvents.
- Biodegradable polymers from renewable resources.

In the end we can say that Green chemistry is Not a solution to all environmental problems But the most fundamental approach to preventing pollution