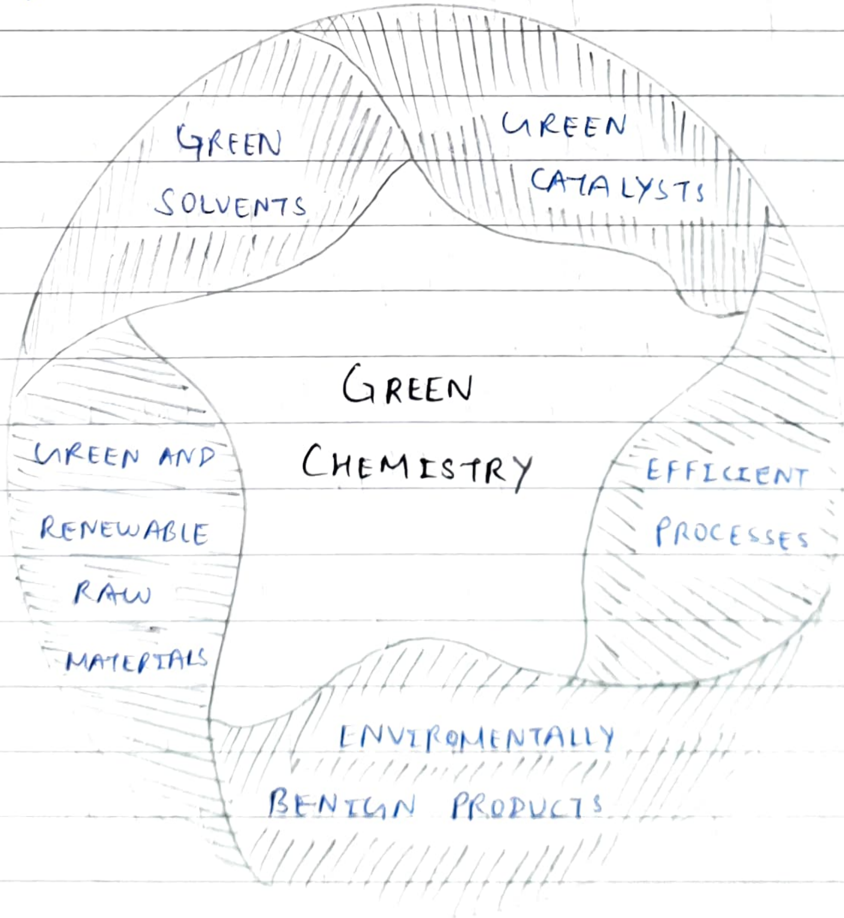
GREEN CHEMISTRY

Definition :-

According to US EPA, Green chemistry is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances. Green chemistry applies across the life cycle of a chemical product, including its design, manufacture, use, and ultimate disposal.

It is also known as sustainable / enviromentally benign chemistry.



Role of Green Chemistry :-

Approaches where green chemistry plays a role :

1. At the most basic level : Pollution prevention
   - Improved operational practices (lowering energy consumption, improving yields)

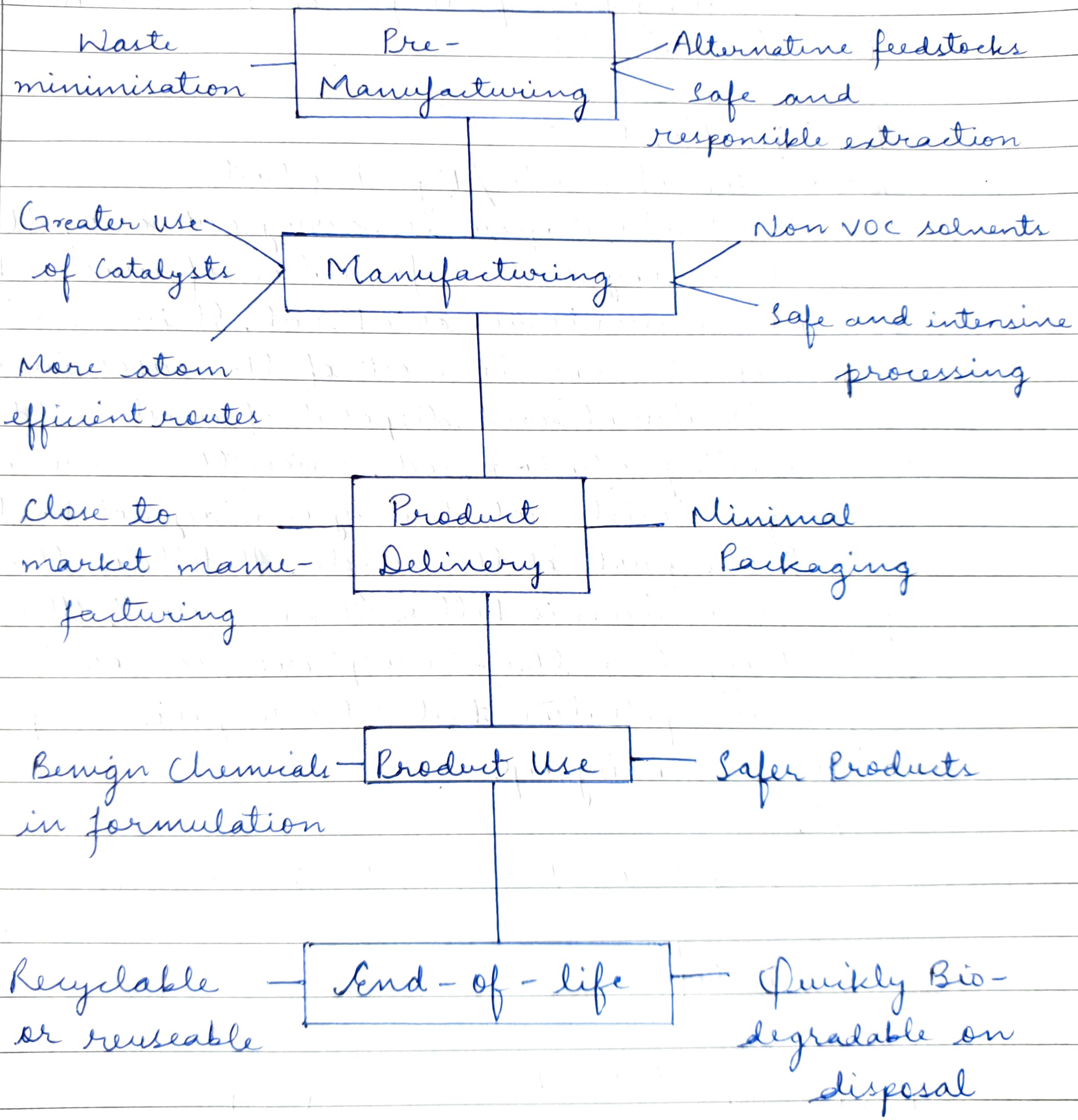
2. Development of greener processes to manufacture unchanged chemical products.
   - Avoid Cl compounds if Cl is not in the final product.

3. Formulation of alternative chemicals for the same application.
   - Use of CFC substitutes

4. Avoidance of chemicals and also use of chemistry for improved environmental performance elsewhere.
   - Molecular markers in plastics for easier identification during recycling.
   - Design of chemical detectors for better monitoring of environmental quality.

Overall, Green chemistry goals at sustainable development which has been defined as —
"Meeting the needs of the present generation without compromising the ability of future generations to meet their own needs".

Green Chemistry : Life Cycle of Product



Basic Principles of Green Chemistry :-

According to the work carried out by Paul T. Anastas, the following basic principles of green chemistry have been formulated :

Principle No. 1 :-

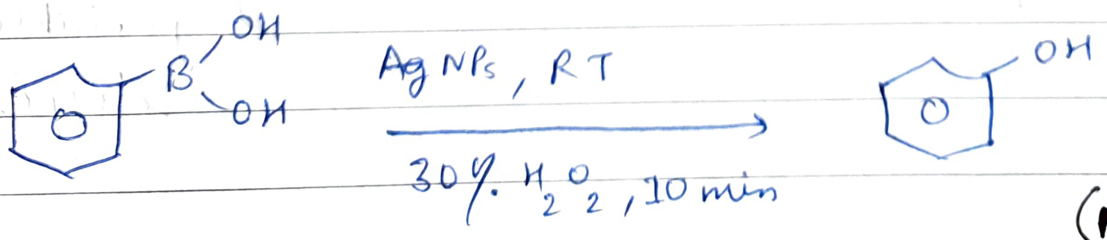
Prevention of Waste / By-Products

It is most advantageous to carry out a synthesis in such a way so that formation of waste (by-products) is minimum or absent. It is essentially important because in most of the cases involved in the treatment and disposal of waste adds to the overall production cost. Even the unreacted starting material (which may or may not be hazardous) form part of the waste. It follows the principle "prevention is better than cure". The waste if discharged in the atmosphere, sea or land not only causes pollution but also requires expenditure for cleaning up.

Example -

$$C_6H_6 + H_2SO_4 + 2NaOH \longrightarrow C_6H_5OH + \underbrace{Na_2SO_3 + 2H_2O}_{\text{Side products}}$$

Green route :-



(No side product

Principle No. 2 :-

Maximum Incorporation of the Reactants (Starting Materials and Reagents) into the final product.

Chemists generally consider that if the yield of a reaction is about 90%, the reaction is good.

$$\% \text{ yield} = \frac{\text{Actual yield of the product}}{\text{Theoretical yield of the product}} \times 100$$

Typical examples like Witting reaction and the Grignard reaction may proceed with 100% yield but they do not take into account the large amounts of by-products obtained.

The reaction or the synthesis is considered to be green if there is maximum incorporation of the starting materials and reagents in the final product.

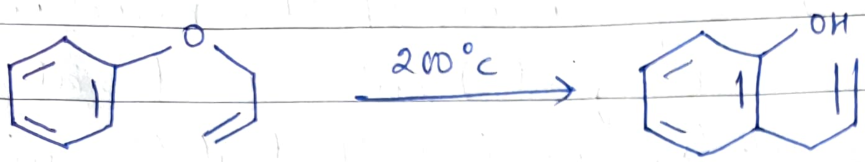
$$\% \text{ Atom utilization} = \frac{\text{MW of desired product}}{\text{MW of (desired product + waste products)}} \times 100$$

The concept of Atom Economy developed by B. M. Trost is a consideration of 'how the reactants end up in the final product.'

The same concept by R.A. Sheldon is given by —

$$\% \text{ Atom Economy} = \frac{\text{FW of atom utilized}}{\text{FW of the reactants used in the reaction}} \times 100$$

① Rearrangement Reaction :-



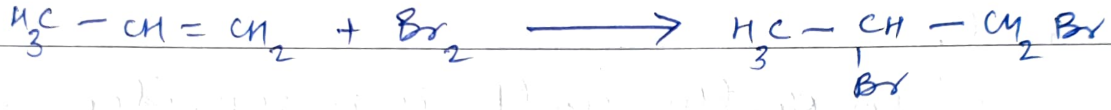
Allyl phenyl Ether   o- Allyl phenol

100 % Atom economical as all the reactants are incorporated into the final product.

② Addition Reaction :-

$$H_3C-CH=CH_2 + H_2 \xrightarrow{Ni} H_3C-CH_2-CH_3$$

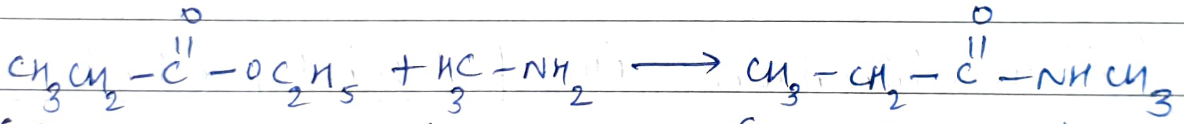
Propene   propane



$$H_3C-CH=CH_2 + Br_2 \longrightarrow H_3C-\underset{\displaystyle Br}{CH}-CH_2Br$$

100 % Atom Economical

③ Substitution Reaction :-



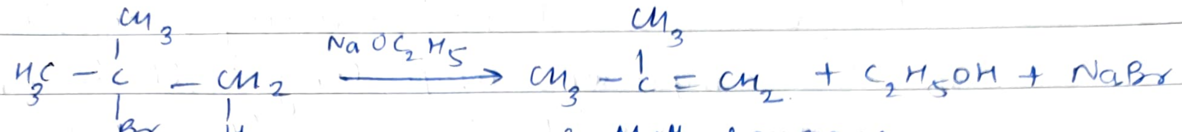
$$CH_3CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-OC_2H_5 + H_3C-NH_2 \longrightarrow CH_3-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-NHCH_3$$

(Ethyl propionate)   (Methyl amine)   (N-methylpropionamide) + CH_3CH_2OH (Ethanol)

	Reactants		Utilised		Unutilised	
	Formula	FW	Formula	FW	Formula	FW
	$C_5H_{10}O_2$	102.132	C_3H_5O	57.057	C_2H_5O	45.061
	CH_5N	31.057	CH_4N	30.049	H	1.008
Total	$C_6H_{15}NO_2$	133.189	C_4H_9NO	87.106	C_2H_5OH	46.069

% Atom Economy $= \frac{87.106}{133.189} \times 100 = 65.40\%$

④ Elimination reaction :-



$$H_3C-\overset{CH_3}{\underset{Br}{C}}-\underset{H}{CH_2} \xrightarrow{NaOC_2H_5} CH_3-\overset{CH_3}{C}=CH_2 + C_2H_5OH + NaBr$$

2-Methylpropane

2-Bromo-2-methylpropane

Atom Economy = 27%

Principle No. 3 :-

Prevention or Minimization of Hazardous products or Less Hazardous chemical synthesis –

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

Some toxic chemicals are replaced by safer ones for a green technology. For example – in the manufacturing of polystyrene foam sheet packing material, chlorofluorocarbons which contribute to O_3 depletion and global warming, have now been replaced by CO_2.

$VOCs + NO + \text{sunlight} \rightarrow O_3 + HNO_3 + \text{Organic compound}$ (partially oxidised)

$CF_2Cl_2 + UV \rightarrow CF_2Cl + \dot{Cl}$

$O_3 + \dot{Cl} \rightarrow O_2 + ClO^{\cdot}$

$ClO^{\cdot} + O \rightarrow \dot{Cl} + O_2$

Overall Reaction : $O_3 + O \rightarrow 2O_2$ (Ozone depletion)

Principle No. 4 :-

Designing Safer Chemicals

Chemical products should be designed to effect their desired function while minimizing their toxicity. A typical example of unsafe drug is thalidomide (introduced in 1961) for lessening the effects of nausea and vomiting during pregnancy (morning sickness). The children born to women taking the drug suffered from birth defects (including missing or deformed limbs). Evidence indicates that only one of the enantiomers has the curing effect while the other isomer is the cause of severe defects.

For designing and producing safer chemicals, chemists are now manipulating the molecular structure to achieve this goal.

Principle No. 5 :-

Energy requirements for Synthesis

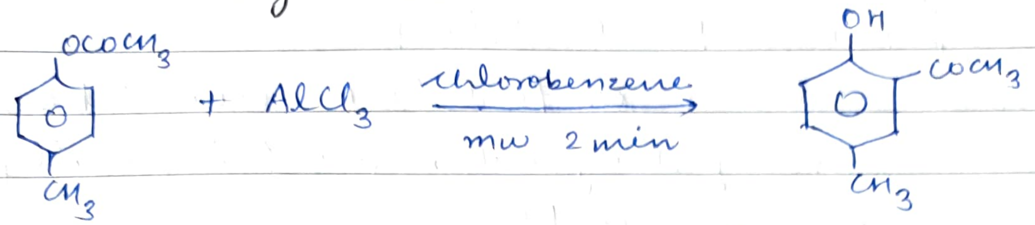
Energy requirements of chemical processes should be recognised for their environmental and economi impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

For Example - Microwave assisted reactions

Oxidation of Toluene -

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

Fries Rearrangement –



(p-Cresyl acetate)

(1-Hydroxy-4-methyl acetophenone)

85 % yield

Principle No. 6 :-

Safer Solvents and Auxiliaries

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

Widely used solvents in synthesis are toxic and volatile alcohol, benzene (known carcinogenic), CCl_4, $CHCl_3$, perchloroethylene, CH_2Cl_2.

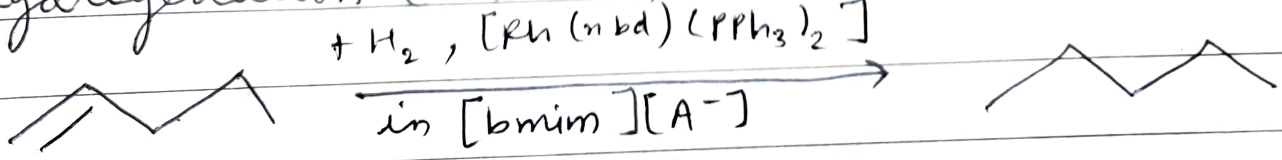
Purification also utilize large amounts of solvents (e.g. chromatography) which adds to the pollution and can be highly hazardous to human health.

An ideal desirable green solvent should be –

- Non-toxic
- Natural
- less hazardous
- Cheap
- Readily available

Example – H_2O, supercritical CO_2, polyethylene glycols (PEG), Ionic liquids

Hydrogenation (5 times faster than in acetone)



$[A^-] = BF_4, PF_6, SbF_6$

Principle No. 7 :-

Use of Renewable Feedstocks

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

90-95% product we used in our daily life are made from petroleum (non-renewable)

- Biodiesel, CNG → Alternative for petroleum in transportation.
- Bio-based plastic like PLA (polylactic acid) made from renewable feedstocks like corn and potato waste.
- Benzene → Adipic acid → Nylon, plasticizers, lubricants

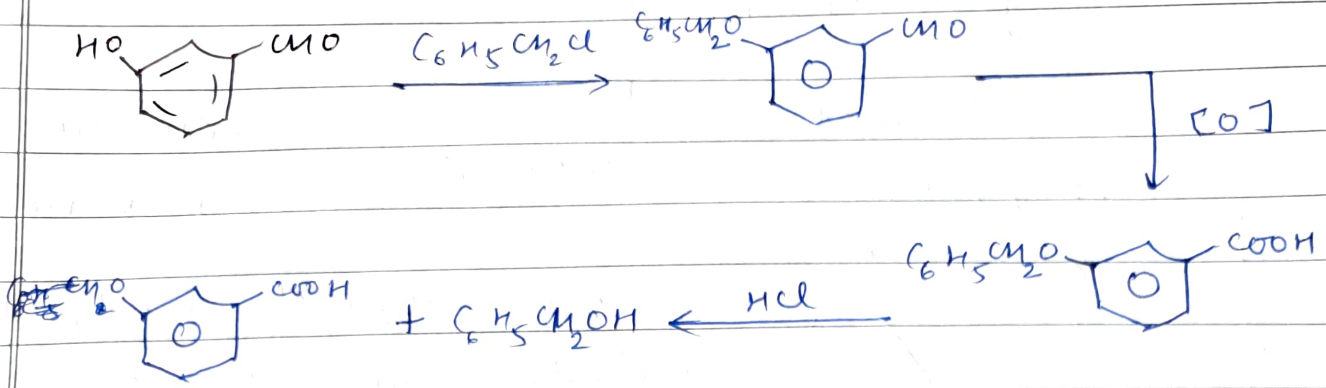
  ↓ replaced by

  Renewable & non-toxic glucose

Principle No. 8 :-

Reduce Derivatives

Unnecessary derivitization (use of blocking groups, protection / de-protection, and temporary modification of physical / chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.



Protecting group → makes reaction chemoselective
→ less atom economical
→ waste generated at the end.

Principle No. 9 :-

Catalysis

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

Example :-

① Better yields.

$$H_3C-CH=CH_2 + H_2 \xrightarrow{Ni} H_3C-CH_2-CH_3$$

propene propane

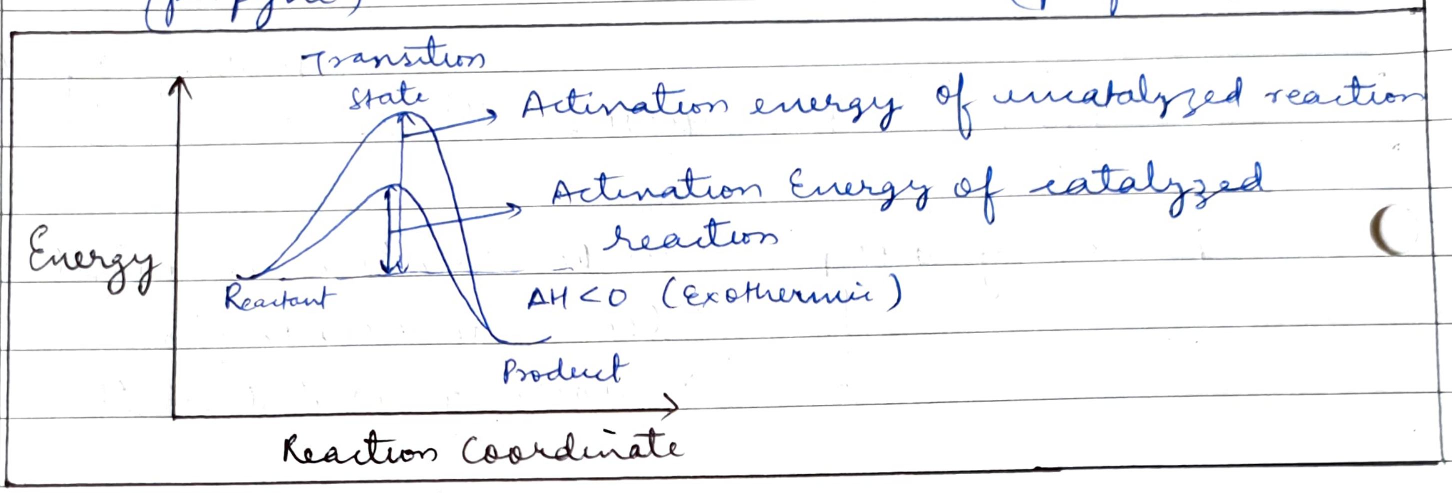
Ⅱ Reaction becomes feasible where no reaction is normally possible

$$HC\equiv CH + H_2O \xrightarrow[H_2SO_4]{HgSO_4} H_3C-CHO$$

(III) Selectivity Enhancement

$$H_3C-C\equiv CH + H_2 \xrightarrow[\text{monoaddition}]{Pd-BaSO_4} H_3C-CH=CH_2$$

(propyne) (propene)

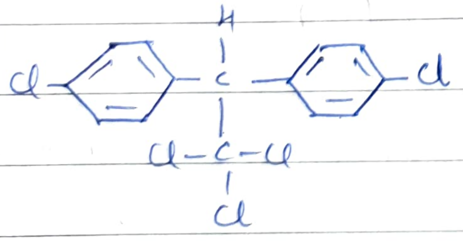


Principle No. 10 :-

Design for degradation

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

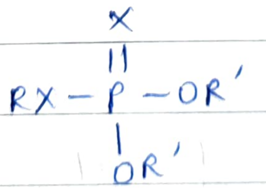
Example — Insecticides



DDT

↓

- Bioaccumulates
- Hazardous

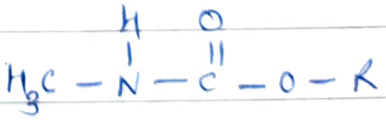


$$RX-\overset{\overset{X}{\|}}{\underset{\underset{OR'}{|}}{P}}-OR'$$

Organophosphate

X = O or S

$R' = CH_3$ or CH_2CH_3



$$H_3C-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-O-R$$

Carbamate

comparatively less persistent

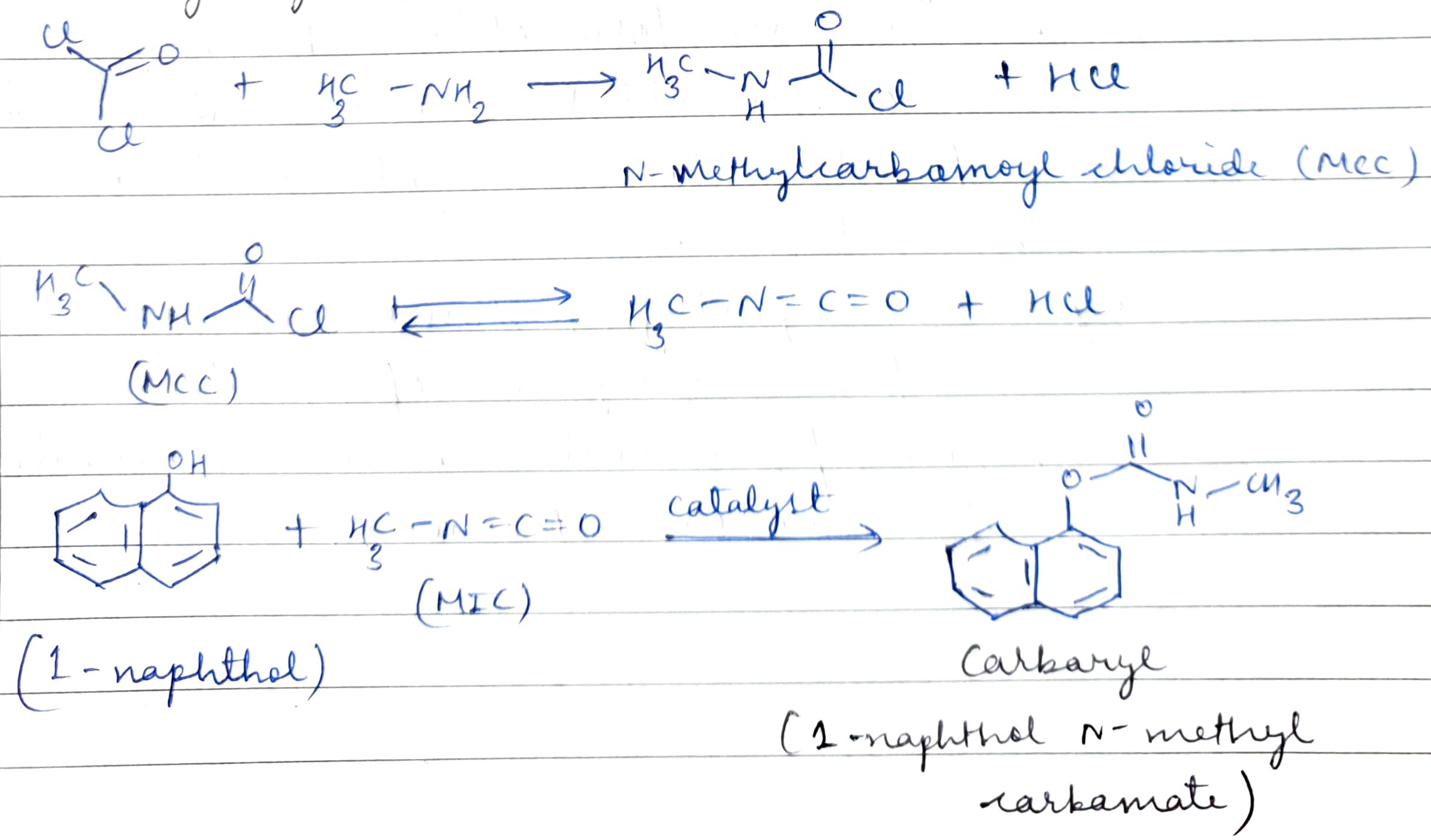
Some of the diacylhydrazines (developed by Rohm and Hass company) are useful as insecticides like – Tebufenozide, Halofenozide, Methoxyfenozide
To facilitate biodegradation, the molecule should have a functional group susceptible to hydrolysis, photolysis or other cleavage.

Principle No. 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.
Example – Bhopal Gas Tragedy (December 1984) in which 40 tons of methyl isocyanate was accidentally released at a Union Carbide pesticide plant, Bhopal.

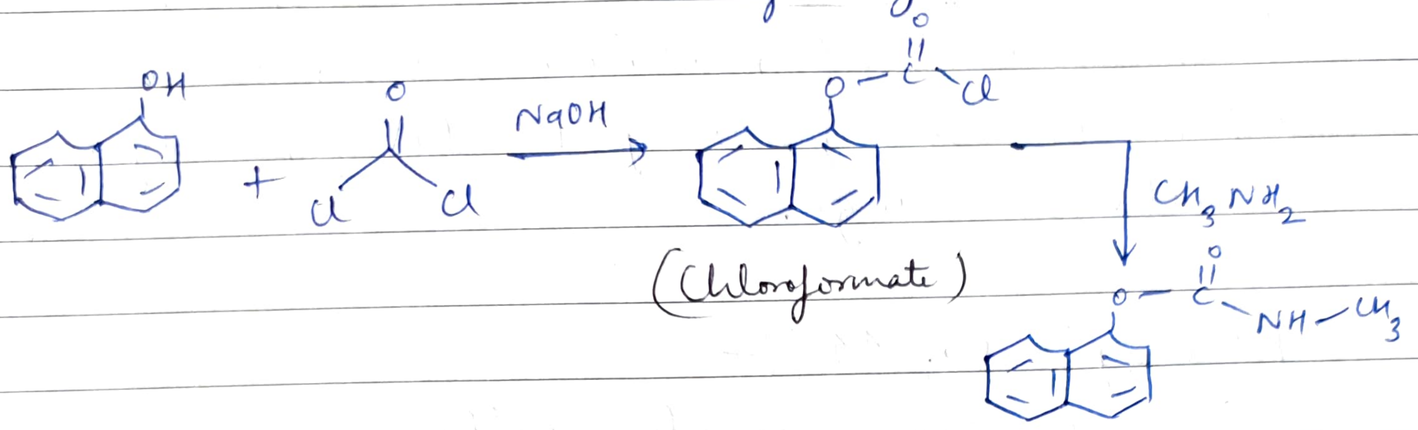
Carbaryl Synthesis at UCIL –



Green route :-

$$CH_3NHCHO \xrightarrow[Ag/O_2]{oxidation} CH_3NCO + H_2O$$

Methyl isocyanate



(Chloroformate)

(Carbaryl)

The hazards posed by toxicity, explosions, fire etc must be looked into and the manufacturing plants should be so designed to eliminate the possibility of accidents during operation.

Principle No. 12 :-

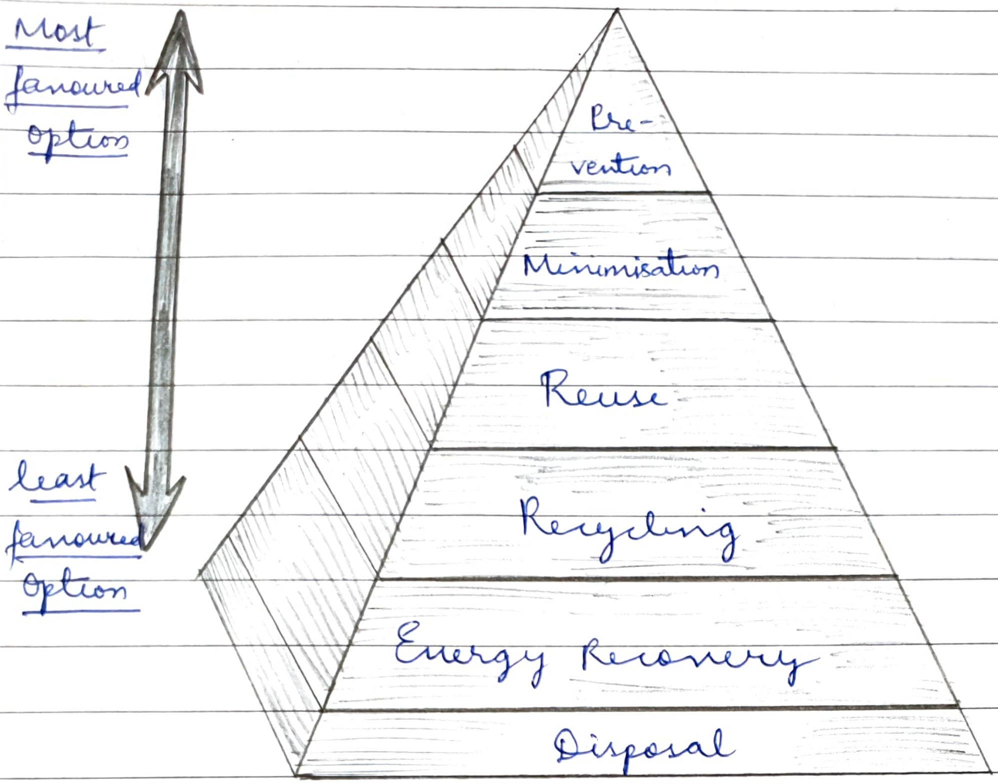
Inherently Safer Chemistry for Accident Prevention

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

Example — ① Recycling of some unreacted reagent for the completion of reaction

(ii) Placement of accurate sensors to monitor generation of hazardous substances.

Waste Management



Conclusion :-

Green chemistry is not a new branch of science. It is a new philosophical approach that through application and extension of the principles of green chemistry can contribute to sustainable development. Great efforts are still undertaken to design an ideal process that starts from non polluting materials. It is clear that the challenge for the future chemical industry is based on production of safer products and processes designed by utilizing new ideas in fundamental research. Furthermore, the success of green chemistry depends on the training and education of new generation of chemists. Student at all levels have to be introduced to the practice of green chemistry. Finally, regarding the role of education in green chemistry

“The biggest challenge of green chemistry is to use its rule in practice”.