CHEMISTRY UNIT-I BAS-102

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Green Chemistry / Clean Chemistry / Sustainable Chemistry

Introduction, 12 principles & importance of green synthesis, Green chemicals. Synthesis of typical Organic Compounds by Conventional & Green Route (Adipic acid & ~~par~~ paracetamol). Environmental impact of Green Chemistry on society.

"The science of utilization of a set of chemistry principles in the design, manufacture & application of chemical products that consumes minimum amount of materials and energy while producing little or no waste material & which reduces or eliminates the use or generation of hazardous substances.

$$\boxed{\text{Reactant}} \xrightarrow{\text{Reaction}} \boxed{\text{Product}} + \boxed{\text{By product}}$$

Reactant:
1. Renewable
2. non-toxic to health & env.
3. to minimize the chemical accident, explosion & fire.

Reaction:
1. use safe
   - Reagents
   - Catalyst
   - eco-friendly solvents
   - Findout reaction Conditions.
   for atom economy.

Product:
- use, Reuse, Recycle.
- leads to suistable development.
- harmless degradat^n product

By product:
- Minimize waste
- real time in process monitoring.

Conventionally ⇒ Risk = f (Hazard × Exposure)

Traditional approach – Reduce or eliminate exposure to hazardous substance.

Green Chemistry approach. – Reduce or eliminate the hazard itself.

Green chemistry is About

Pollution prevention on the molecular scale.

At all three steps

(1) Companies manufacture products.

(2) Consumer use the product

(3) When the products & their packaging are recycled or disposed.

It is about Reducing – 1. Environmental Impact.
2. Energy
3. Hazard.
4. Risk
5. Materials
6. Waste
7. Cost.

In Traditional approch

Risk = Hazard × Exposure

Risk = Hazard × (Dose × time)

this is how risk calculated traditionally and focuses on limiting the exposure of a hazardus material for avoiding risk.

Green chemistry Approach :

Reduce or eliminate the hazard itself.

12 Principles of Green Chemistry

1. Prevent waste.
2. Design safer chemicals & products.
3. Design less hazardous chemical syntheses.
4. Use safer solvent / Reaction conditions.
5. Increase energy efficiency
6. Use Renewable feedstock
7. Design chemicals & product that degrade after use.
8. Analyze in real time to prevent pollution.
9. Use catalysts.
10. Maximize Atom economy
11. Avoid chemical derivatin
12. Minimize the potential for Accidents.

Principles of Green Chemistry

1. Prevent waste or by-products

It is better to prevent waste than to treat or cleanup waste after it has been created.

It is most important principle than principles of 'how' to achieve it.

2. Design Safer Chemicals & products.

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

Safer (Greener) chemicals are,

(i) Safer for the atmosphere (form smog or deplete ozone layers)

(ii) Recyclable & biodegradable.

(iii) Safer with regard to accidental potential.

(iv) less toxic than products they replace.

Chemists can meet the goal of designing safer chemicals by combining chemistry knowledge related to molecular structure & properties with toxicological data regarding chemical toxicity.

3. Design Less Hazardous Chemical Syntheses.

Synthetic methods should be designed to use & generate substance that posses little or no toxicity to human health & environment.

Some pointers can be

1. Atom economical
2. Based on natural process, such as fermentation, biomimetic synthesis.
3. Use of greener feed stock that are renewable or innocuous.
4. Use of environment friendly reagents, microorganism, biocatalyst
5. It consume less energy, simple & safe
6. If it has high yield & selectivity.

eg : (i) Metathesis Reaction : (Swapping, closer of rings) "Polymerisation")
(ii)

4. Use safer solvent / Reaction Conditions.

The design & utilization of solvents that have reduced potential for damage to the environment. These solvents should serve as alternatives to currently used volatile organic solvents, chlorinated solvents & solvents that damage the natural environment.

Characteristic of Ideal "Green" solvent.

(i) The ideal solvent has the reactivity that fits the reaction
(ii) It allows for easy precipitation / sepration of product.
(iii) It safely degrade / evaporate after use.
(iv) Minimal environmental impact.
(v) low toxicity & flammability.

Preferred.	Usable	Undesirable.
① Water	Toluene	Dimethyl formamide
② isopropylalcohol	IsoparG	Dioxane
③ Acetone	Heptane.	Dimethyl acetamide
④ Ionic liquids eg.- Quaternary ammonium Quaternary phosphonium N-alkyl pyridium	Dimethyl sulfoxide (DMSO)	Hexane
	Tetrahydrofuran (THF)	Chloroform
	Acetonitrile.	

⑤ Supercritical CO_2 [above critical Pressure & critical temp. is SCF.] - density near liquid & viscosity near gas.

30.98°C & 73 atm.

Advantages.
(i) Improved mass & heat transfer. b/c of High diffusion rate & low intensity)
(ii) Easy removal of solvent for recycling.
(iii) A potentially large operating window in supercritical region.
(iv) The possibility of fine tuning solvent properties by varying temprature & pressure.

Ionic liquid Advantages.

(i) They have very low vapour pressure.

(ii) They can act both as solvent & as catalyst.

(iii) They are stable at higher temperature ($\geq 300°c$) thus it is possible to carry out high temp. reaction at low pressure

(iv) Properties (viscosity, mpt. acidity / basicity) can be varied as per requirement.

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5. Increase Energy Efficiency

Energy requirements should be recognized for their environmental & economical impacts & should be minimized synthetic methods should be conducted at ambient temp. & pressure.

- arrange a synthesis to have the fewest number of steps.
- lowest cost starting material.
- or any other design parameter.

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6. Use Renewable Feed stocks.

The use of feedstocks that are both renewable rather than depleting & less toxic to environment & human health.

qualities.

(i) Relatively safer material.

(ii) Should place minimal demands on the earth's resources.

(iii) Its acquisition & refining should be safe.

(iv) It should be renewable.

⇒ Source : method & environmental impacts.

⇒ Sepration: of desired feedstock component from waste matters.

⇒ Conversion: of isolated feedstock material to desired product.

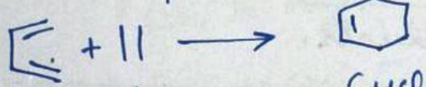
10. Maximize Atom Economy.

Atom economy is a measure of the efficiency of a particular reaction.
Synthetic methods should be designed to maximise the in-corporation of all atoms of reactant molecule used in the process into the desired final product.

$$\% \text{ Atom Economy} = \frac{\text{Mass of atom in desired product}}{\text{Total mass of atoms in reactant}} \times 100$$

$$\% \text{ yield} = \frac{\text{Mass of product obtained (actual)}}{\text{Theoretical mass of the product}} \times 100$$

For Green Synthesis, the atom economy must be very high, approaching or equal to 100%.
less or no by product.



Butadiene ethene Cyclohexene.

% Atom economy = 100 %.

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11. Avoid chemical derivative.

Unnecessary derivatization (Use of blocking groups, protection/deprotection, temporary modification of physical/chemical process.) should be minimized or avoided if possible, because such steps require additional reagents & can genrate waste.

→ This can be done by the use of enzymes.
Enzymes are so specific they will react only the one site of the molecule, leaving the rest molecular part. & hence protecting groups are often not required.

eg. of Biological feed stocks.

1. Carbohydrates
2. Cellulose
3. Lignin
4. Lipids.
5. Oils & fats.

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7. Design Chemicals & product That degrade after use.

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

⇒ Biodegradation, hydrolysis & photolysis can be designed into chemical products.

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8. Analyze in Real time to prevent pollution.

Analytical methodologies need to be further developed to allow for real-time, in-process monitoring & Control prior to the formation of hazardous substance.

The effective application of process analytical chemistry directly contributes to the safe & efficient operation of chemical plants world wide.

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9. Use Catalysts.

A catalyst is defined as a "substance that changes a velocity of a reaction without itself being changed in the process." It lowers the activation energy of the reaction but in so doing it is not consumed.

→ used in small amount.

→ Can be recycled.

→ doesn't generate any waste.

12. Minimize the potential for Accidents.

Safety can be defined as the control of recognized hazard to achieve an acceptable level of risk.
This is also known as saftey principle.

~~Saft~~ Saftey at
(i) substance choosen
(ii) form of substance choosen
(iii) Process of reaction.

to minimize the potential for chemical accidents, Including releases, explosions. & fires.

in Traditional approach

$$\text{Risk} = \text{Hazard} \times \text{Exposure}.$$
$$\text{Risk} = \text{Hazard} \times (\text{Dose} \times \text{time})$$

This is how risk calculated traditionally & focus is on limiting the exposure of a hazardous material for avoiding risk.

Green chemistry approach:
Reduce or eliminate the hazard itself.

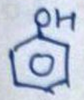
Environmental Impact. of Green Chemistry on society.

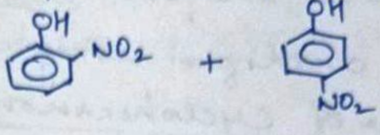
1. Many chemicals end up in environment by intentional release (eg. pesticide) by unintended releases (i.e. during manufacturing or disposal)
   Green chemicals either degrade to innocuous products or are recovered for further use.
2. Plants & animals suffer less harm from toxic chemicals
3. lower potential for global warming, ozone depletion, smog formation.
4. less chemical disruption of ecosystem.
5. less use of landfills, especially hazardous waste landfills.

Paracetamol.

Conventional Method.

Step 1 Phenol. $\xrightarrow[\text{Nitrating Mixture}]{HNO_3 + H_2SO_4}$ o nitrophenol + p nitrophenol.

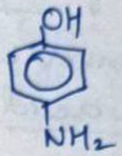




Step 2.

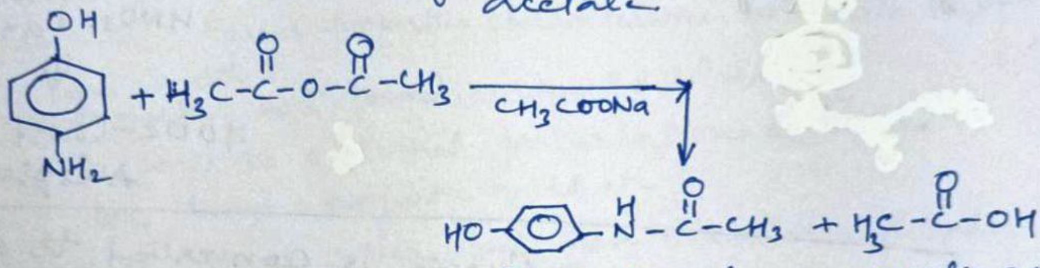
p nitrophenol $\xrightarrow{\text{NaBH}_4\text{(Sodium borohydride) or NH}_4\text{OH (hydroxylamine)}}$ paminophenol.

↑
(Reduse pnitropheno)



Step 3. paminophenol. $\xrightarrow[\text{by acetic anhydride}]{\text{acetylation}}$ Paracetamol.

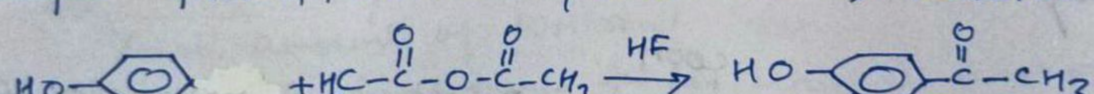
presence of sodium acetate



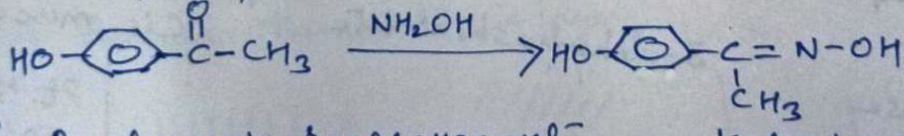
Paracetamol acetic acid.

Green Synthesis.

Step 1 phenol + acetic anhydride $\xrightarrow{HF}$ 4, hydroxy acetaphenon ketone



Step 2. 4hydroxyacetaphenone $\xrightarrow{\text{hydroxilamine}}$ Ketoxime



Step 3. Beckmann's rearrangment Ketoxime

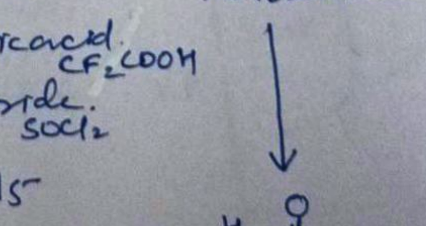
in presence of trifluroaceticacid. CF_3COOH

or

thionylchloride. $SOCl_2$

or

Amberlyst 15

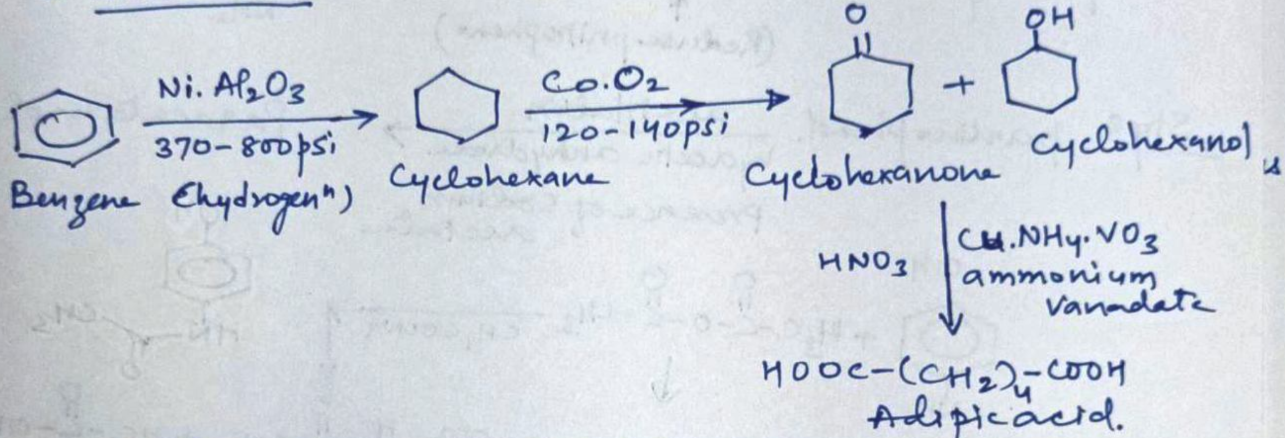


Adipic Acid.

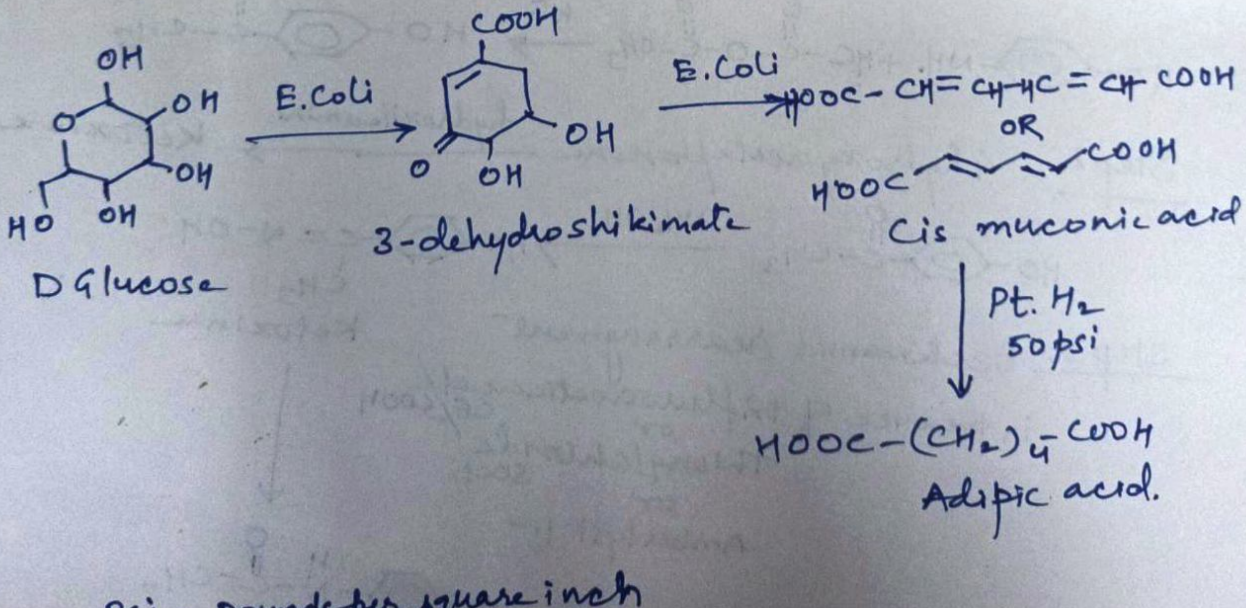
→ Benzene is hydrogenated using $Ni\text{-}Al_2O_3$ Catalyst using 370–800 psi to cyclohexane

→ This is oxidized using Co(Cobalt) catalyst to a mixture of cyclohexanone & cyclohexanol.

→ Then Converted to adipic acid using ammonium vandate & nitric acid.



Green Route : D glucose is converted to ~~cis~~ Cis muconic acid using E.Coli, which is further hydrogenated to adipic acid using hydrogen gas.



Psi – pounds per square inch