" GREEN CHEMISTRY "

* It is the design of chemical products and processes that reduce or eliminate use and generation of hazardous substances.

* Principles of green chemistry:

i) it is better to prevent waste than to treat waste after it is formed.
The by-products and non-reacted started materials constitute waste. Chemical synthesis should be designed to minimise waste formation. Because sometimes, treating waste becomes so expensive that overall production cost ↑ tremendously. Also, hazards associated with waste storage, transportation & treatment is minimized.

ii) Synthetic methods should be designed to maximise incorporation of all material in process into final product.
- Maximum yield and maximum efficiency should be achieved

iii) Wherever praticable, synthesis should be designed to use & generate substances that possess little or no toxicity to human health & environment.
For a particular process, a no. of reagents are available, but we choose reagent such that they not only pose less risk but also generate benign by-products. for eg. in manufacture of polystyrene foam sheet packing material CFC's have been replaced by CO_2 as blooming Agent.

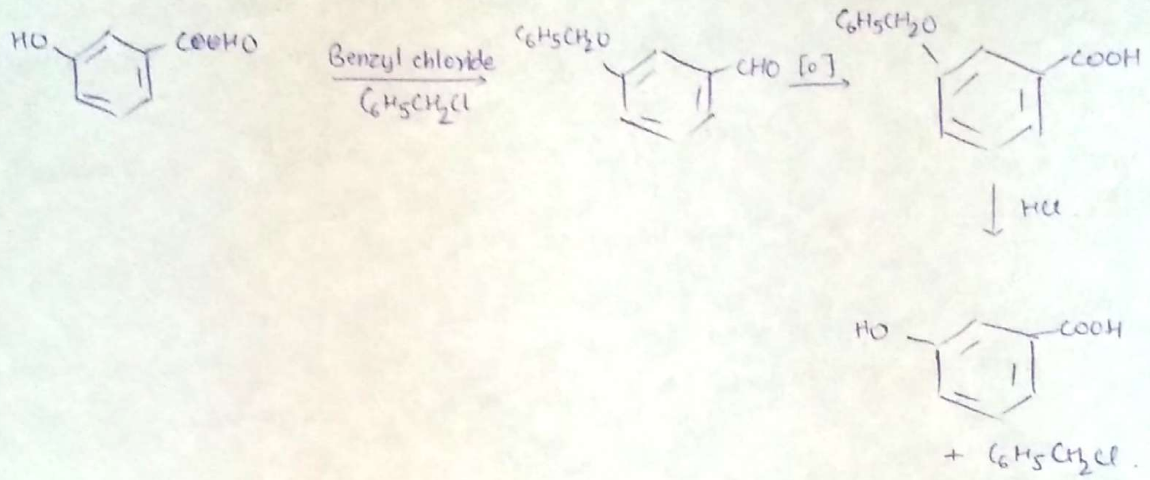
iv) Chemical products should be designed to preserve efficacy of function while reducing toxicity.
The rxn products should be fully effective with no toxic effect. eg Thalidomide a drug used for reducing effects of vomiting during pregnancy resulted in birth defects in children. Its use has been banned.

v) The use of Auxillary substances (ie. solvent, separating agents) should be made unnecessary wherever possible & innocuous (less harmful) when used.
eg in dry-cleaning process for clothing, liquid CO_2 has replaced perchloroethylene (hazardous) for dissolving grease. Efforts should be made to reduce volume of solvent used.

vi) Energy requirements should be recognized for environmental & economic impacts and should be minimized.
Chemical rxn should be conducted at ambient temp. & pressure. In exo-rxn cooling is required which adds to total cost. Energy also req for purification

vii) A raw material or feedstock should be renewable rather than depleting.
eg. production of adipic acid has now seen replacement of benzene by glucose with rxn carried out in water.

viii) Derivatives (blocking Agents / protection/deprotection grps) should be avoided whenever possible.
Derivatization results in increase in no. of steps required in process & which in turn ↑ use of reagent & can generate more waste. eg. Benzyl-chloride (a known chazard) is used as protection group for 'OH' group. Atom economy of such rxn is usually low.



ix) use of catalysts over stoichometric reagents.
Since catalysts are highly selective, they reduces the waste formation. They reduce temp of transformation, avoid unwanted side rxn and hence serves the purpose of Green technology. They are required in low amounts, whereas stoichiometric reagents are used in excess & work only once

x) Products should be biodegradable after use.
They should breakdown after use and should not accumulated in the environment. eg. Insecticide DDT, has been banned as it is non-biodegradable.

xi) Analytical technologies should be developed.
The quick detection of harmful substance help in quick curative action.

xii) substances used in chemical process should be chosen to minimise potential for chemical accidents.
The substances should be safe even if some accident may take place, they should be no Harm to environment.
Bhopas gas tragedy posed a great challenge.

* ATOM ECONOMY

Concept of Atom economy is Basically a method of expressing efficiency of a particular rxn. The greater the value of atom economy of a rxn, better is the rxn to convert all reactant atoms to desired product.

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

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

i) Substitution rxn:

$$\underbrace{CH_3-CH_2-CH_2-OH + NaBr + H_2SO_4}_{275g} \longrightarrow \underbrace{CH_3-CH_2-CH_2-Br}_{\substack{\text{(desired product)} \\ = 137\,g.}} + NaHSO_4 + H_2O$$

$$\text{Atom economy} = \frac{137}{275} \times 100 = 50\%$$

ii) Elimination rxn:

$$\underbrace{CH_2(H)-C(CH_3)(Br)-CH_3 + CH_3CH_2ONa}_{205} \longrightarrow \underbrace{CH_2=C(CH_3)-CH_3}_{56} + CH_3CH_2OH + NaBr$$

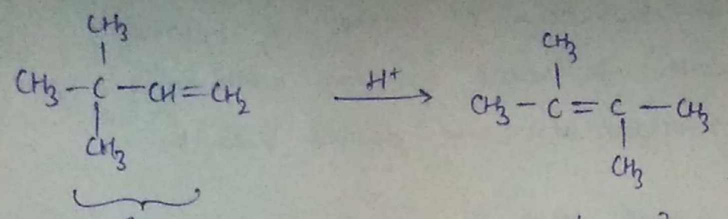
$$\text{Atom economy} = \frac{56}{205} \times 100 = 27\%$$

iii) Addition reactions.

$$\underbrace{CH_2=C(CH_3)-CH_3 + HBr}_{137} \xrightarrow[\text{peroxide}]{\text{no}} \underbrace{CH_3-C(CH_3)(Br)-CH_3}_{137.}$$

$$\text{Atom economy} = \frac{137}{137} \times 100 = 100\%$$

iv) Rearrangement reactions.



84 $\quad\quad$ 84

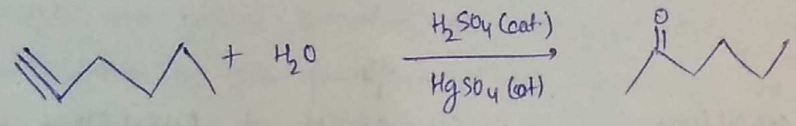
$$\text{Atom economy} = \frac{84}{84} \times 100 = 100\%$$

NOTE 1: Atom economy of rearrangement rxn are always better than that of elimination rxn because in elimination rxn. some part of reactants gets eliminated and forms side-product whereas in rearrangement rxn, no side product is formed.

NOTE 2: H^+ in above rxn acts as catalyst & is recovered at the end of rxn, so it is not to be added in calculation of mass of Reactant.

* ATOM ECONOMY OF SOME MORE RXN.

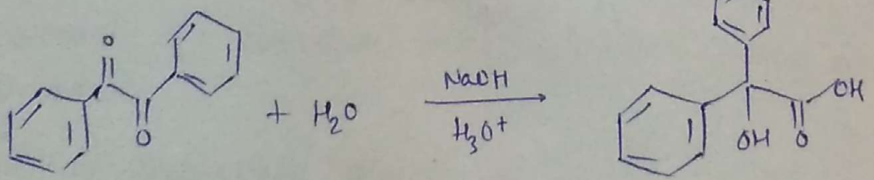
v) atom economy for Hg^{+2} catalyst hydration of Alkene. (catalysed rxn)



82.15 $\quad$ 18.01 $\quad$ 100.16

$$\%\ \text{Atom economy} = \frac{100.16}{82.15 + 18.01} \times 100 = 100\%$$

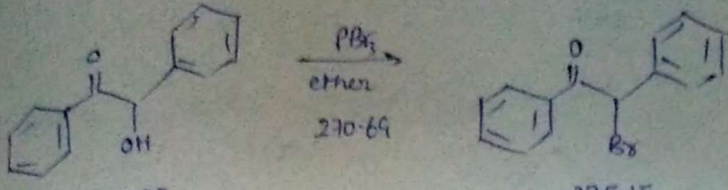
vi)



210.24 $\quad$ 18.01 $\quad$ 228.25

$$\%\ \text{Atom economy} = \frac{228.25}{18.01 + 210.24} \times 100 = 100\%$$

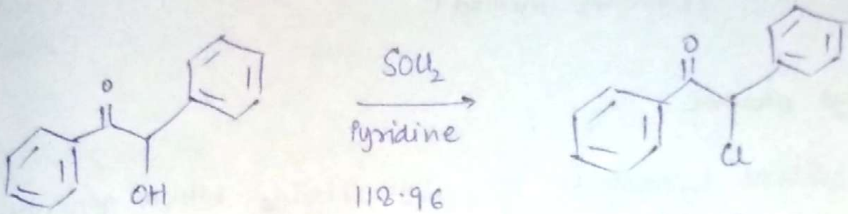
viii) bromination of secondary alcohol with PBr_3



212.25 275.15.

$$\text{Atom economy} = \frac{275.15}{212.25 + 270.69} \times 100 = 57\%.$$

viii) bromination of Secondary alcohol with $SOCl_2/Py$.



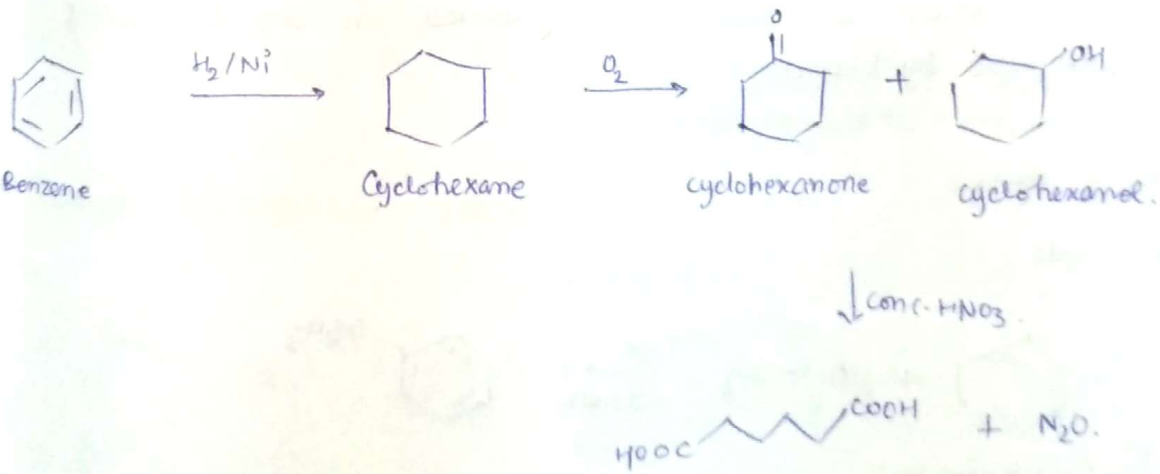
212.25 230.69.

$$\% \text{ Atom economy} = \frac{230.69}{212.25 + 118.96} \times 100 = 70\%.$$

* GREEN METHODS OF SYNTHESIS.

i) Synthesis of Adipic Acid.

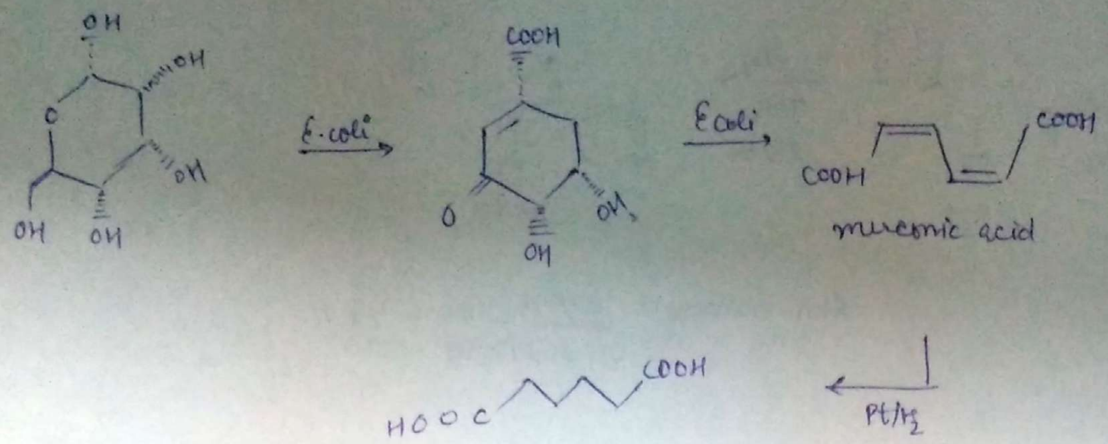
Traditional method :



* Risks involved : Benzene is used as starting material, which is known to be carcinogenic.

So, now, it is ppd. from Adipic Acid

biosynthetic pathway :



(Adipic Acid)

(Greener method).

ii) Production of allyl alcohol.

Traditional route : Alkaline hydrolysis of allyl chloride which generates HCl

$$CH_2=CHCH_2Cl + H_2O \longrightarrow CH_2=CHCH_2OH + HCl$$

Greener route : Two step formation as given below :

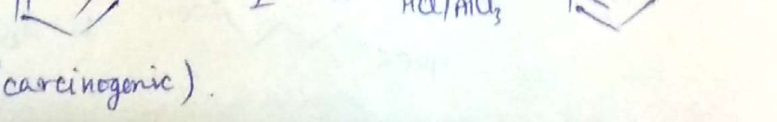
$$CH_2=CHCH_3 + CH_3COOH + \frac{1}{2}O_2 \longrightarrow CH_2=CHCH_2OCOCH_3 + H_2O$$

$$CH_2=CHCH_2OCOCH_3 + H_2O \longrightarrow CH_2=CHCH_2OH + CH_3COOH.$$

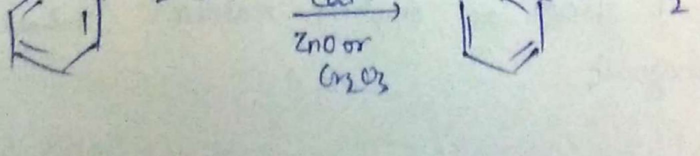
Benefits : CH_3COOH added in step 1 is recovered in step 2. leaving no undesirable by-products.

iii) Production of styrene.

Traditional route :



(carcinogenic).



Greener method : single step conversion of Xylenes to Styrene (better Atom Economy)

(iii) Production of Styrene oxide

Traditional method : Chlorohydrin route.

$CH_2=CH_2 + Cl_2 + H_2O \longrightarrow Cl-CH_2-CH_2-OH + HCl$

$Cl-CH_2-CH_2-OH + Ca(OH)_2 \longrightarrow CH_2-CH_2$ (O) $+ CaCl_2 + 2H_2O$

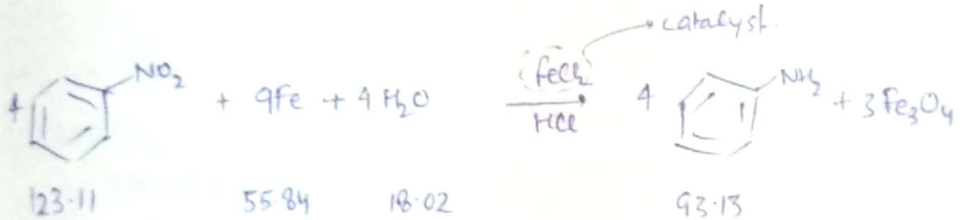
% Atom economy = 44/189 ×100 = 23%.

Green method : Catalytic route.

$CH_3CH_2=CH_2 + H_2O_2 \xrightarrow{cat.} CH_2-CH_2$ (O) $+ H_2O$.

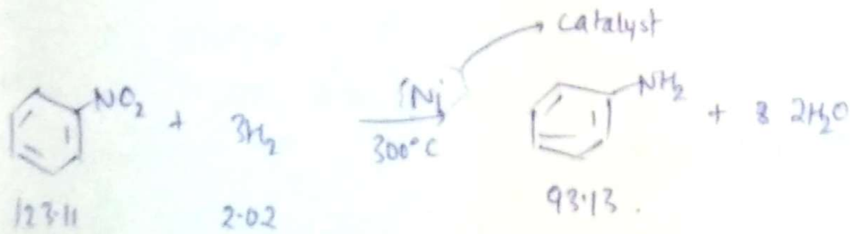
% Atom economy = $\frac{44}{44+18} \times 100 = 70.96\%$.

iv) Traditional Beckhamp process :



% Atom Economy = $\frac{4 \times 93.13}{4\times123.11 + 9\times55.84 + 4\times18.02} \times 100 = 35\%$.

Nickel catalysed hydrogenation process.



% economy = $\frac{93.13}{123.11 + 3\times2.02} \times 100 = 72\%$.

NOTE : Equation should be balanced while calculating Atom Economy.

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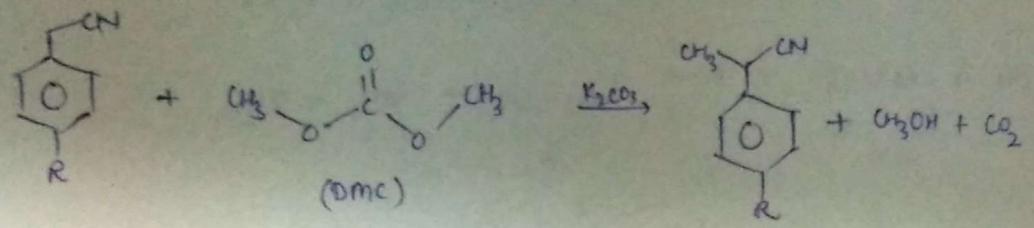
* GREEN REAGENTS

[non-toxic, biodegradable and give maximum atom economy].

Conventionally, methylation rxn were carried by using methyl halide or methyl sulphates which are toxic and synthesis is undesirable. Now, DMC (dimethyl carbonate - A green reagent) is used.



* using safer chemicals.

Conventionally, organotin compounds were used in large ships to prevent accumulation of Barnacles (resist movement of ship) but these are toxic and harm surrounding marine life.

Now, Sea-Nine is a non-toxic alternative used to prevent accumulation of Barnacles.

* Green solvents. (safer solvents)

A solvent is a liquid, solid or gas that dissolves another solid, liquid or gaseous solute to form a solution. Organic solvents are used in dry cleaning (perchloroethylene), as nail polish removers & glue solvents (acetone), in detergents (citrus terpenes) & in perfumes (ethanol) etc.

- But all these are found to be toxic, flammable, volatile, hazardous to environment. (alcohol, benzene, CCl_4, $CHCl_3$ etc.). Their purification leads to large amount of wastes. ∴ these are replaced by green solvents namely :

  i) ionic liquids

  ii) supercritical CO_2

  iii) supercritical water

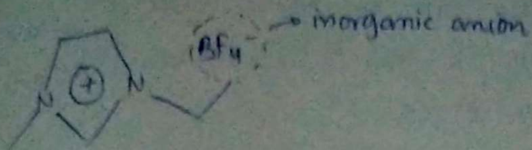
  iv) solvent-free systems.

i) Ionic liquids. (ILs)

The class of materials which consists entirely of ions & are liquid below 100°C. It includes an organic cation & inorganic anion. They are non-volatile & have no vapour pressure. and can be recycled easily.

- RTILS – If they are liquid at room temp. they are called room temp. ILs.

eg.



Ethyl methyl imidazolium tetrafluoroborate [emim][BF_4]

* Ionic liquids as reaction media

These are used in a no. of rx^n listed below:

i) Alkylation rx^n.

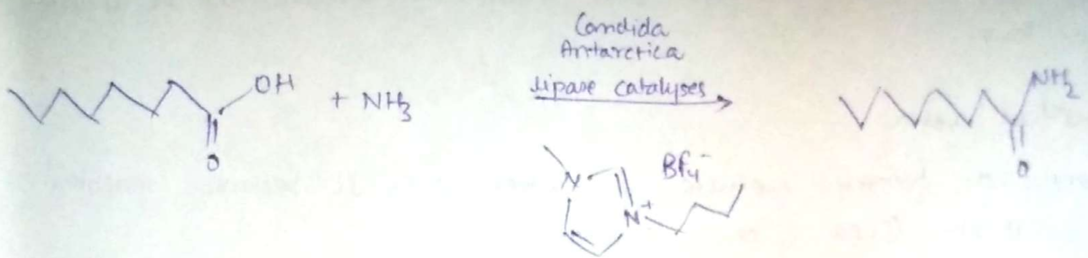
ii) F-C rx^n

iii) Alkene polymerisation

iv) Biotransformations

• BIOTRANSFORMATIONS IN IL'S

Process of Ammoniolysis:



• Rx^n rate is better than that carried out in organic solvent.

* Advantages of Ionic liquids.

i) Good solvents for organic, inorganic & polymeric compounds.

ii) Anions & cations can be tuned for wide range of solvent properties.

iii) Very low vapour pressure.

* Disadvantages of ILs.

i) Expensive as compared to other solvents.

ii) Involves use of other solvents for its preparation, purification & separation.

iii) Some are toxic.

* Supercritical CO_2 (Sc-CO_2).

• low viscosity & surface tension.
• unique ability to diffuse
} Advantages
• inexpensive as CO_2 is obtained as By-product in other rx^n.
• easily evaporated.

- If Temp & pressure are both ↑ from STP to above critical values, it can adopt properties midway b/w a gas & a liquid. & behaves as supercritical fluid. ∴ called supercritical CO_2.

* Applications (uses) of $Sc\text{-}CO_2$.

- ~~defac def~~ decaffeination using $ScCO_2$.

$$\underset{\text{(with caffeine)}}{\text{Coffee beans}} \xrightarrow{Sc\text{-}CO_2} \underset{\text{(without caffeine)}}{\text{coffee beans}}$$

i) due to high density, dissolves 97% - 99% of caffeine.

- used as a solvent for dry-cleaning.
- Since, it is non-toxic & non-flammable ∴ used as extraction solvent for creation of essential oils.
- Extraction process has advantage over steam-distillation as it is used at low-Temp.

* Supercritical water

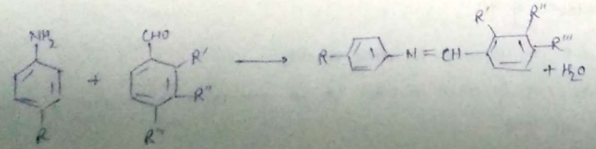
Many compounds becomes soluble in water when it becomes supercritical at 374°C & 218 Atm. (Clean & cheap solvent).

* Water as reaction medium.

- cheap, readily available, plentiful.
- Limited use because of low-solubility of organic substrates.

* Solvent-less chemistry (Solid-state rx^n / dry media rx^n).

$$\text{Solid A} + \text{solid B} \xrightarrow{\text{grind}} \text{Solid C}.$$



- limited no of rx^n possible
- Exothermic rx^n creates problems.
- solvents still required for separation, purification etc.
- reactants may not mix homogeneously
- high viscosity in reactant system.

* Evaluation of feedstocks. (Raw materials).

The first step of green chemistry is the nature / profile of feedstock. so that it may not produce toxic products. The things that are needed to be kept in mind are :

i) origin of feedstock

> mined
> synthesized
> Natural
> recycled

ii) Sustainability

> Renewable
> Depleting

iii) Impact on human health & environment.

> Hazardous
> Innocuous (less harmful)