Green Technology and Green Chemistry

↳ mid 20th century

Chemical manufacturing

→ sources of drugs, antibiotics, plastics, fuels, ~~agri~~ pesticides, insecticides, fertilisers, synthetic fabric (nylon, rayon, polyester)

Green ~~technology~~ Chemistry is environment friendly chemical synthesis in which schemes are designed to minimize pollutn.

Green Technology

- Green ~~Technology~~ Chemistry and its Basic principles aims at reducing the environmental pollutn by inovving various synthesis chemical.

12 basic principles

1. PREVENTION OF WASTE
   → chem synthesis should be designed in a way to minimize waste products formed
   → preventatn of waste generation; waste storage, transportatn and treatment is minimized to
2. ATOM ECONOMY
   → chem synthesis should be done to maximize the incorporatn of starting materials and ~~final products~~ reagents in final product.

3. MINIMIZATION / PREVENTION OF HAZARDOUS CHEM SYNTHESIS

→ synthesis should be designed to use or generate substn which can provide minimum to no toxicity to wealth and environment.

4. DESIGN SAFER CHEMICALS

→ synthesis should be in such a way that they should be fully activ without having toxic effects.

5. USE OF SAFER SOLVENTS & AUXILLARIES

→ auxilary substn (solvents, seperatn agents etc.) should be avoided.

→ if these chemicals are necessary, safer chemicals should be used. (H_2O or liq. CO_2)

→ CCl_4, $CHCl_3$, $Cl_2C=CCl_2$: harmful to health, can create dangerous like explosives or fire hazards.

→ liq. CO_2 instead of $Cl_2C=CCl_2$ for dissolving grease.

6. DESIGN FOR INCREASE IN ENERGY EFFICIENCY

→ chemicals ~~stout~~ rxn should be carried out at ambient ~~temp~~ and pressure to minimize environmental economic impacts.

→ process should be designed so that no need for seperatn or purificatn.

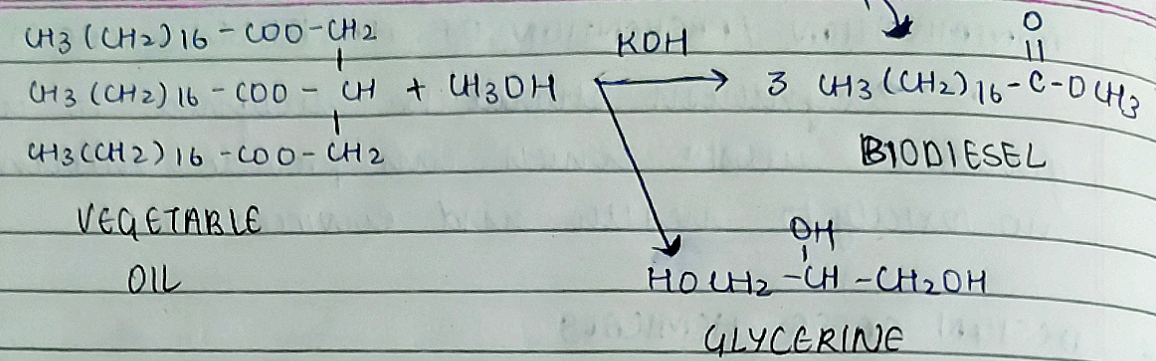
7. SELECTION OF RENEWABLE FEEDSTOCKS AS STARTING MATERIAL

→ Raw matr and foodstocks should be preffered over depleting ones

→ BIODIESEL (Methyl or Ethyl ester of fatty acid)

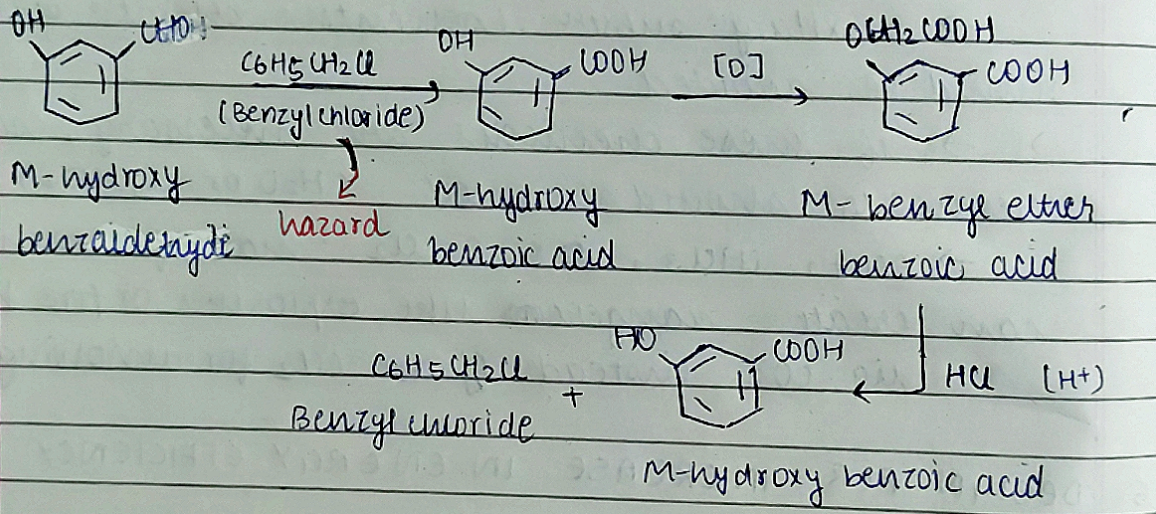
- clean fuel as contains no ~~S, O~~ sulphur S, aromatics & has 10% built in oxygen & making it easy to burn.

can be used in pure form or blended



8. AVOID CHEMICAL DERIVATIVES

→ blocking grp, protection / deprotectn or any temporary modificatn of phys / chem processes should be avoided.



* less atom economic as waste is generated

9. USE OF CATALYST & NON STOICHIOMETRIC REAGENTS

→ catalytic rxn are HIGHLY SPECIFIC & are needed in very small amts.

→ energy efficient rxn. (low temp)

→ stoichiometric reagents are used in excess and work only once & hence should be avoided.

(1) $CH \equiv CH$ (acetylene) + H_2O $\xrightarrow{HgSO_4 + H_2SO_4}$ CH_3CHO (acetaldehyde)

- not possible without catalyst

(2) $CH_3C \equiv CH$ (propyne) $\xrightarrow[PdBaSO_4]{+H_2}$ $CH_3CH = CH_2$ (propene)

- selectivity increased

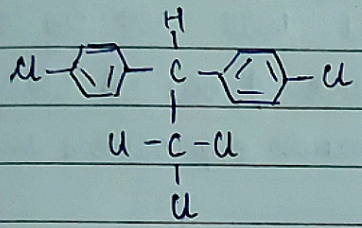
(propene)

(3) $CH_3CH=CH_2 + H_2 \xrightarrow{Ni\ catalyst} CH_3CH_2CH_3$ (propane)

- better yield is obtained

10. PRODUCTS DESIGNED SHOULD BE BIODEGRADABLE

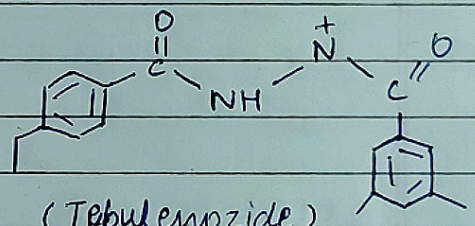
→ products should be designed ~~as~~ so that they breakdown into safer substⁿ & not accumulate



(DDT) → harmful

→ DDT, aldrin, dieldrin remain in environᵗ for long periods as they are non biodegradable.

→ diacetylhydrazines (Tebufenozide, halofenozide etc.) are useful insecticides and biodegradable.



(Tebufenozide)

→ useful.

11. STRENGTHENING OF ANALYTICAL TECHNIQUES FOR POLLUTION PREVENTION

→ in-process real-time monitoring & control should be designed during synthesis to monitor progress of rxn if it is complete or not, so by-products can be minimized and detected.

12. DESIGN OF MANUFACTURING PLANTS TO MINIMIZE THE POTENTIAL FOR ACCIDENTS

→ forms of chem (solid, liq, gas) should be chosen to minimize potential for chemical accidents, ~~but~~ also explosions, fires and release of toxic subst.

CASE STUDY

2011: Japan earthquake, tsunami, and Fukushima nuclear disaster.

→ Japan experience a powerful earthquake & tsunami, claiming 20,000 lifes.

→ Fukashima Daiichi power plant, was severely damages by earthquake and tsunami knocking out its crucial cooling system, resulting in ~~world's~~ explosions and meltdowns

ATOM ECONOMY

- method of expressing efficiency of rxn.

Objective: most efficient output to obtain with least amount of wastage

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

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

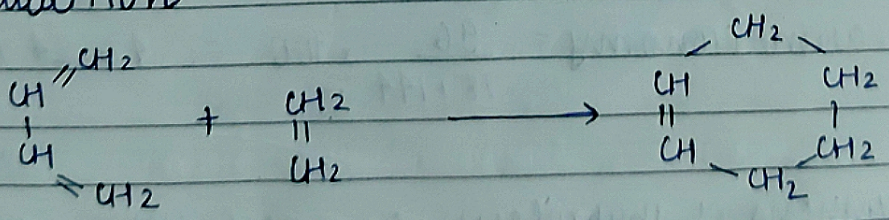
REARRANGMENT RXNs

(MW = 134.175 g) (MW = 134.175 g)

$$\% \text{ atom economy} = \frac{134.175}{134.175} \times 100 = 100\ \%$$

ADDITION REACTIONS

a) cycloaddition



(M.W = 54 g) (MW = 28 g) (M.W = 82 g)

$$\% \text{ atom economy} = \frac{82}{54+28} \times 100 = 100\ \%$$

b) catalytic addition → catalyst can be fully recovered after rxn

$CH_3CH=CH_2 + H_2 \xrightarrow{Ni} CH_3CH_2CH_3$

(M.W = 42g) (M.W = 2g) (M.W = 44g)

% atom economy = $\frac{44}{42+2} \times 100 = 100\%$

SUBSTITUTION RXN

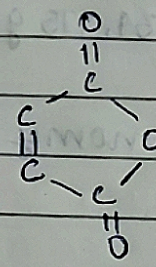
(desired prod)

$CH_3CH_2C(=O)-OC_2H_5 + CH_3NH_2 \longrightarrow CH_3CH_2C(=O)-CH_2NH_2 + C_2H_5OH$

(M.W = 102.132g) (31.057g) (87.106 g) (40.083g)

% atom economy = $\frac{87.106}{102.132 + 31.057} \times 100 = 65.40\%$

OXIDATION RXN

benzene (78g) + 4.5 O_2 (MM = 144g) →  + $2CO_2$ + $2H_2O$

(96g)

(desired prod.)

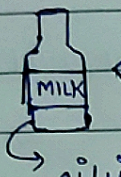
% atom economy = $\frac{96}{78+144} \times 100 = 43.24\%$

Synthesis of Ibuprofen : uses 6 steps with an atom economy of only 40.1%

1990s : HCC developed new 3 stage process with atom economy of 77.4%

ZERO WASTE TECHNOLOGY

- methodologies are devised for synthesis so that there are no by-products formed during a rxn.
- or if any waste by products can be used as raw materials.



→ Normal waste method : Landfills

→ zero waste method : Recycled and reduced to its constituents.

manufacture of NH_3 : CO_2 ↑ ⇒ ~~doesn't contribute to greenhouse effect.~~ mixed with natural gas units is used in making POLYSTYRENE FOAM SHEETS.

ozone depleth

⇒ replaces CFC's, ~~reduce~~ reducing the adverse impact on environment.

⇒ CO_2 is ECONOMICAL, easy to handle, & doesn't form smog or depletes ozone layer.

TOOLS OF GREEN TECHNOLOGY

Obj: reduce ~~toxicity~~ toxicity in environment.

TOOLS OF GREEN TECH

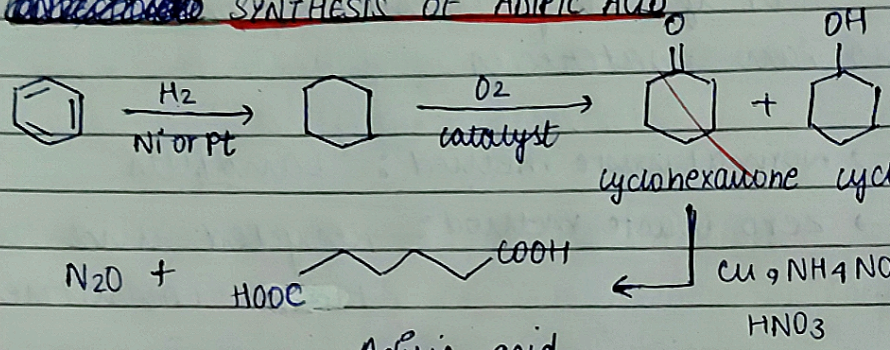
- Green starting material
- Green reagents
- Green reactn
- Green chem Products
- Green Methodoligies

GREEN STARTING MATERIALS

- it is non toxic, preferably renewable and does not degrade the quality in environment.

SYNTHESIS OF ADIPIC ACID

Conventional Method

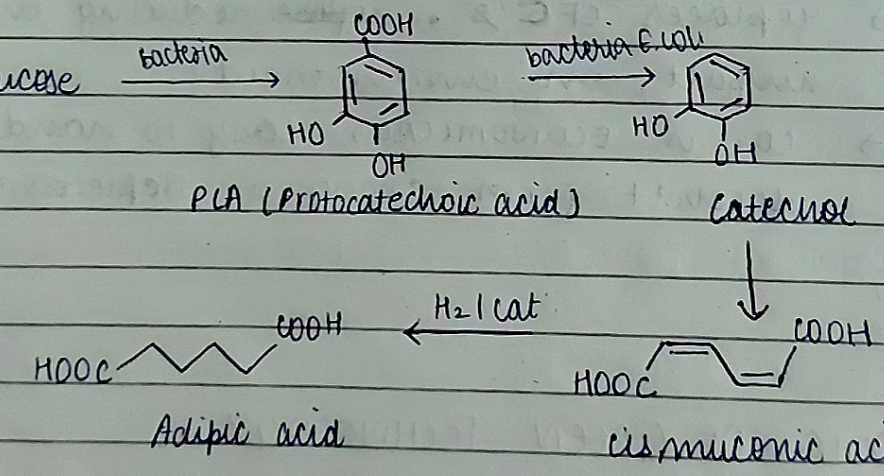


Adipic acid

- in synthesis of nylon, plasticisers & lubricants prepared from benzene (carcinogenic)

GREEN SYNTHESIS OF ADIPIC ACID FROM D-GLUCOSE

Green synthesis



Adipic acid

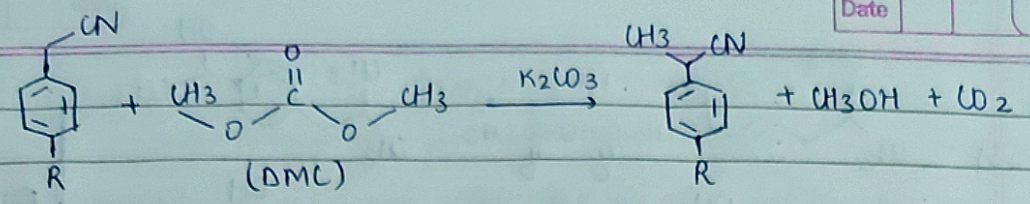
cis,muconic acid

GREEN REAGENT

- is easily available (from natural ~~sou~~ renewable resources), non toxic, give maximum atom economy & waste prd. are non toxic.

METHYLATION REACTIONS

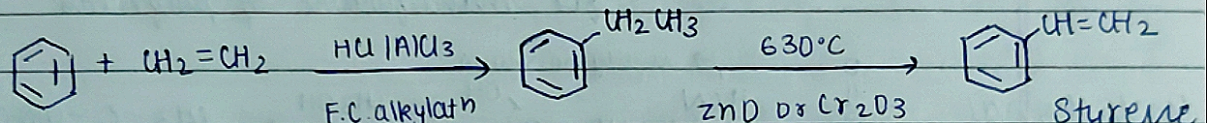
- carried by using Methyl halides CH_3X or methyl sulphate which are very toxic, hence synthesis is undesirable.



→ Tundo developed a method to methylate active methylene cmpds using DMC: dimethyl carbonate without producing any inorganic salts.

STYRENE (monomer of polystereene)

FIDEL CRAFTS ALKYLATION



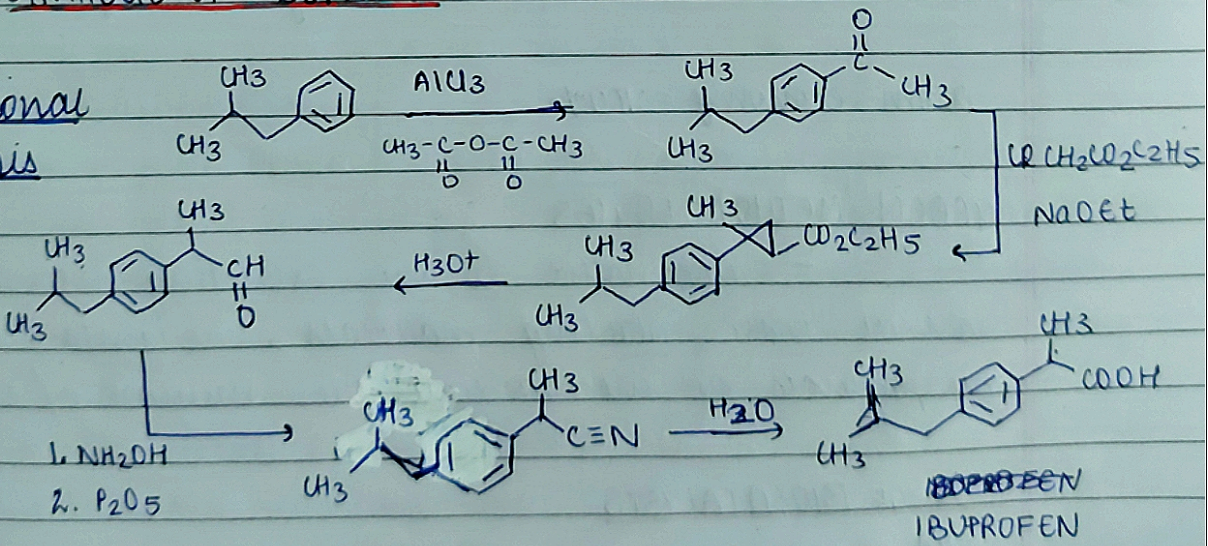
→ green synthesis dev. by Chapman a single step is used to convert mixed xylenes to Styrene.

GREEN REACTIONS

– based on the "concept of Atom economy"

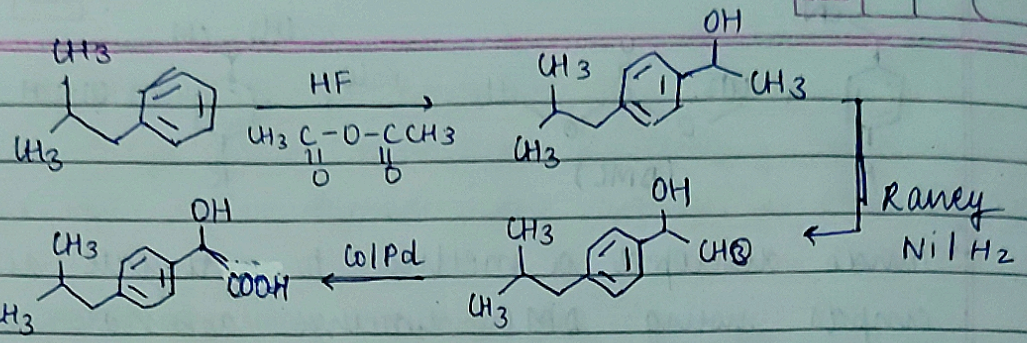
SYNTHESIS OF IBUPROFEN

Conventional synthesis



atom economy = 40.1%

Green synthesis



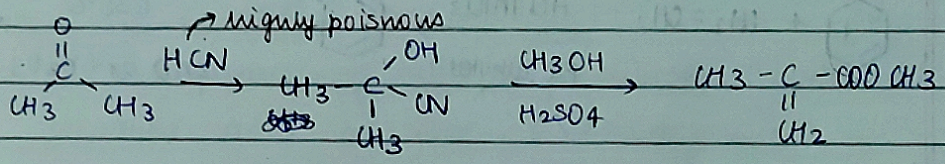
IBUPROFEN

atom economy = 77.4 %

SYNTHESIS OF METHYL METHACRYLATE :

- for manufacture of polymers

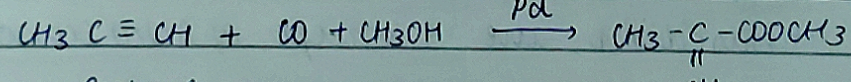
Conventional synthesis



Acetone — Methyl Methacrylate

atom economy = 74 %

Green synthesis



Propyne — Methyl Methacrylate

atom economy = 100 %

GREEN METHODOLOGIES

– alternative to the exisisting methods, so that toxic starting materials, reagents, catalysts, by products or intermediate are minimize / eliminated

USE OF BIOCATALYSTS

advantages : • rxns performed at ambient temp & pressure
• most rxn carried in aqueous medium.
• conversions are normally single step conversion.
• atomic economy is maxm². • stereospecific conversion

Biocatalysts (enzymes)

OXIDOREDUCTASES
→ catalyze oxdn reductn rxns.

HYDROLASES
→ catalyse hydrolytic rxns

ISOMERASES
→ responsible for isomerizatn rxn

TRANSFERASES
→ catalyze the transfer of various functn groups

LYASES
→ carry out the addn & elimination of small molecules of sp^3 carbon atoms

LIGASES
→ catalyse the formatn of cleavage of sp^3 hybrd. C.

USE OF AQUEOUS MEDIUM AS SOLVENTS

→ adv. of using water as a solvent instead of organic solvents is that ~~it is~~ it is:

- cheaply available
- safe (non flammable)
- non-carcinogenic
- simple in operation

rxns. that use aq. medium

DIELS ALDER RXN
→ hetrocyclic cmpds with N or O containing dienophiles

MICHAEL RXN
→ 2-Methyl-cyclopentane-1,3 dione when reacted with vinyl ketone in water gave a 5-6 fused ring system without using a basic catalyst.

CLAISEN REARRANGMENT
→ Thermal rearrangment of Allyl vinyl ether to give aldehyde in pure water

ALDOL CONDENSATION
→ rxn of 2-alkyl-1,3, diketones with aq. for maldehyde using 6-10 M aq. K_2CO_3 to form vinyl ketone.

GREEN CHEMICAL PRODUCTS

- those which serve the same function without being toxic or breaking down into toxic subst^{n}.

- ex: many insecticides use organochlorines, organophosphates and carbamates: ~~although they are less persistent~~
- aldrin, dieldrin (organo-Cl) get incorporated into the food chain.
- DDT is less persistent in environment, but they readily decompose in the environment & tend to be toxic.
- diacetyl hydrazine (insecticides) is non toxic.
- Tributyltin (TBT), conventional antifouling agent used on boats.

used on boats to nulls to reduce the build up marine organisms, such as algae, plants, diatoms etc.

DCOI {4,5 dichloro-2-n-octyl-4 iso thiazolin-3-one}

↳ antifouling agent which is less persistent in marine environment as well as the product of metabolism are non toxic.

Rohm & Hass developed.