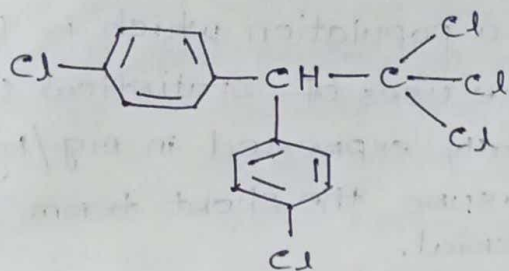


Book { Green Chemistry $\Rightarrow$ V.K. Ahluwalia
Green Chemistry $\Rightarrow$ Chandrakanta Bandyopadhyay

■ Introduction of Green Chemistry:

Silent Spring

1962 by Rachael ~~Kennan~~ Carson



(DDT)

Environmental pollution is an incurable disease. It can only be prevented.

1969 - NEPA [National Environment Policy Act]

$\rightarrow$ Barry Commoner

The

● Current status of Chemistry and the Environment:

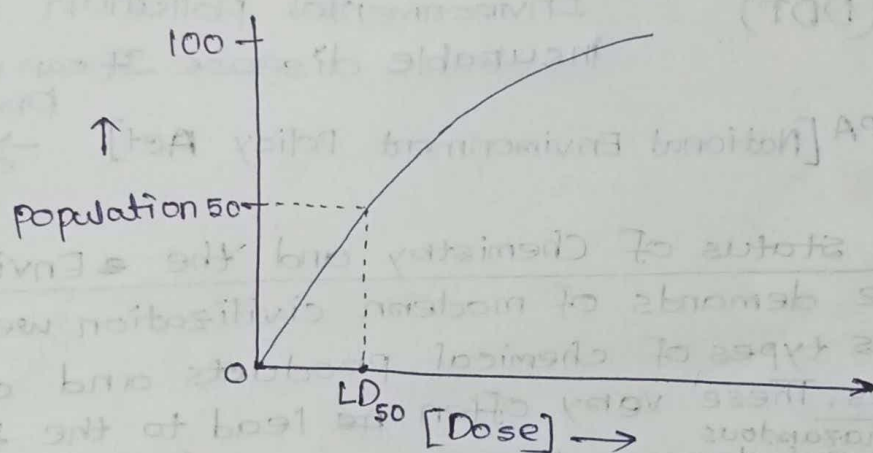
To meet the demands of modern civilization we need varieties types of chemical products and chemical industries. These very often ~~are~~ lead to the formation of ~~hazardous~~ ^{hazardous} substances and sometimes we are also to use hazardous substances. To prevent or minimize the formation and use of such hazardous substances, the chemists are required to develop the novel technologies. This need has inspired the generation of new branch of Chemistry, called Green Chemistry.

■ Toxic chemicals:

The list of toxic chemicals are too long, Here we shall only mention some. It has been already mentioned that some elements are essential to biological system, while some elements are toxic. However, the essential ~~elements~~ ^{elements} i.e., Fe, Cu, Zn, Mo, Co, V, Mn, Na, K, Ca, Mg, F, etc may also be toxic upto a certain level.

Metal	Fe	Zn	Cu	Mn	F	Mo	I	Na	K	Ca	P
Normal range (mg/ per day) for adult human being	10-15	15	2-3	3-5	1.5-3	150 μ g	150 μ g	5-10 mg/day	3-4 mg/day	1 mg/day	1 mg/day

LD₅₀ : LD₅₀ values represent the minimum dosages of a substance require to result in an average lethality of 50% of a population which is large enough to allow the uses of statistical treatment. LD₅₀ value is generally expressed in mg/kg. LD₅₀ is one way to measure the short term poisoning potential of the material.



■ Effect of toxic substances :

- 1) Enzyme inhibition
- 2) Cell membrane disruption
- 3) Disruption of carbohydrate and liquid metabolism
- 4) Inhibition of respiration
- 5) Mutation in genetic material

■ Observable physiological effect :

- 1) Malfunction (Fail to Function normally of central nervous system) : Coma, Ataxia (inability to coordinate voluntary movements), paralyseis, paresthesia, (loss of sensation) etc.

2) Change in ^{signs} vital ~~science~~ like body temperature, blood pressure, pulse rate, etc.

3) ~~Carcinogenesis~~ Carcinogenesis

4) Mutagenesis

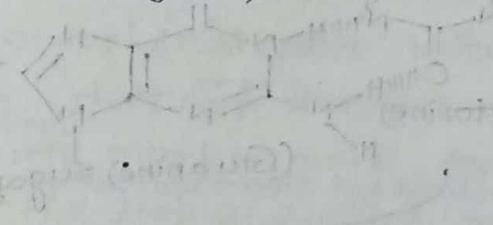
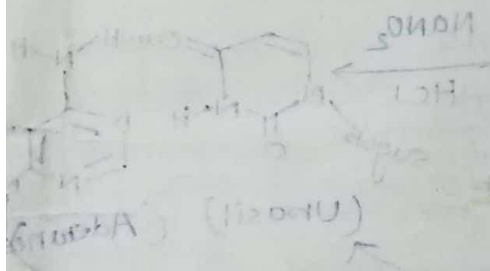
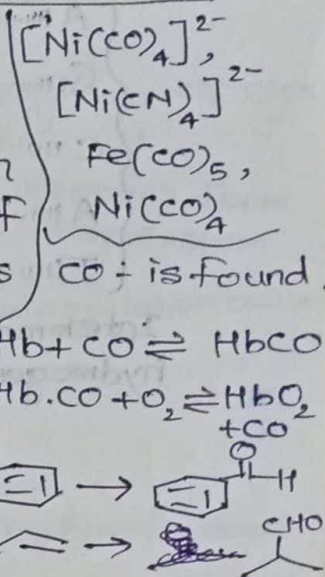
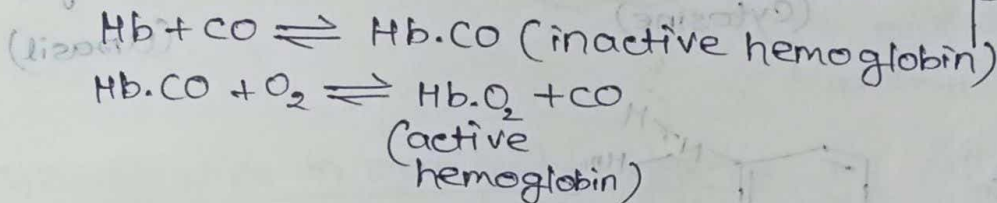
5) Effects on immunosystem.

Reversible and Irreversible effect of toxicity :

Reversible effect :

Some toxic chemicals can irreversibly damage the biological system & some can damage reversibly. The poisoning action of CO is not cumulative and in fact it binds reversibly with hemoglobin (Hb).

In fresh air (where the partial pressure of O_2 is high and partial pressure of CO is negligible) the hemoglobin bound CO is replaced by O_2 . Thus, the activity of CO is restored.



25/02/23
 ■ Some irreversible effect of toxic chemicals: online

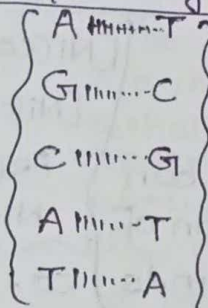
Food additive $\Rightarrow$ NaNO_2 is used

$\downarrow$
 it comes to drinking water

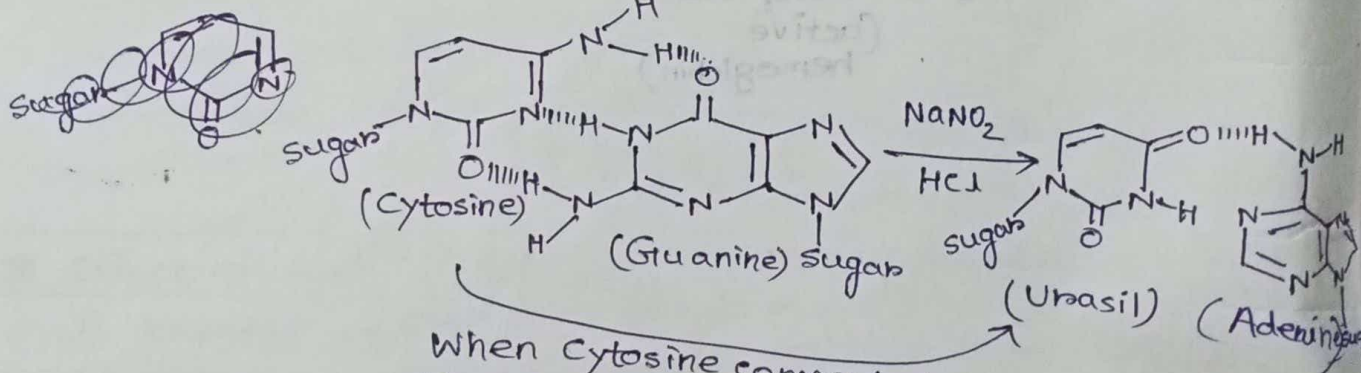
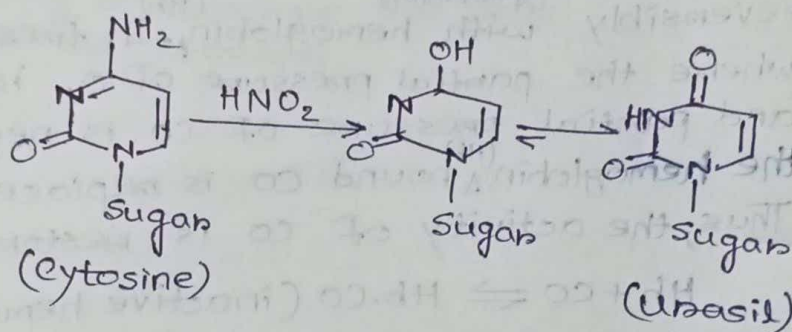
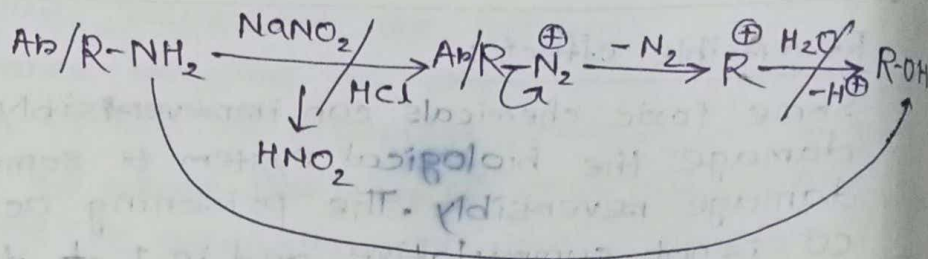
It affects the base pairing sequence in DNA.

$\downarrow$
 It alters genetic code $\Rightarrow$ Mutation

Base pairing



Intermolecular hydrogen bond

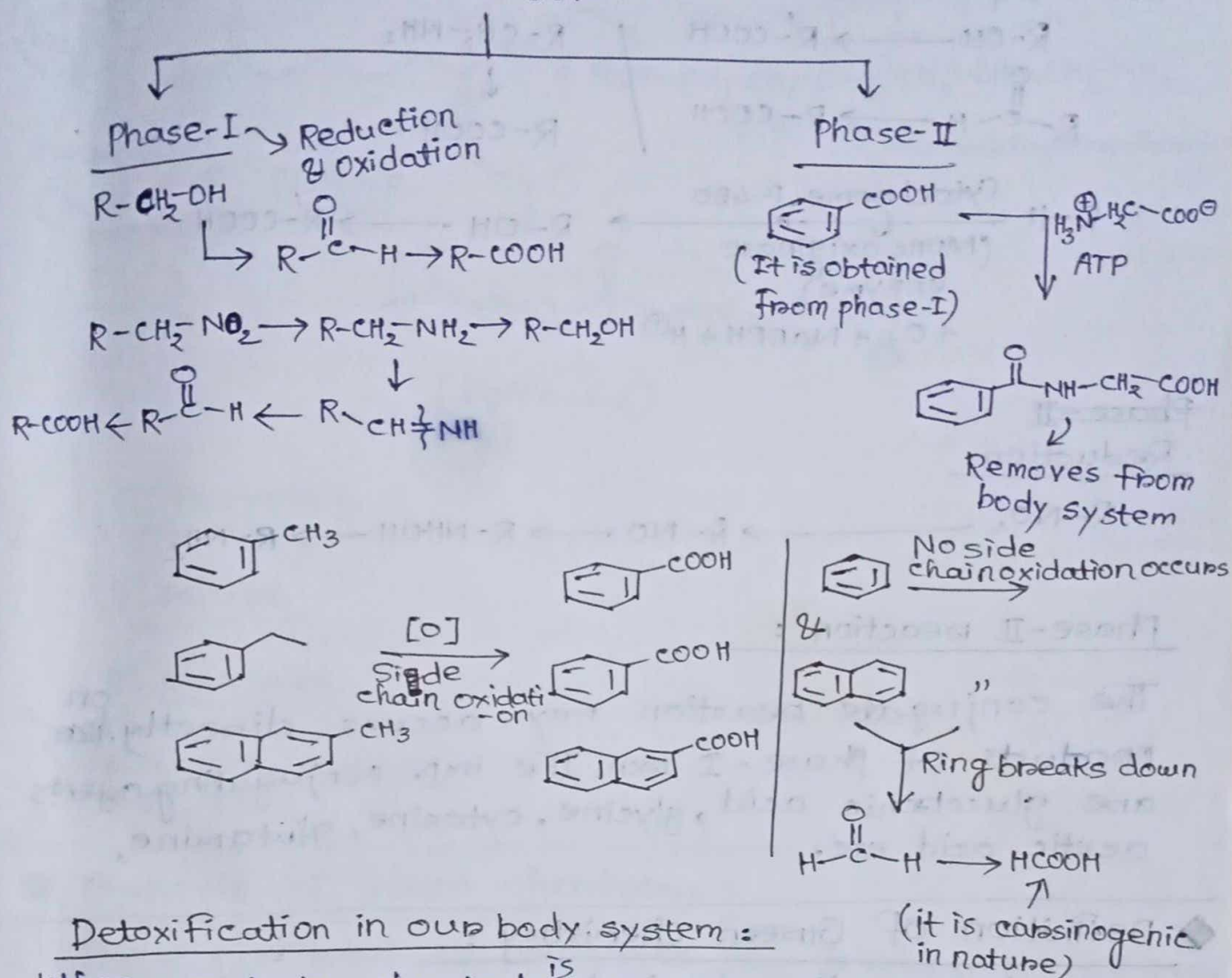


When Cytosine converts to urasil, then urasil tries to bind with Adenine. Thus, base pairing sequence changes. It is permanent damage.

HNO_2 (Nitrous acid) can cause deamination. The three nucleobases adenine, guanine and cytosine contain the $-\text{NH}_2$ group that can be replaced by $-\text{OH}$ group in the reaction with the HNO_2 . From the food additives, NaNO_2 and NaNO_3 , nitrous acid can be produced in biological system. Deamination of DNA bases can change the DNA base sequence. For example, the amino group in Cytosine is converted to keto group and effect of H-bonding occurs, that is shown above.

Detoxification in our body system

via metabolism



Detoxification in our body system :

When a toxic chemical ^{is} entered into a living body, the system attempts to detoxify through metabolism. Some ~~metabolized~~ ^{metabolized} products may be more toxic than as in the case of benzene or polycyclic aromatic hydrocarbons. However, the living system may not be always able to ~~remove~~ remove the toxic chemicals. In such case, it may be required to detoxify the substances by some therapy.

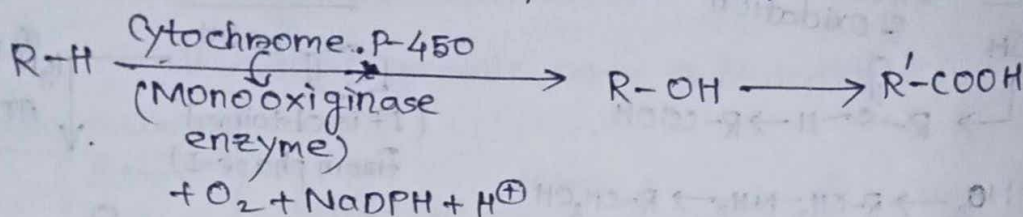
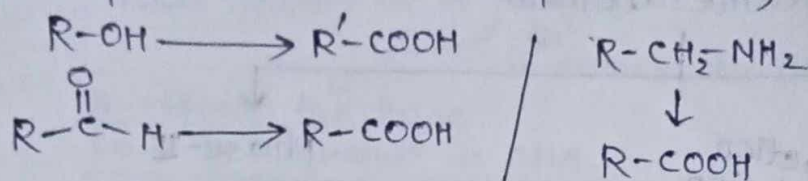
Metabolism for detoxification passes through phase-I and phase-II reaction.

Phase-I reaction :

Oxidation, Reduction and Hydrolysis, Common type of enzyme catalyzed reaction ^(NADPH) occurring in phase-I, to introduce suitable functional groups, $-OH$, $-SH$, $-COOH$, $-NH_2$.

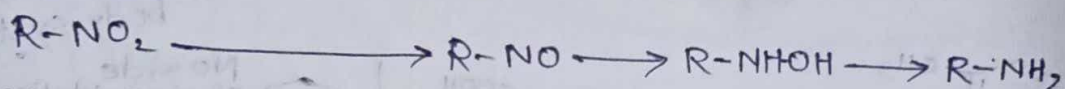
Oxidation

Some representative examples are,



Phase-II

Reduction



Phase-II reaction :

The conjugate reaction may occur directly on products of phase-I rxn. The imp. conjugating agents are gluconic acid, glycine, cytosine, glutamine, acetic acid etc.

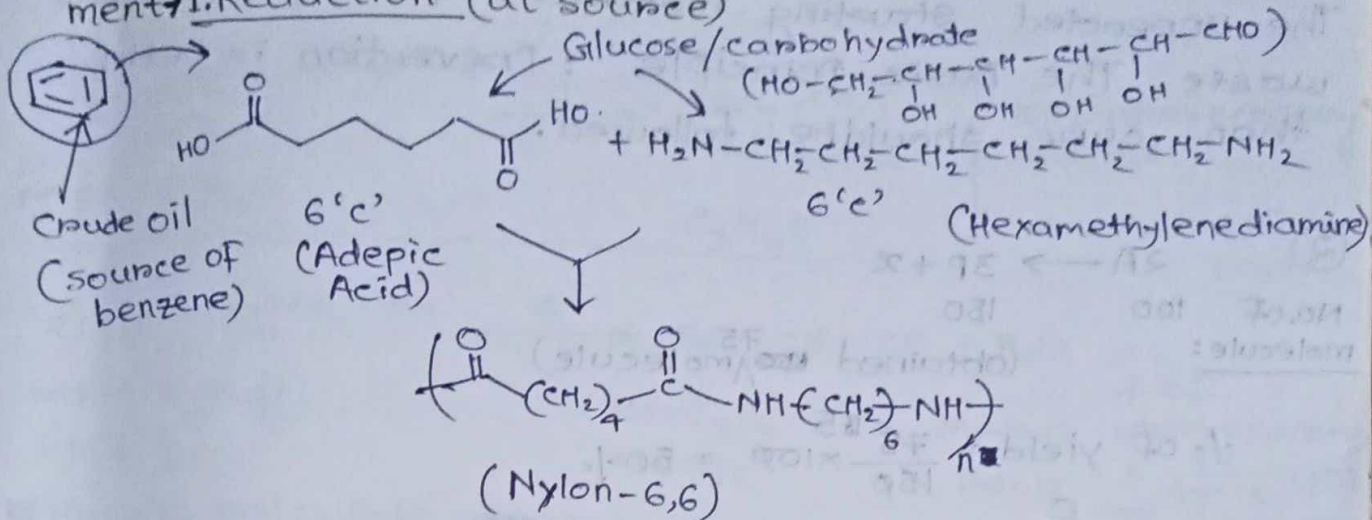
◆ Definition of Green Chemistry :

It designs the chemical processes & products that reduce or eliminate the use and formation of hazardous substances. This is also called as, sustainable chemistry (~~other~~ Another name of Green Chemistry).

◆ Purposes of Green Chemistry :

- 1) Ecofriendly chemical technology $\Rightarrow$ Green chemistry ^{aims} ~~acts~~ to protect environment for that biologically friendly technique should be used. Thus, it is also called as, Environmentally Benign chemistry. (non-harmful in effect)
- 2) Replacement of organic solvent and to minimize the waste products.
- 3) To minimize the energy consumption.
- 4) Eco-Friendly chemical product uses.

■ The term '4R's for integral waste management' 4/3/23



2. Recycling

3. Reuse

4. Recovery

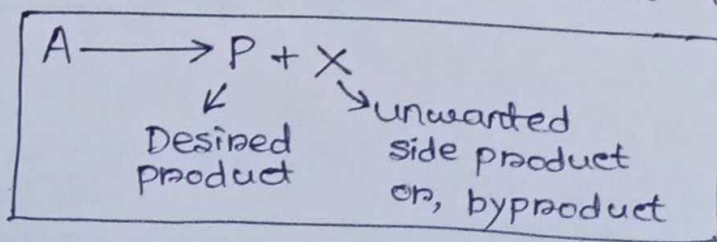
These are called as '4R's'.

■ Principle of green chemistry :

There are total 12 principles for development of prevention of pollution to protect our environment. Using these 12 principles, we are preserving our environment by benign chemical synthesis.

According to Paul T. Anastas, the following 12 principles of green chemistry have been formulated.

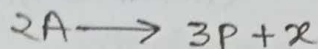
- ① It is better to prevent waste than to treat or, clean up waste after it is formed (to minimize the waste product formation). This is related to zero-waste technology (ZWT). It is better to carry out



a synthesis, so that formation of waste is minimum or, absent. It must be kept in mind that, in most of the cases, the cost involved in the treatment & disposal of

waste ^{adds to} the overall cost of the production.
 The unreacted starting materials form part of the waste. The basic principle: Prevention is better than cure should be followed.

②

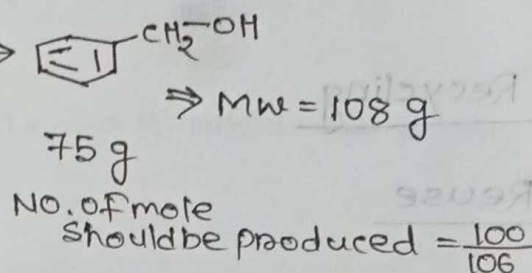
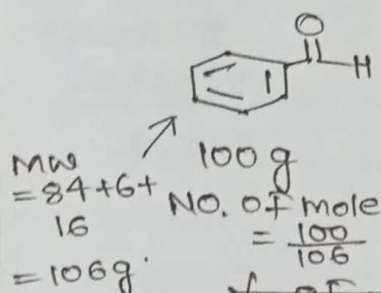


No. of molecule: 100

150

(obtained ~~100~~ ⁷⁵ molecule)

$$\% \text{ of yield} = \frac{75}{150} \times 100 = 50\%$$

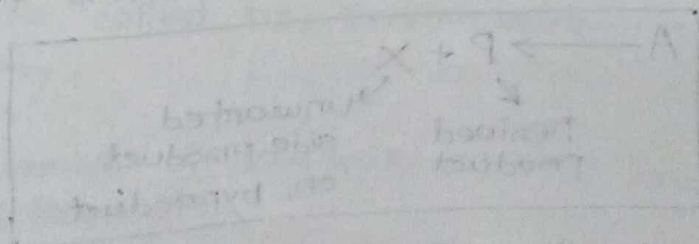
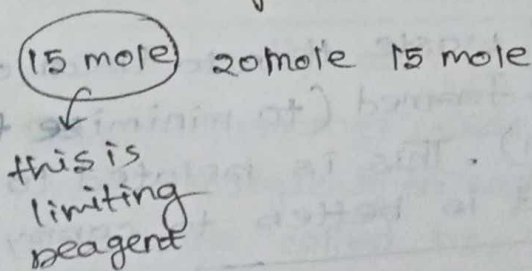
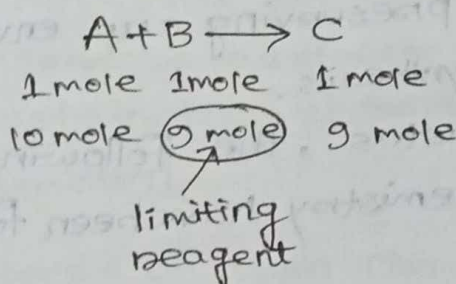


No.

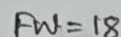
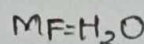
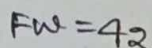
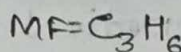
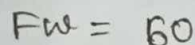
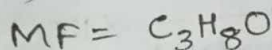
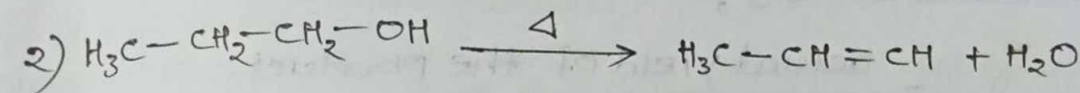
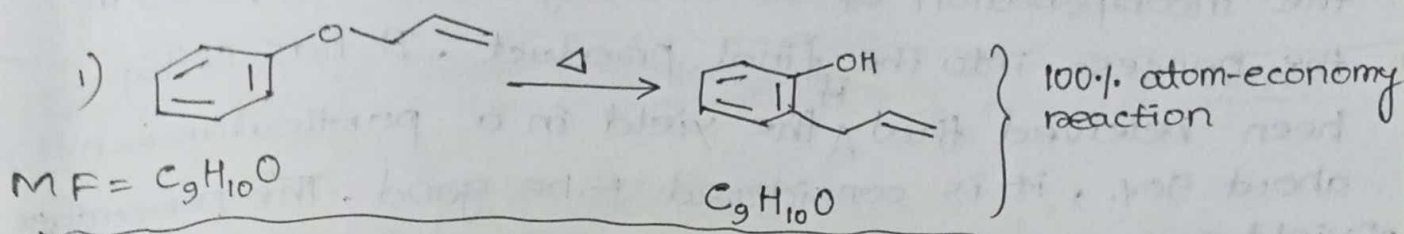
No. of mole produced

$$= \frac{75}{108}$$

$$\therefore \% \text{ of yield} = \frac{\frac{75}{108}}{\frac{100}{106}} \times 100$$



V.V.I Atom economy :

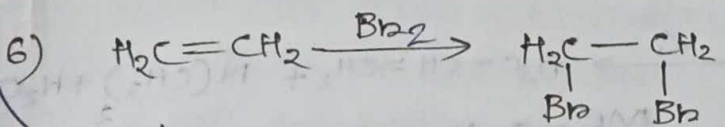
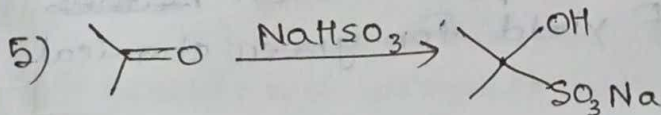
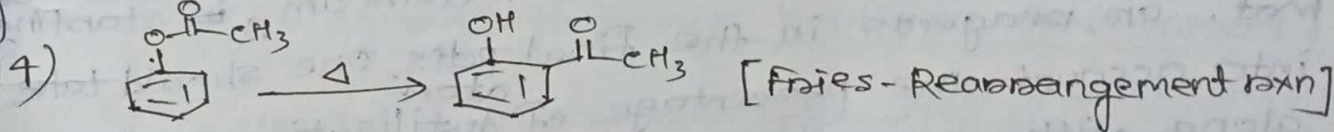


% of atom economy
 $= \frac{42}{42+18} \times 100$
 or, $\frac{42}{60} \times 100$

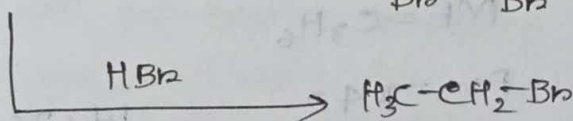
How to calculate percentage of atom-economy?

Percentage of atom utilisation of percentage of atom economy = $\frac{\text{Formula weight (FW) of desired product}}{\text{Formula weight (FW) of desired product} + \text{FW of waste product} + \text{FW of byproduct}} \times 100$

$$= \frac{\text{Formula weight (FW) of desired product}}{\text{Sum of FW of all reactants used in the reaction}} \times 100$$



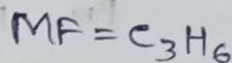
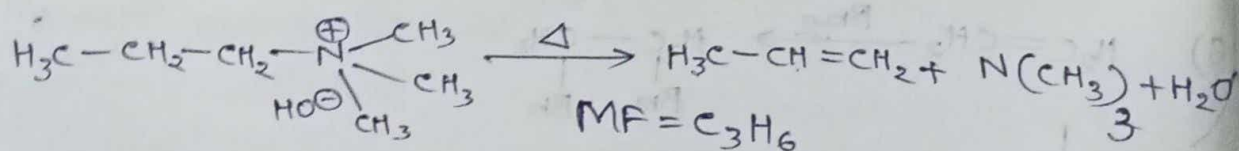
100% atom economy



Synthetic materials should be designed to maximize the incorporation of all starting materials, used in the process, into the final product. It has so far been believed that ^{if} the yield in a particular rxn is about 90%, it is considered to be good. The percentage of yield is calculated as,

$$= \frac{\text{actual yield of the product}}{\text{theoretical yield of the product}} \times 100$$

The above calculation implies that, if one mole of starting ~~reaction~~ material produces one mole of pds, the yield is 100%. However, such a synthesis may generate significant amount of waste or by products which is not visible in above calculation. Such a syn- ~~thesis~~ ^{thesis} even though is 100% yield of reaction, is not considered to be a green synthesis. Always considering percentage of atom economy. For example, reaction like Grignard reagent & Wittig rxn may proceed with 100% yield of reaction, but they do not take into ~~atom~~ account for the large amount of byproducts obtained. A rxn or, a synthesis is considered to be green if there is maximum ^{incorporation of} ~~starting~~ ^{starting} mat. or, reagents in the final pds. One should take into account the percentage of ^{atom} utilisation ~~rather~~ along with percentage of yield for green chemical synthesis.

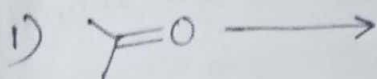


$$\text{FW} = 842$$

$$14 + 36 + 9 + 18 = 59$$

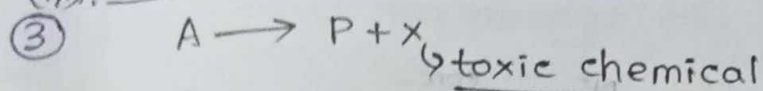
$$\therefore \% \text{ of yield} = \frac{42}{42 + 59 + 18} \times 100$$

$$= \frac{42}{119} \times 100 = 35.29\%$$



(iii) Principle of Green Chemistry:

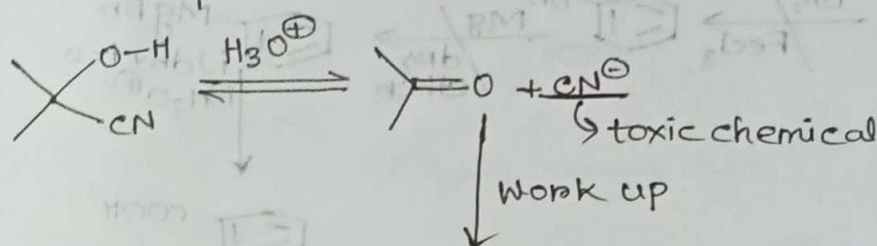
8/3/23



Prevention

⑥ If the toxic chemical is generated, then the effect of its toxicity should not work on human health or, environment

⑦ The process should be designed in such a way that generation of X will be minimum.



Work up

The ketone compound is isolated in organic layer. + Aqueous layer (CN^-)

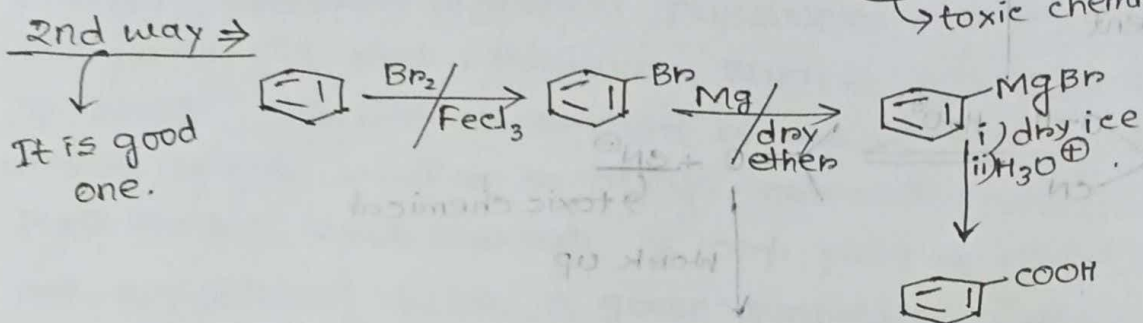
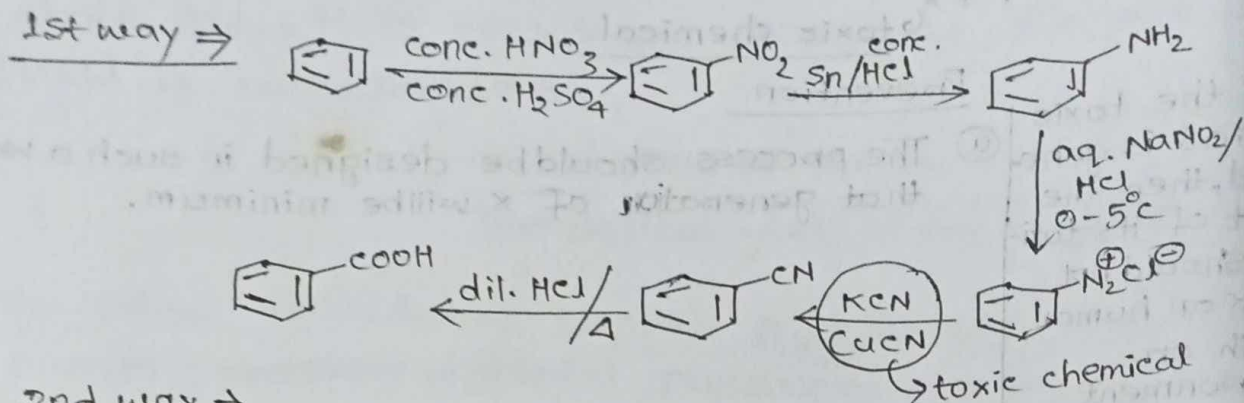
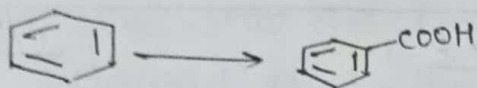
Sodium hypochlorite (bleach)

CN^- will be destroyed

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

one of the most important principle of green chemistry is to prevent or, at least to minimize the formation of hazardous products which may be toxic and or, environmentally harmful. In case hazardous products are formed, their effects on the workers must be minimized by the use of protective clothing, respirator, etc. These, of course, will add the cost of production. At times, it is found that, the controls may fail, and there may be more risk involved. Green chemistry, in fact, offers a scientific option to deal with such situations.

④ Say we are going to prepare benzoic acid from benzene.



Use of non-toxic chemical products :

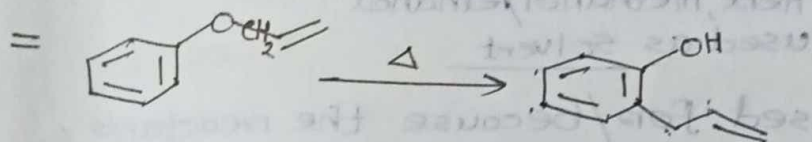
Chemical products should be designed to preserve ~~the~~ efficacy of function while reducing toxicity. In many chemical industries, not only the waste product, but the starting materials are also quite hazardous to the workers & environment. It is extremely important that chemicals, synthesized or developed (i.e., dyes, paints, cosmetics, pharmaceuticals, etc) should be safe to use. A typical example of unsafe drug is ~~thalidomide~~ Thalidomide (introduced in 1961) for reducing the effects of nausea ~~nausea~~ and vomiting during pregnancy. The children, born to woman taking Thalidomide suffers birth-defects. Subsequently, the use of Thalidomide was banned, the drug withdrawn & strict regulations passed for ^{testing} all new drugs. With the advancement of technology, the designing and production of safer chemicals has been possible. In fact, it is possible to manipulate the molecule str to achieve the goal.

Another example for 4th principle:

Adepic acid ~~(C6H10O4)~~ $\text{HOOC}-(\text{CH}_2)_4-\text{COOH}$, is widely used in polymer industries. Benzene, which is very toxic

material, is used for preparation of Adepic acid. Now, Adepic acid is prepared from glucose which is developed by Drath and Frost.

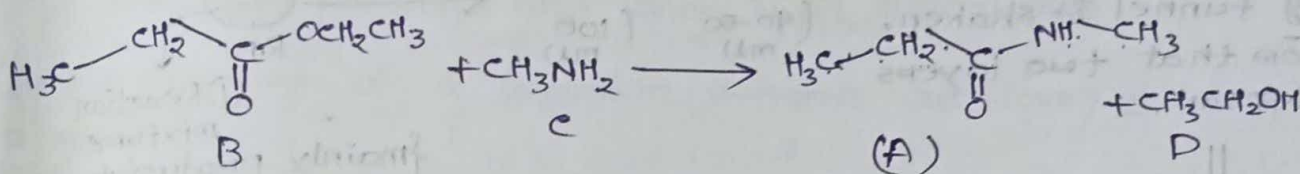
Q Find out the percentage of atom-economy of 11/3/23 the following reaction.



$$\% \text{ of atom economy} = \frac{\text{Formula weight of desired product} \times 100}{\text{FW of reactants used in the reaction}}$$

$$= \frac{108 + 16 + 10}{134} \times 100$$

$$= 100\%$$

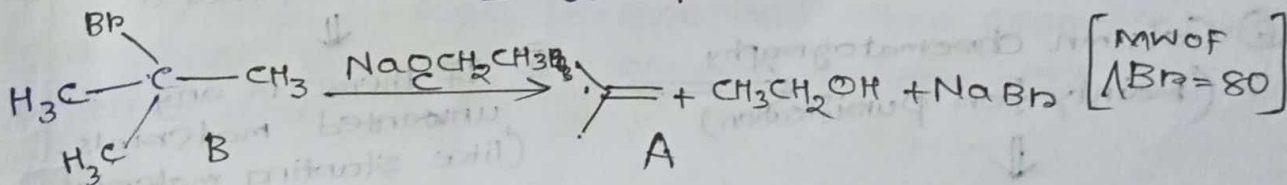


$$\% \text{ of Atom economy} = \frac{\text{FW of A}}{\text{FW of all reactants (A+D)}} \times 100$$

$$= \frac{48 + 16 + 9 + 14}{87 + (24 + 6 + 16)} \times 100$$

$$= \frac{87}{133} \times 100$$

$$= 65.4\%$$



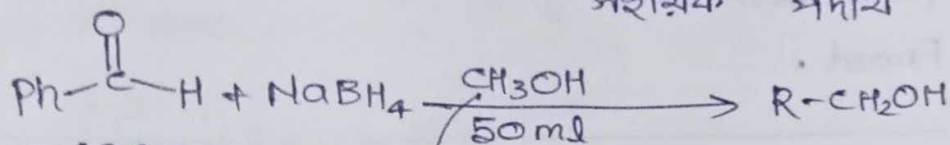
$$\% \text{ of atom economy} = \frac{\text{FW of A}}{\text{FW of B + FW of C}} \times 100$$

$$= \frac{48 + 8}{(48 + 9 + 80) + (23 + 16 + 24 + 5)} \times 100$$

$$= \frac{56}{205} \times 100$$

$$= 27.32\%$$

⑤ Minimum use of auxiliary substances: प्रशन्नक प्रदार्श



10 gm

(aldehyde)

Reduction

Primary alcohol

Here, methanol/ethanol used as solvent

solvent are mainly used for/because the reactants are coming to each other, by travelling through the solvent.

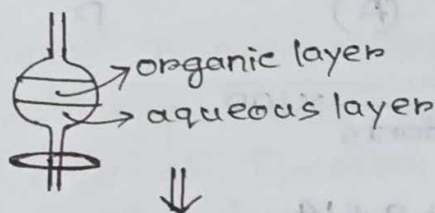
After the completion of the reaction $\Rightarrow$ Workup $\downarrow$

Then transfers

this to a separating

-g funnel & shaken.

For that two layers appear.



② H_2O + ethylacetate
(40-50 ml) (100 ml)



① Reaction mixture

{mainly product + slight amount of starting material}

③ Organic layer is collected

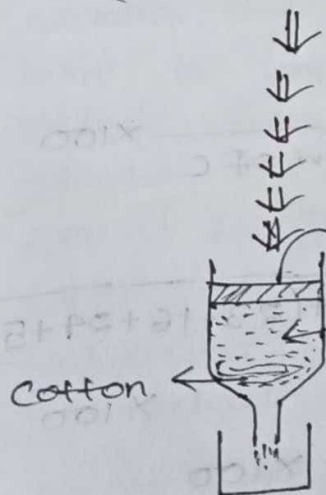
{ It contains product + starting material + ethylacetate }

$\Rightarrow$ ④ Organic layer (which contains ethylacetate)

is evaporated

⑥ Column chromatography (mainly for purification)

⑤ If there is any unwanted materials (like starting material or, side product) then purification should be done.



① Silica gel (one type of sand)

② Silica bed containing organic molecules {like product, side product, starting material}

③ solvent (generally ether)

The compound, which is most stable in illutant. (Solvent used that will come first).

④ pure organic or, required compound is collected.

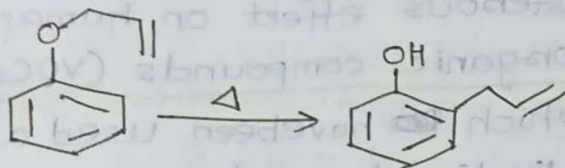
⑥ Evaporation of solvent

◆ The unnecessary product used :-

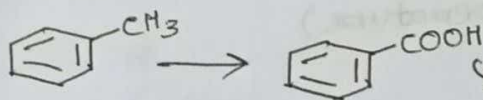
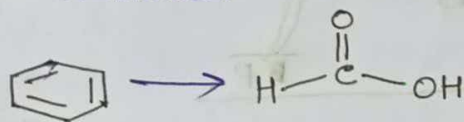
- ① The solvent used for the reaction. Here it is methanol.
- ② During work up, after completion of reaction, extracting solvent (ethyl acetate here) is used as unnecessary compound.
- ③ During purification silica gel, elutant^(solvent), Auxiliary substances (solvents, separating reagents etc).

The use of auxiliary substances should be made unnecessary whenever possible and when used innocuous.

Good example of a reaction where auxiliary substances are not used.



A no. of solvents like CH_2Cl_2 , $CHCl_3$, Perchloroethylene, CCl_4 , benzene, and other aromatic hydrocarbon have been used due to their excellent solvent properties. However, halogenated solvent have been identified as, suspected human carcinogens. Also, benzene and other aromatic hydrocarbons are believed to promote cancers of human & other animals.



It is used in preservative purposes like jam, jelly.

A solvent selected for a particular reaction should not cause any environmental pollution and health hazards. The use of liq. CO_2 should be explored. If possible, the reaction should be carried out in aqueous phase or, without use of solvent in solid phase.

Solvents : CH_3OH , benzene, $\text{CH}_3\text{CH}_2\text{Cl}$, CHCl_3

most dangerous solvent

toluene, $\text{CH}_3\text{CH}_2\text{OH}$,
DMF

less toxic

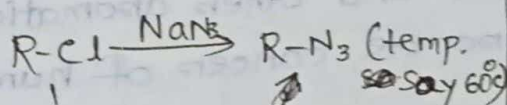
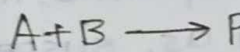
Green solvent

liq. CO_2 , H_2O

No use of solvent is the most harmless.

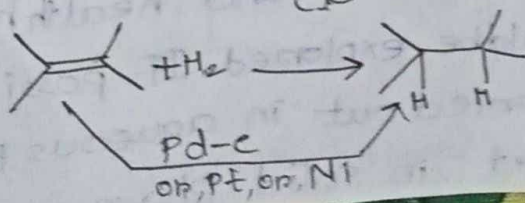
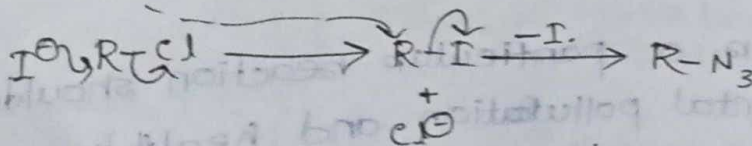
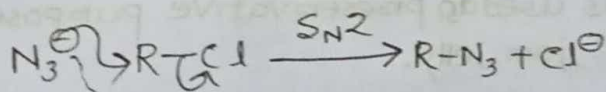
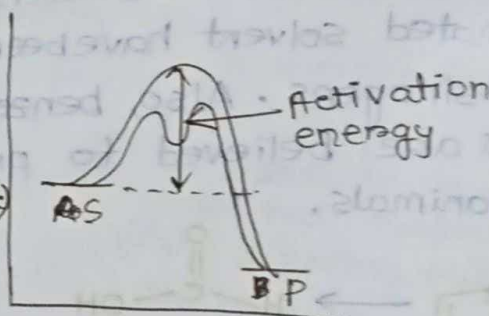
A lot of concern has been expressed about the use of solvent which have direct hazardous effect on the environment. One, such example is Chlorofluorocarbons (CFCs) which have been widely used as cleaning agents, blowing agents and as refrigerants. These CFCs are responsible for depleting of ozone layer which in turn has disastrous effect on human survival. Even, the volatile organic compounds (VOCs) like CCl_4 , CH_3Cl , CHCl_3 , etc which have been used as solvent in number of application have dangerous effect in the atmosphere.

③ Minimum energy consumption :



In presence of NaI catalyst

(room temperature)

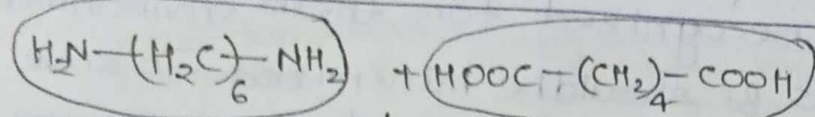


Q. How catalyst is playing role in green chemistry principle

Energy requirement should be recognized for their environmental & economic impacts & should be minimized. To save energy, synthetic methodology should need more & more moderate conditions and ambient temperature and pressure are the best choices. It needs suitable catalysts that will accelerate the reaction rate even at low temperature. In any chemical synthesis, requirement of energy should be kept to an minimum. For ex, if the st. material & reagents are soluble in particular solvent, the reaction mixture has to be heated to reflux for completing the reaction. In such cases, the time required for the completion of the reaction should be minimum. So that, least amt. of energy is required.

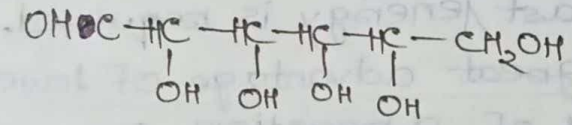
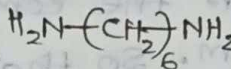
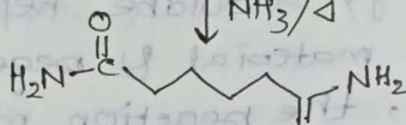
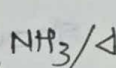
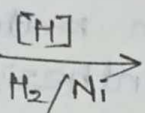
cu-22 The use of catalyst has the great advantage of lowering the requirement of energy of a reaction. In case of final product is not pure, it has to be purified by distillation, recrystallisation or, ultrafiltration. All the steps required energy. The process should be designed in such a way that there is no need for separation & purification. It is possible, the energy of a reaction supplied photochemically, by using microwave or, sonication.

7 Use of renewable resources :



Non-renewable resource

Nylon 6,6

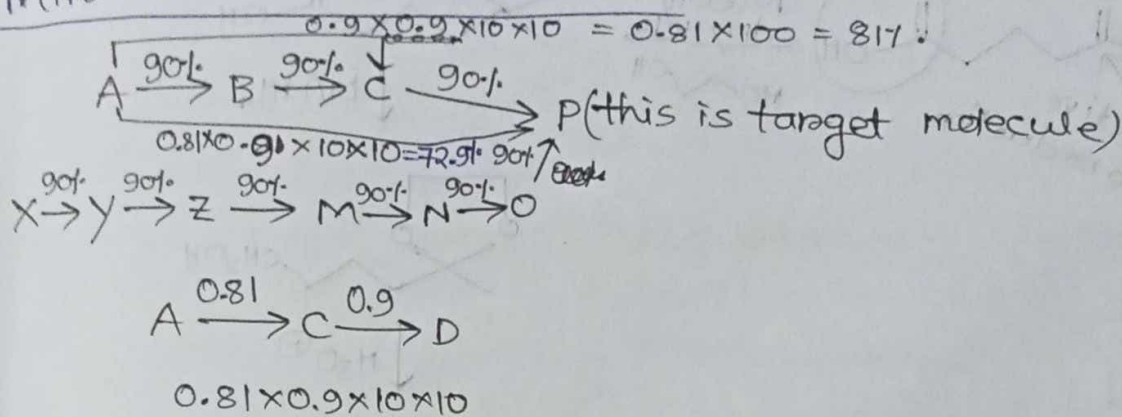


A raw material or, feed stock should be renewable rather than depleting, whenever technically and economically, practically. The renewable resource (i.e., biomass) rather than non-renewable resources (crude oil) should be used as the raw material.

Petrochemicals are mostly obtained from petroleum oil which is a non-renewable source, since its formation takes millions of years from animal & vegetable remains. Biopolymers & bioplastic may be obtained by using the microorganisms which can use lower fatty acid to produce the biopolymers like PHA (PolyHydroxy-Alkanoid), PHB (Poly-beta-Hydroxy-butyrate).

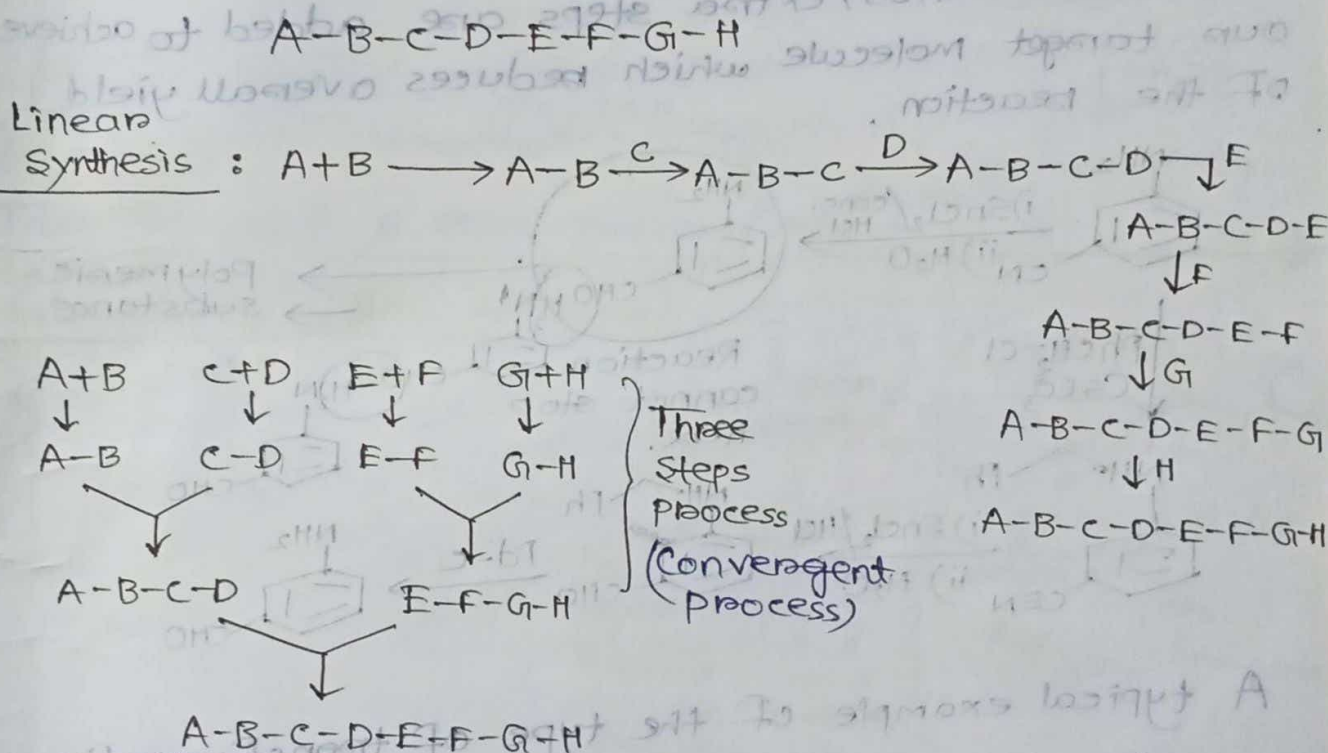
Substances like CO_2 and CH_4 gas are available in abundance, these are considered as renewable starting materials.

⑧ Minimization of steps :



Thus, if we increase the no. of steps to get one particular target molecule, the overall yield of the reaction decreases which is not desirable.

Convergent synthesis of peptide :

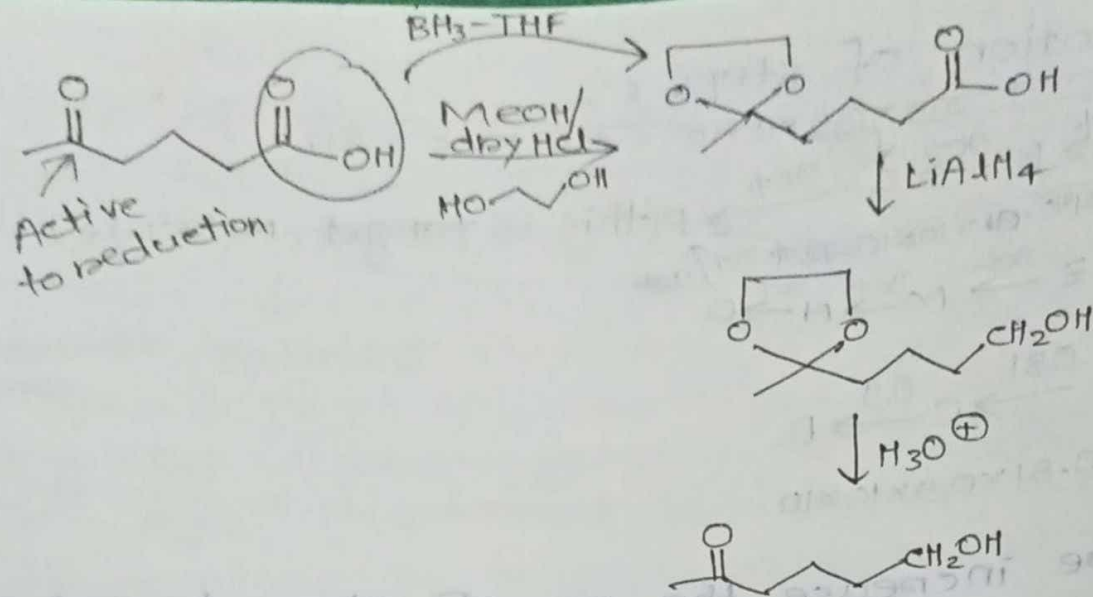


Overall yield = $0.9 \times 0.9 \times 0.9 \times 10 \times 10 \times 10$

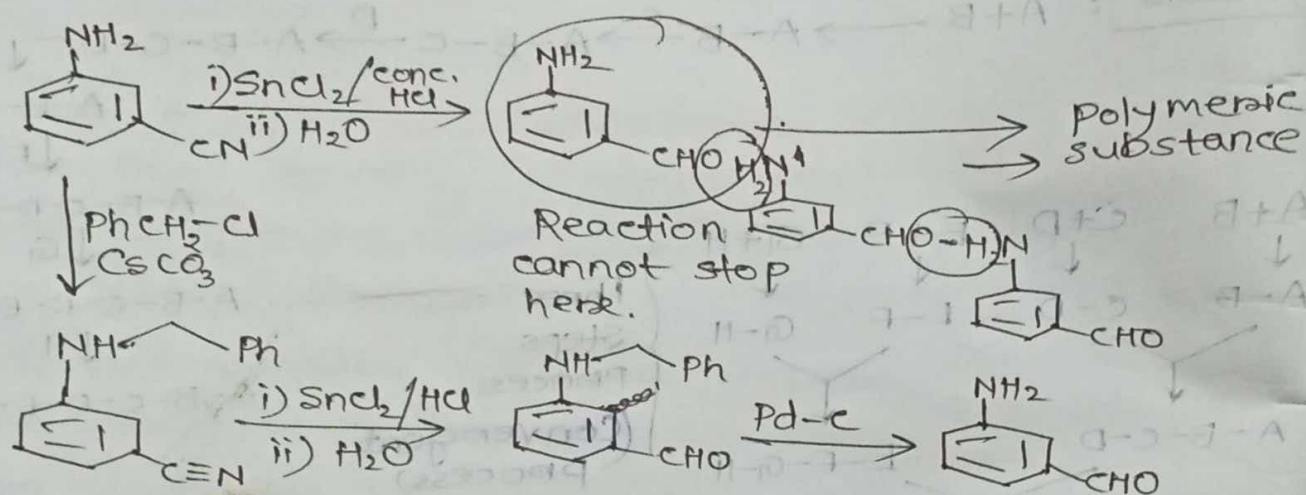
for overall yield, for octapeptide synthesis, using convergent way is $0.9 \times 0.9 \times 0.9 \times 10 \times 10 \times 10 =$

Thus, convergent synthesis of peptide is more effective than linear synthesis.

unnecessary derivatisation (blocking group protection, deprotection, temporary modification of physical & chemical processes) should be avoided, whenever possible.

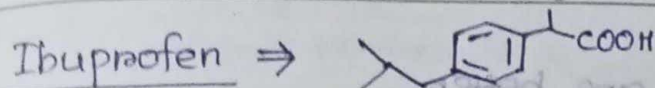


For organic synthesis, we need very often protection of some functional group. Finally, we again need their deprotection. Thus, extra steps are added to achieve our target molecule which reduces overall yield of the reaction.



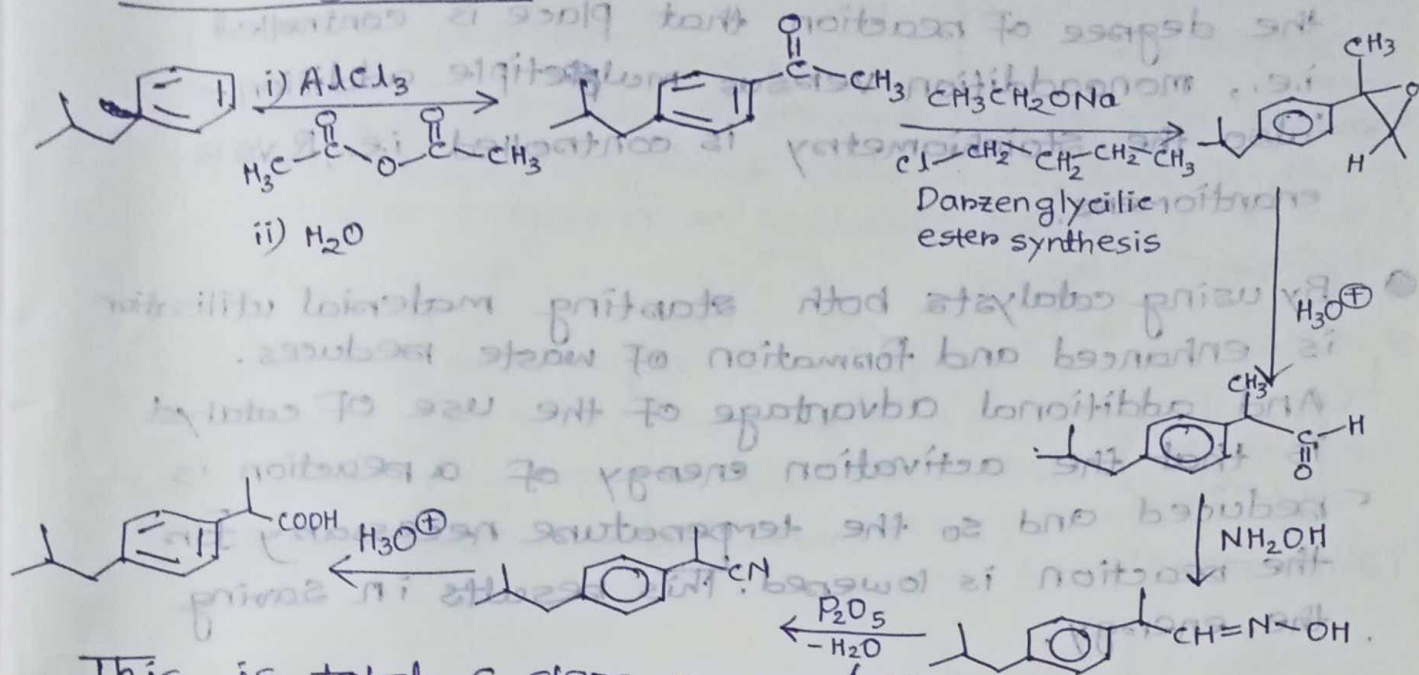
A typical example of the type of transformation would be protection of amine by making benzyl ether in order to carry out the transformation of another group, present in the molecule. After the reaction is complete, -NH_2 group can be regenerated to cleavage of benzyl ether. As protecting group is not incorporated into final product, their use makes a reaction less atom economical. Thus, use of protecting groups should be avoided.

One application of principle (VIII) i.e. minimization:



Preparation of ibuprofen:

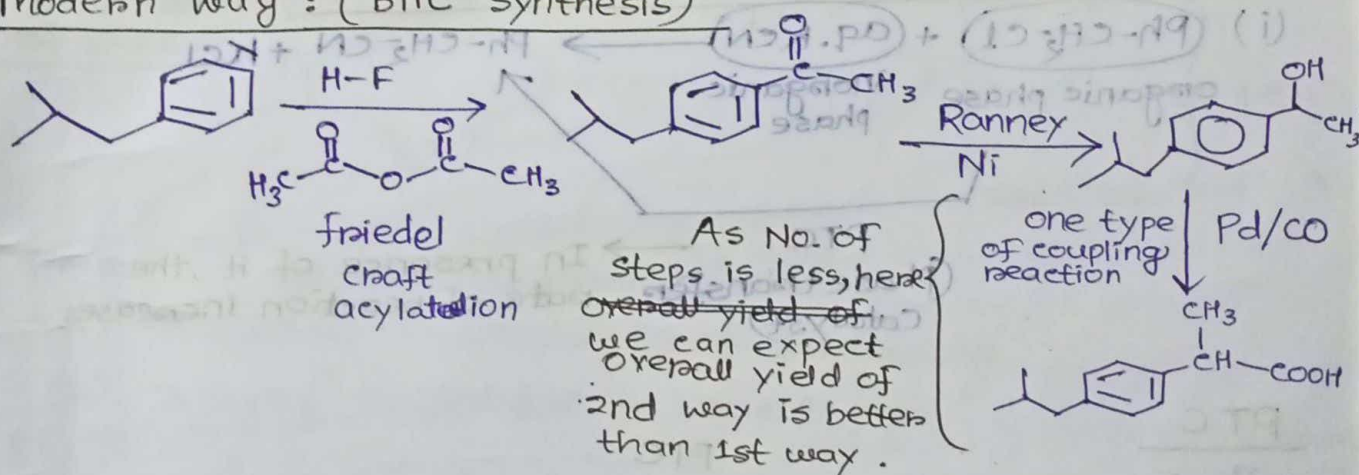
Boot's synthesis (total 6 steps process)



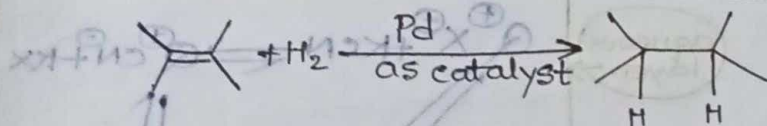
This is total 6 steps process/way.

2nd way:

Modern way: (BHC synthesis)



Principle-9: Use of catalytic reagent (used as very small quantity):



But if Pd (catalyst) is used stoichiometrically, then 1st of atom economy will be less (or, low).

- Catalytic reagents (as selective as possible) are superior to stoichiometric reagents because of —
 - 100% atom economy because the true catalysts are fully reversed without any change in their chemical & physical properties.

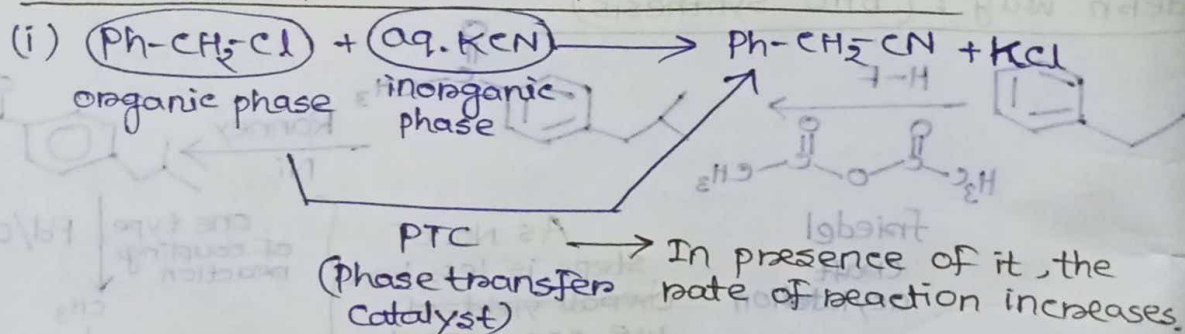
(ii) Catalysed reactions are faster i.e., energy save is possible.

(iii) Reaction's yields are better.

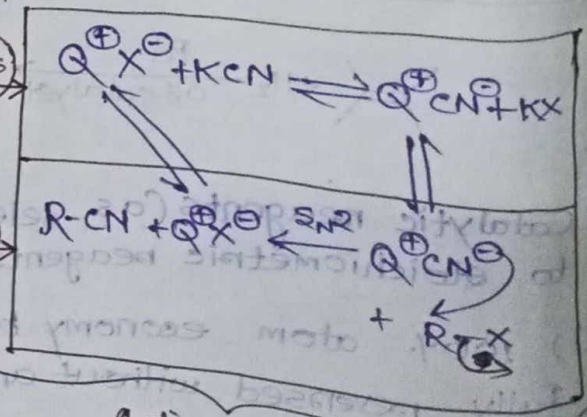
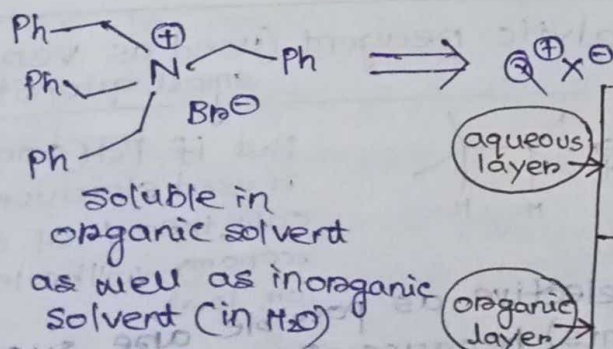
● Catalysts are selective in their action, in that the degree of reaction that place is controlled i.e., monoaddition versus multiple addition + also the stoichiometry is controlled i.e., R vs. S enantiomers.

● By using catalysts both starting material utilisation is enhanced and formation of waste reduces. And additional advantage of the use of catalyst is that the activation energy of a reaction is reduced and so the temperature necessary for the reaction is lowered. This results in saving the energy.

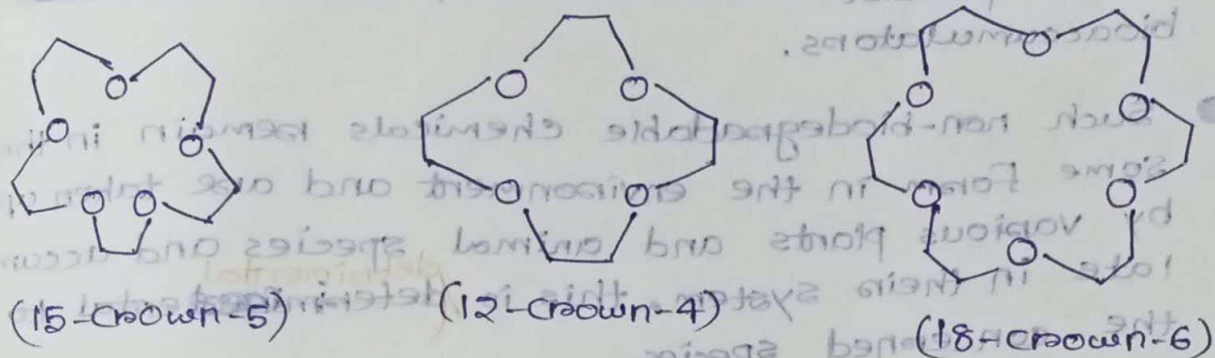
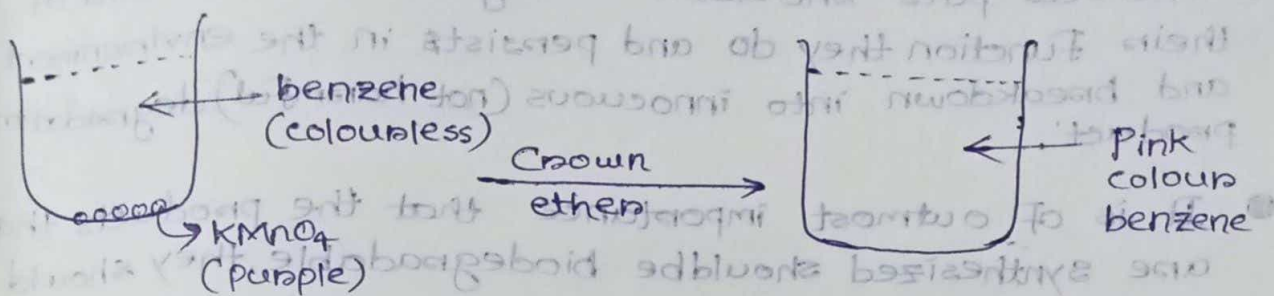
◆ Some example of catalytic reactions :



PTC
CU-22

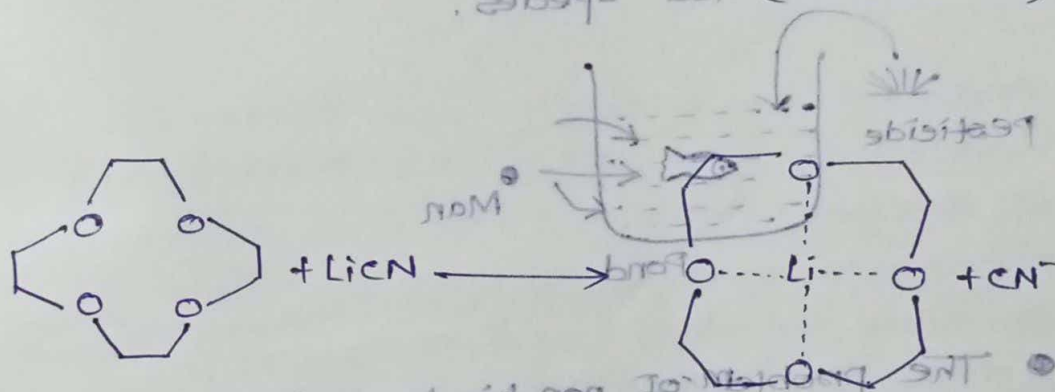


Action of phase transfer catalyst which issued as catalytic amount.



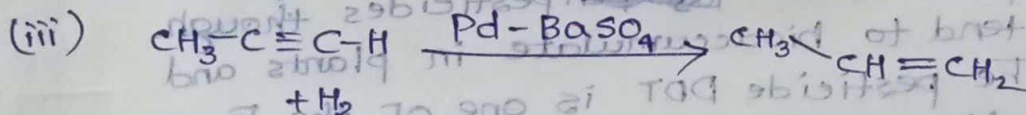
CV-22

Mechanism
of role:



Here crown ether is playing its dual

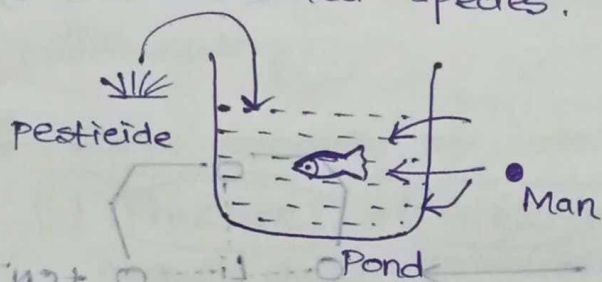
- (i) Increases nucleophilicity of nucleophile
- (ii) It helps to soluble the nucleophile in organic phase



Principle - 10 :

Lifetime of a chemical product :

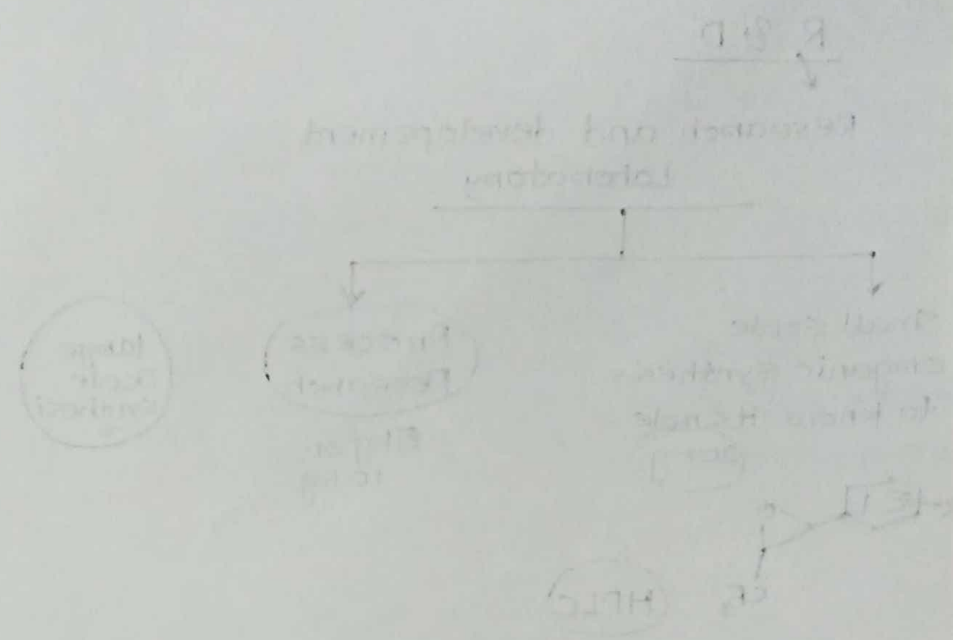
- Chemical p_{dt}s should be designed that at end of their function they do and persists in the environment and breakdown into innocuous (not harmful) degradation product.
- It is of outmost importance that the products that are synthesized should be biodegradable, they should not be persistent chemicals or, persistent chemicals bioaccumulators.
- Such non-biodegradable chemicals remain in the some form in the environment and are taken up by various plants and animal species and accumulate in their system, this is ~~detrimental~~ ^{detrimental} to the concerned species.



- The problem of non-biodegradability is generally associated with pesticides, plastic & a host of other organic molecules.
- Most of the pesticides in use are organohalogen based compounds, this ~~are~~ ^{are} pesticides though effective tend to bioaccumulate in plants and animals. The pesticide DDT is one of the first pesticide which bioaccumulated in plants and animals. Whenever a chemical is being designed it should be made sure that it will be bio-degradable. It is now possible to place functional groups and other features in the molecule which will facilitate its degradation.
- Functional groups, which are susceptible to hydrolysis, photolysis or, of cleavage have been used to ensure that p_{dt} will be biodegradable.

It is equally important to make sure that the biodegradable degradation products should not possess any toxicity and be ~~detrimental~~ ^{detrimental} to the environment.

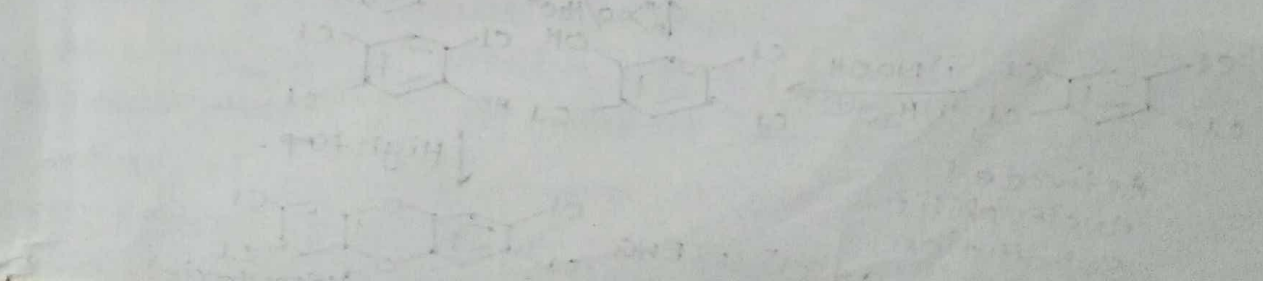
need time, in process monitoring and control for the formation of hazardous substances.



Analytical methodologies and technologies have been developed which allow the prevention & minimization of the generation of hazardous substances in chemical processes. One need to have accurate and reliable sensors, monitors and analytical techniques which can access the hazardous that are present in process stream. Using various techniques, chemical processes can be monitored for generation of hazardous by-products & side reactions. These procedures can prevent any incident which may occur in chemical plants.

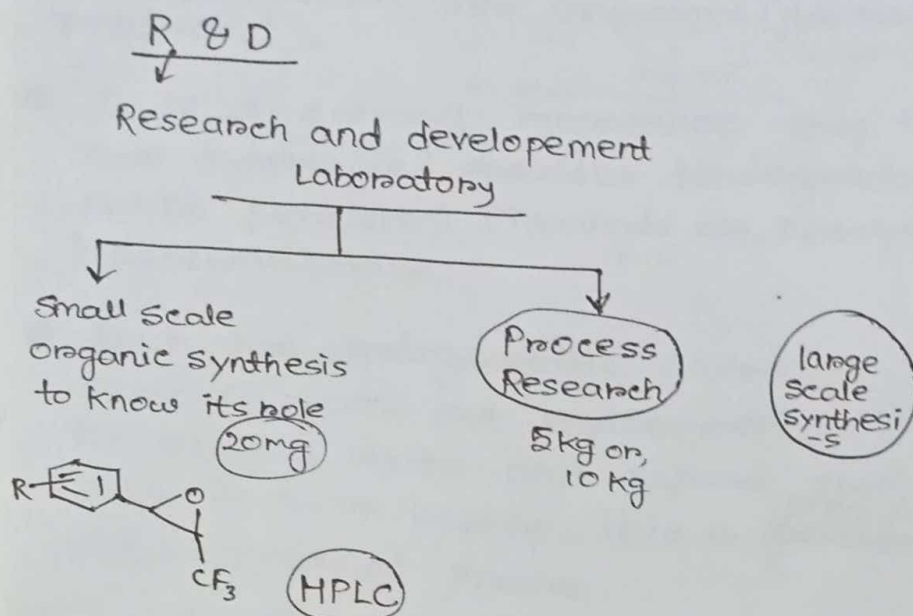
Principle-12

Substances & the forms of substance use in chemical process should be chosen so as to minimize the potential for chemical accidents including explosions and fires.



Principle No. - 11

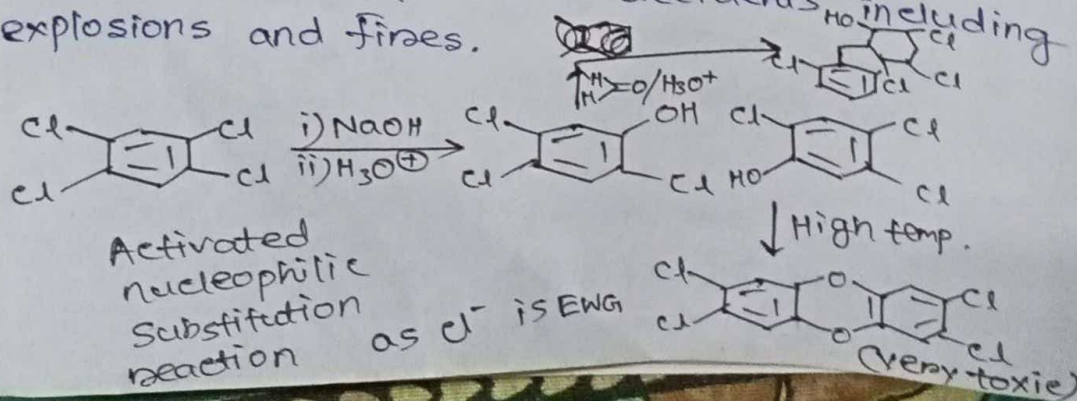
Analytical methods need to be further developed for real time, in process monitoring and control prior to the formation of hazardous substances.



Analytical methodologies and technologies have been developed which allow the prevention & minimization of the generation of hazardous substances in chemical processes. One need to have accurate and reliable sensors, monitors and analytical techniques (HPLC) to access the hazardous that are present in process stream. Using various techniques, chemical process can be monitored for generation of hazardous by-products & side reactions. These procedures can prevent any incident which may occur in chemical plants.

Principle-12

substances & the forms of substance use in chemical process should be chosen so as to minimize the potential ^{for} chemical accidents including releases explosions and fires.



Seveso disaster

Seveso disaster was an industrial incident that occurred around 12:37 p.m. on 10th July, 1976 in a small chemical manufacturing plant in Italy. It ^{resulted in} ~~resulted in~~ the highest known exposure to 2,3,7,8-tetrachlorodibenzo-p-dioxin ^(TCDD) ~~(TCDD)~~ in residential pollution which ^{gave} ~~gave~~ rise to numerous scientific studies & standardized industrial safety regulation. This incident was ranked 8th in a ^{list} ~~rank~~ of the worst manmade environmental disasters. The chemical 2,4,5-trichlorophenol was being produced there from 1,2,4,5-tetrachlorobenzene by nucleophilic substitution reaction with sodium hydroxide. The 2,4,5-trichlorophenol was intended as an intermediate for hexachlorophene.

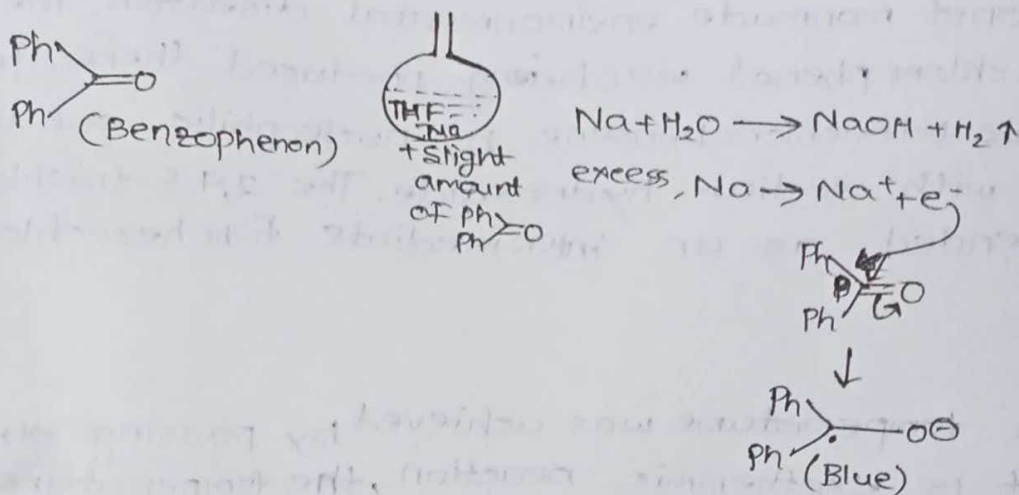
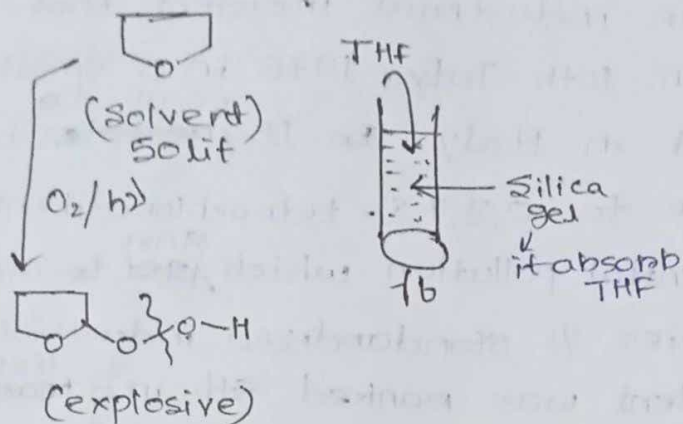
Reaction temperature was achieved by passing steam. ~~The~~ As it is exothermic reaction, the temperature reached to 230°C , which gave toxic TCDD.

Bhopal disaster

Bhopal disaster / Bhopal gas tragedy was a chemical accident ~~on~~ on the night of 2-3rd December, 1984 at the union carbide india limited, pesticide plant in Bhopal, Madhya Pradesh, India. Considered, the world's worst industrial disaster, over 5 lakh people in the small town around the plant was exposed to the highly toxic gas methyl isocyanate (MIC gas). Estimates vary on the death toll with the official number of immediate deaths been ~~2000~~ 2259. ~~The~~

The occurrence of accident in the chemical industries must be avoided. The accidents in Bhopal & Seveso and many others have resulted a loss of ~~1000~~ thousands of life. At times, it is possible to increase accident potential ~~at~~ inadvertently in an attempt to minimize the generation of waste in order to prevent pollution. It has been noticed that ~~it~~ in an attempt to recycle solvent from a process increases the potential for chemical

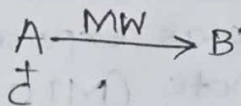
accidents or, fires.



In fact, a process must balance the incident ^{on, accident} prevention with a desire ^{or, preventing} pollution. A possible course is not to use volatile solvent, instead solids ^{or, low} vapour pressure substances are used.

Some green techniques:

i) Application of microwave ~~or~~ Irradiation

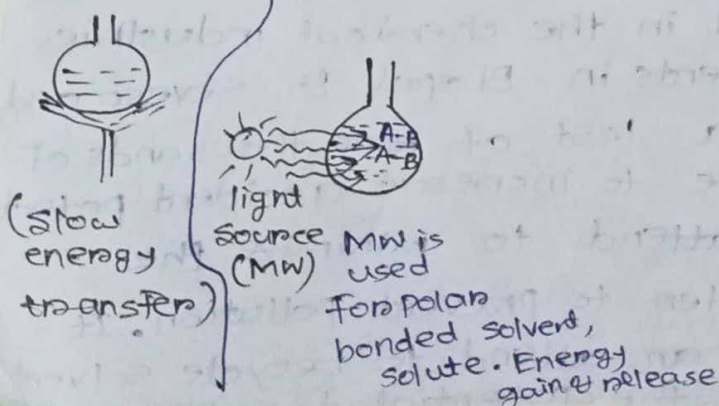


(300 MHz - 300 GHz)
 1 mm to 1 m

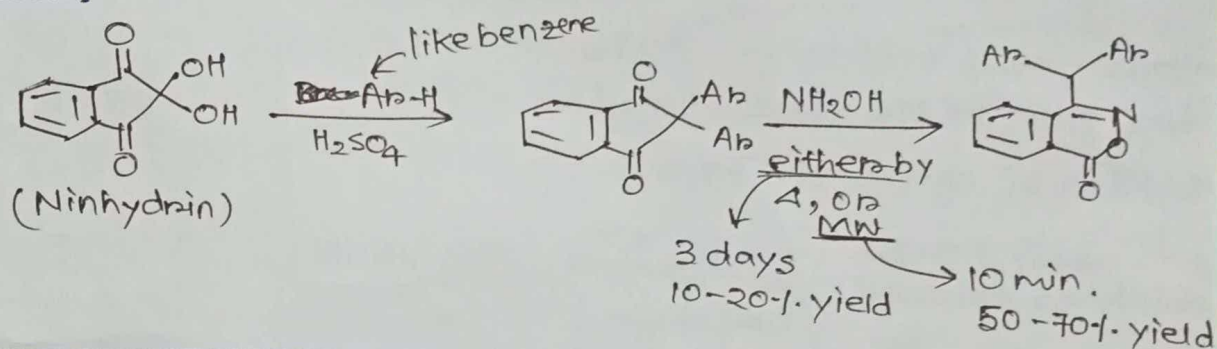
Energy supplied

Conventional

Unconventional

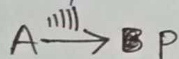


These unconventional energy sources are now being used in chemical transformations. Many chemical transformations can be carried out by using microwave irradiation^(MWI). The selective absorption of microwaves ($10^9 - 10^{11}$ Hz) by the polar molecules leads to reaction rate acceleration. In fact, ^{the} reactions experiencing polar transition state are favoured by MWI. Generally, polar solvents which can easily absorb MWI should be used. The advantages in using these techniques are, quick reaction, no requirement of prolonged heating or reflux, As time requirement for this type of reactions using MWI is less, the generation of side products will not occur.

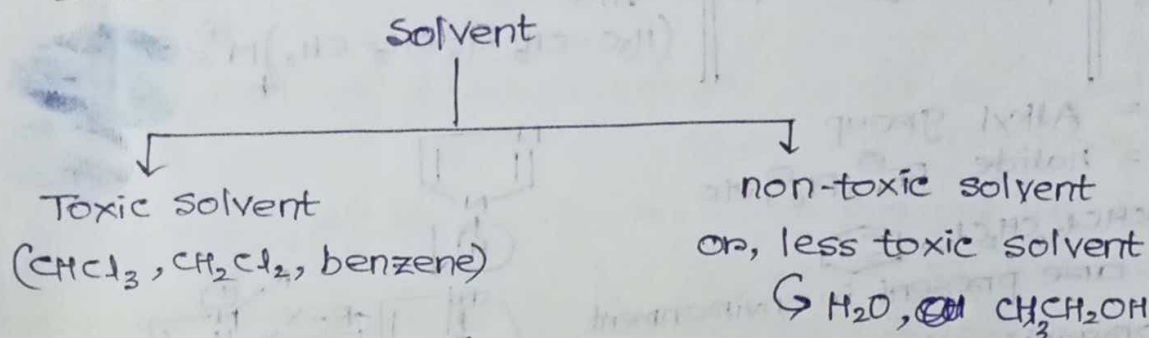


ii) Use of ultrasound in chemical process :

Chemistry is known as Sonochemistry.

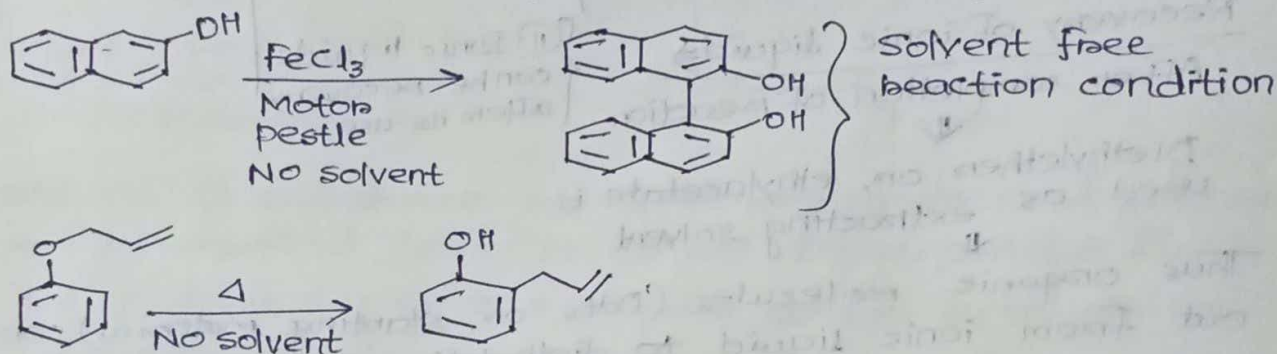


~~The use~~ ultrasound covers the range 20 kHz to 10 MHz ⁱⁿ sonochemistry it generally ^{uses} the range 20 kHz to ~~100 kHz~~ 100 kHz. Soundwave cannot directly interact with the molecular vibration because the wave range of soundwave is much longer than the molecular dimension. In fact, sonication in homogeneous solution produces ~~aqueous~~ acoustic cavitation which is responsible for chemical effects. A solvent medium irradiated with ultrasonic waves leads to production and collapse of microbubbles. This phenomenon is called as acoustic cavitation. During the propagation of ultrasonic wave through a solvent medium, the oscillating particles produces the region of compression & rarefaction ~~fraction~~ ^(reduction of high intensity density) (release) the region of rarefaction collapse. Collapse of these

Green Chemistry Technology $\Rightarrow$ III) Solvent free Organic Reaction

Whether the toxic or, less toxic solvent is used these will be waste after reaction.

If we design one reaction which is solvent free reaction, the waste amount will be reduced, these will be very good way. But, solvent free organic synthesis design is difficult.



Use of organic solvent is objectionable from the stand point of environment hazard. In fact the best solvent is no solvent but no solvent condition faces the problems like heat & mass transfer, mixing of reactants, etc. To overcome ~~these~~ ^{these} barriers in solvent free reaction, the technique the mechanochemical mixing (i.e., grinding), microwave irradiation are commonly used.

IV) Use of green solvent $\Rightarrow$

$\hookrightarrow$ less toxic or, non-toxic liquid

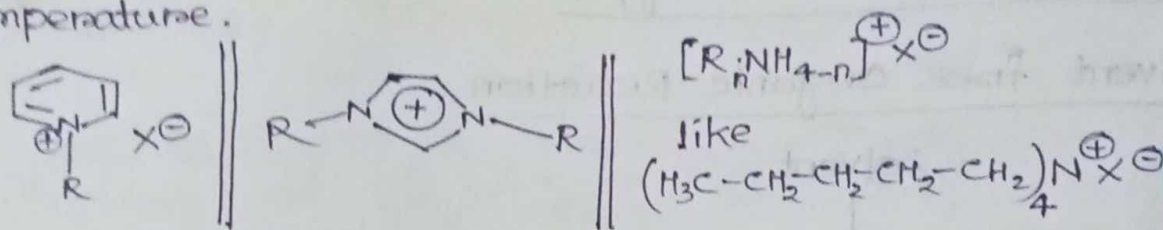
The hazardous organic solvents need replacements. The eco-friendly reaction medium are water, polyethylene glycol, super-critical CO_2 and super critical H_2O , etc.

V) Use of room-temperature ionic liquid $\Rightarrow$

↓

Ionic substances which are liquid at room temperature.

When substances is ionic in nature, its melting point should be high. Thus, they are generally solid at room temperature.



R = Alkyl group
X = halide, BF_4^- , PF_6^- , etc

$\text{CHCl}_3, \text{CH}_2\text{Cl}_2, \text{C}_6\text{H}_6$ are present in environment
organic solvent (volatile in nature)

No solvent molecules is coming but
Ionic liquid (non-visible)

① thus here environment is not contaminated with such ionic liquid solvent

Recovery of ionic liquids

After completion of reaction

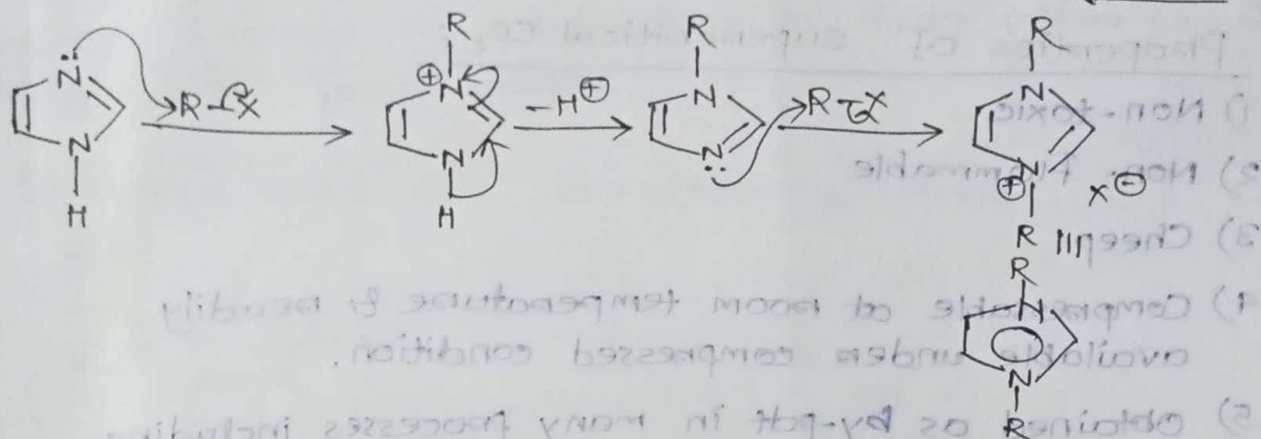
Diethylether or, ethylacetate is used as extracting solvent

② Ionic liquids can be recovery after its use.

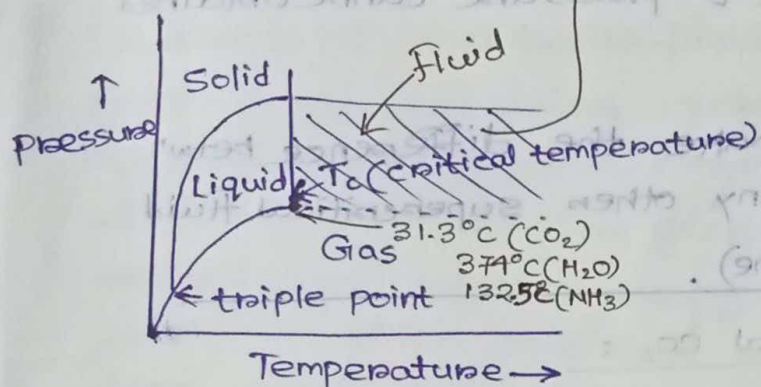
Thus organic molecules (Pds or, starting material) comes out out from ionic liquid to diethylether (due to high polarity of ionic liquid, they are not soluble in diethylether).

Commonly used organic solvents are generally volatile organic compounds that causes several environmental hazards in smog production in air, ozone depression, health hazards, etc. The ionic liquids are the green alternatives these are non-volatile, non-co-ordinary but polar, immiscible with organic solvents. These ionic liquids are generally organic salts like alkyl ammonium salts, N-alkyl pyridinium salt, etc. These non-volatile organic liquids can be easily recovered after use they can be required by purified the product can be isolated from ionic liquid by using some common solvent like ether, diethylene, ethyl lactone in separating funnel.

9/4/23



■ Super critical Carbondioxide (SC- CO_2) or, (S- CO_2) :



The state of a substance at a temperature and pressure above its critical point is called supercritical fluid, where the distinct liq & gas phases do not exist. It can effuse through solids like a gas and can dissolve materials like a liquid. Critical temp. of a substance is the temp. at or above which the gas cannot be liquified by increasing pressure. With increasing temperature, the kinetic energy of the molecule increases & becomes difficult to liquify. At the triple point, all three phases (solid, liquid and gas) co-exist. However, the liquid-vapour boundary terminates at a point having critical temp. & critical pressure: this point is called critical point. Above this region, it is called critical fluid. A supercritical fluid exhibits properties in between a gas & a liquid.

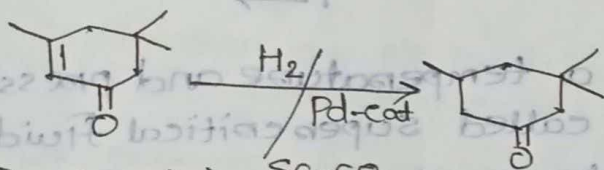
If the temperature & pressure both increased from STP to be at or above critical point for CO_2 , it can adopt properties midway between a gas and a liquid. Most specifically, it behaves as a supercritical liq above its critical temp. & critical pressure.

Properties of supercritical CO₂:

- 1) Non-toxic
- 2) Non-Flammable
- 3) Cheap
- 4) Compressible at room temperature & readily available under compressed condition.
- 5) Obtained as by-product in many processes including fermentation of biomers.
- 6) Critical temperature & pressure can be obtained comparatively easily.

The above properties make the difference between supercritical CO₂ with any other supercritical fluid (SC-N₂O, SC-NH₃, SC-n-butane).

Utility of supercritical CO₂:

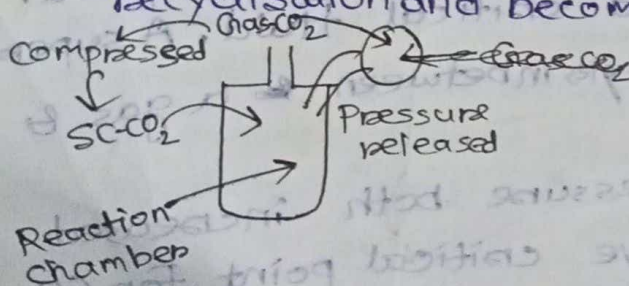


(Isophorone)

CU-22

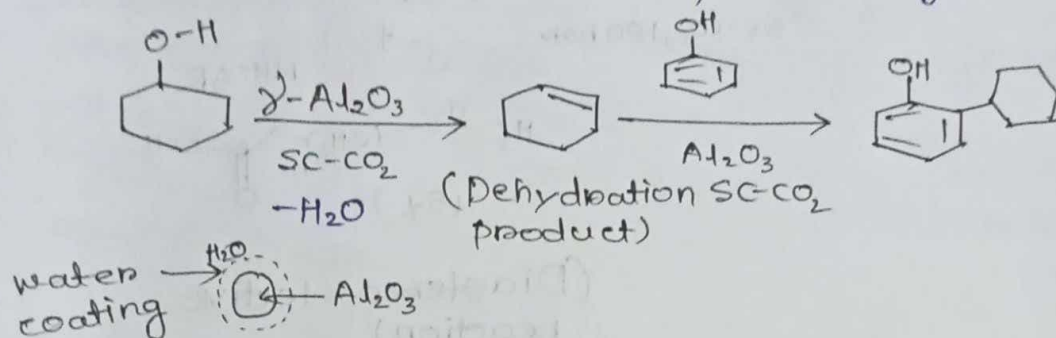
1) 3,3,5-trimethylcyclohexanone (TMCH) is used in the paint industry. It can be prepared in industrial scale by Pd-catalysed hydrogenation of isophorone in supercritical CO₂.

During the recovery of TMCH from SC-CO₂, it needs the removal of pressure. The released CO₂ is required to compress again for recycling and becomes expensive.



② SC-CO_2 is used in extraction of fatty acid, triglyceride from nature.

③ It can be used as dry cleaning solvent

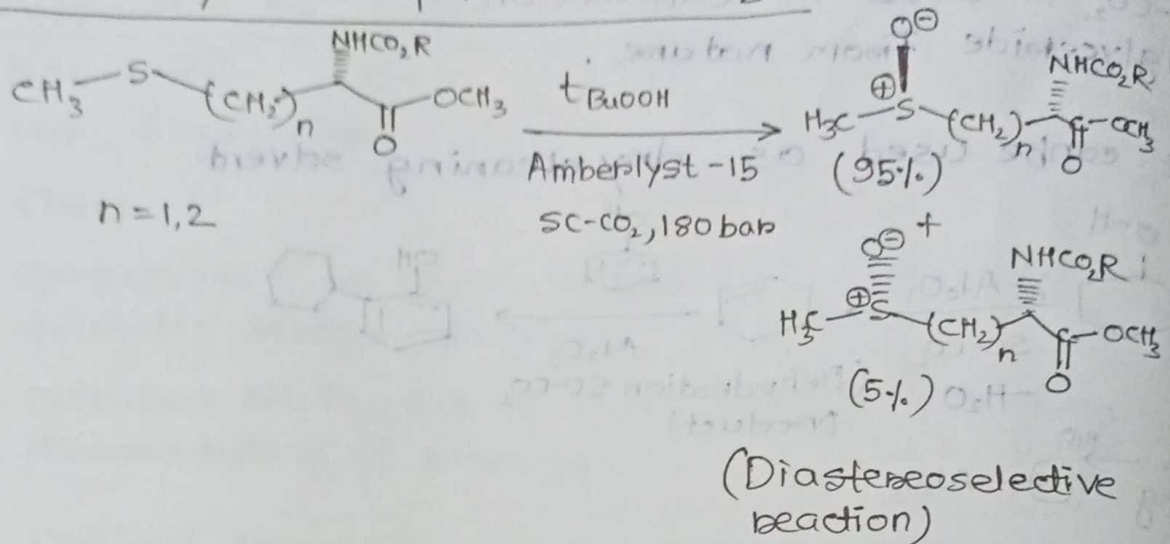


④ Synthesis of cyclohexyl phenol or cyclohexylphenol can be performed using cyclohexene as alkylating agent, but cyclohexene is more costly than cyclohexanol, which can be used for generation of cyclohexene by dehydration reaction using $\gamma\text{-Al}_2\text{O}_3$ as catalyst and later alkylation of phenol with cyclohexene can be done using same catalyst.

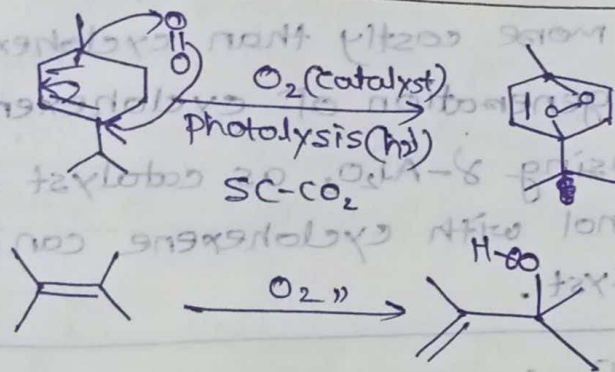
Drawbacks of SC-CO_2 :

- 1) Although use of SC-CO_2 in reaction medium increases yield, regioselectivity and stereoselectivity of many reactions compare to the use of common organic solvents, but all are accomplished in very small scale and using dilute solution. Commercial scale reactions (large scale reaction) in SC-CO_2 are very difficult to carry out or, accomplished. The reactions are performed in batch processes using shield autoclaves.
- 2) Properly devised laboratory (well equipped lab.) is better in this respect. Ionic liq. is better in this respect.
- 3) Inadequate solubility of reagents & catalysts in supercritical CO_2 is another limitation. The reactions, passing through polar transition state are very slow in supercritical CO_2 .

■ Selectivity of supercritical CO₂ :



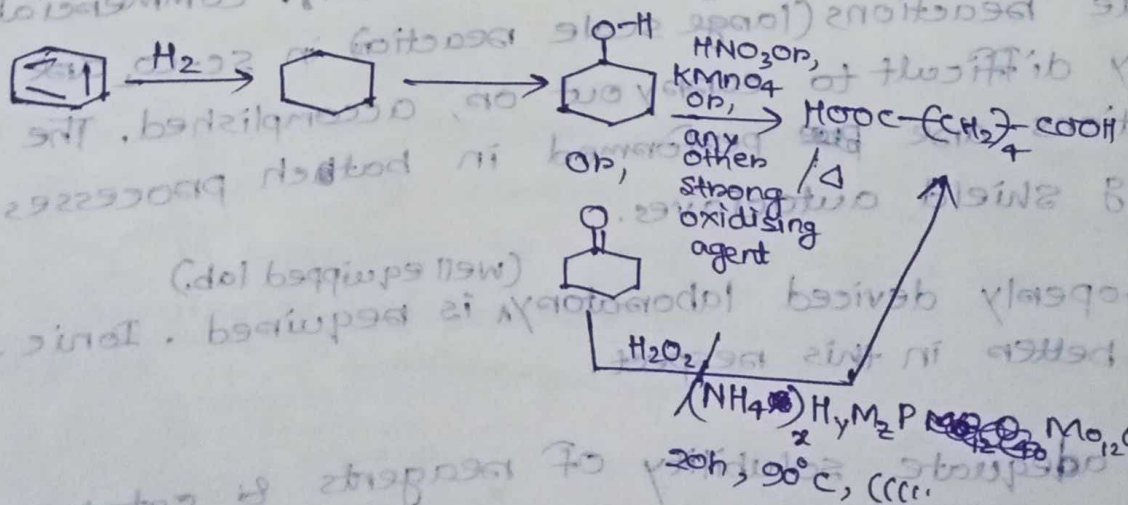
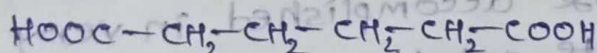
■ Use of SC-CO₂ as solvent during photolysis:

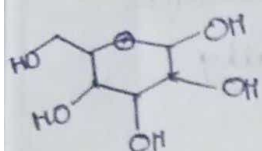


■ Green Synthesis of some compounds :

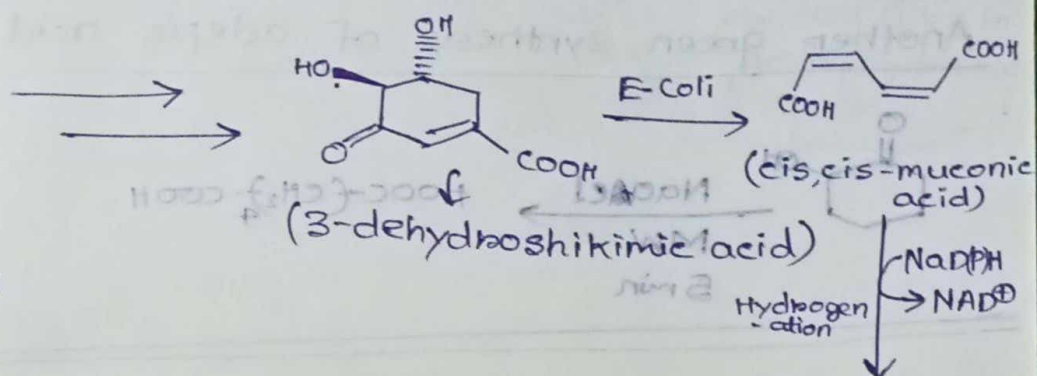
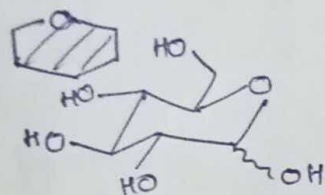
CV-22

1) Adepic Acid synthesis:

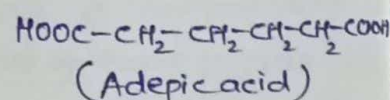




(Carbohydrate like glucose)



Bio.

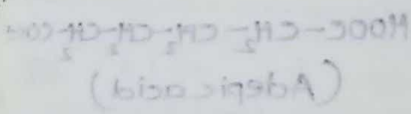
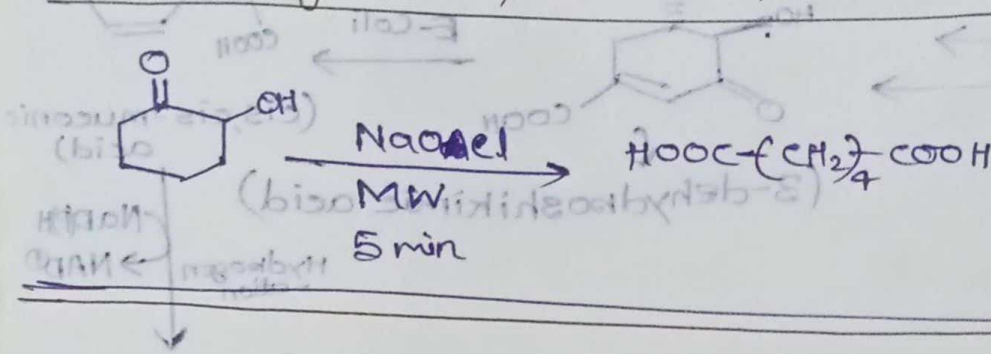


The above method is called as bioengineering process of adepic acid synthesis / green synthesis of adepic acid.

Adepic acid is primarily used in synthesis of Nylon 6,6 & globally 1.9×10^9 kg of adepic acid is required ~~clearly~~ yearly. The common method for the production of adepic acid is by ^{oxidation} ~~oxid~~ of a mixture of cyclohexanol and cyclohexanone, which is generally obtained from ~~oxid.~~ of cyclohexane. The source of cyclohexane is reduction of benzene, and benzene is obtained from non-renewable fossil fuels. Oxidation of cyclohexanone, cyclohexanone is carried out by using HNO₃, KMnO₄, ~~not~~ O₂, Ozone (O₃) or, NaOCl as oxidising agent. Most of the processes are not at all environmentally acceptable. To get alternative green synthesis of adepic acid, H₂O₂ was considered as environmentally benign oxidising agent because it is safe, gentle, clean, cheap & readily available. But, different catalyst used with H₂O₂ are expensive & complex. Moreover the yield of the reaction is not satisfactory (say 90% when (NH₄)₂HyM₂PMo₁₂O₄₀ is used). An environmentally compatible process for the synthesis of adepic acid has been established using microbial catalyst with

enzymatically converts glucose to cis,cis-muconic acid & subsequently hydrogenated catalytically to adipic acid.

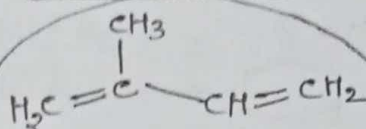
Another green synthesis of adipic acid:



The above method is called as biorefining process of adipic acid synthesis/green synthesis of adipic acid. Adipic acid is primarily used in synthesis of Nylon 6. Globally 1.9 x 10⁶ kg of adipic acid is produced annually. The common method for the production of adipic acid is by oxidation of a mixture of cyclohexanol and cyclohexanone, which is generally obtained from oxidation of cyclohexane. The source of cyclohexane is reduction of benzene, and benzene is obtained from non-renewable fossil fuels. Oxidation of cyclohexanone, cyclohexanone is converted out by using KMnO₄, K₂Cr₂O₇ or NaOCl as oxidizing agent. Most of the processes are not at all environment friendly. To get alternative green synthesis of adipic acid, H₂O₂ was considered as environment friendly oxidizing agent because it is safe, gentle, cheap & readily available. But, different catalysts with H₂O₂ are expensive & complex. Moreover, yield of the reaction is not satisfactory (say 40-50%). An environmentally friendly process for the synthesis of adipic acid is used (H₂O₂ is used). An environmentally friendly process for the synthesis of adipic acid is used (H₂O₂ is used).

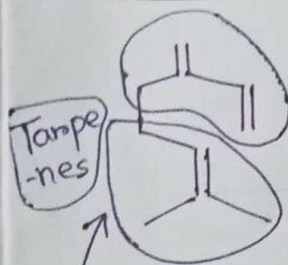
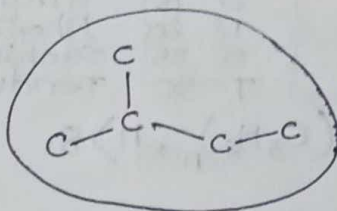
Terpenes & Terpenoids:

Isoprene

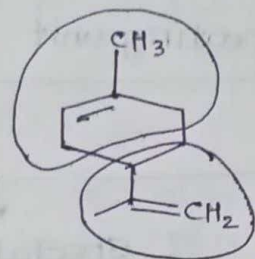
 C_5H_8

If this unit is repeated in a natural product (like in essential) having only hydrocarbon (hydrogen & carbon)

Terpenes

Examples: $\text{C}_{10}\text{H}_{16}$ β -Myrcene

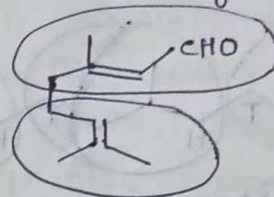
Limonene



having O containing group $\Rightarrow$ terpenoids

alcohol, ketone, aldehyde, ester, ether.

Example: citral (present in lemon grass)



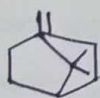
Classification of terpenes depending upon no. of isoprene unit $\Rightarrow$

A) Hemiterpene: Only simplest isoprene (C_5H_8)

(m) B) Monoterpenes: having two isoprene units (10 carbon atoms)

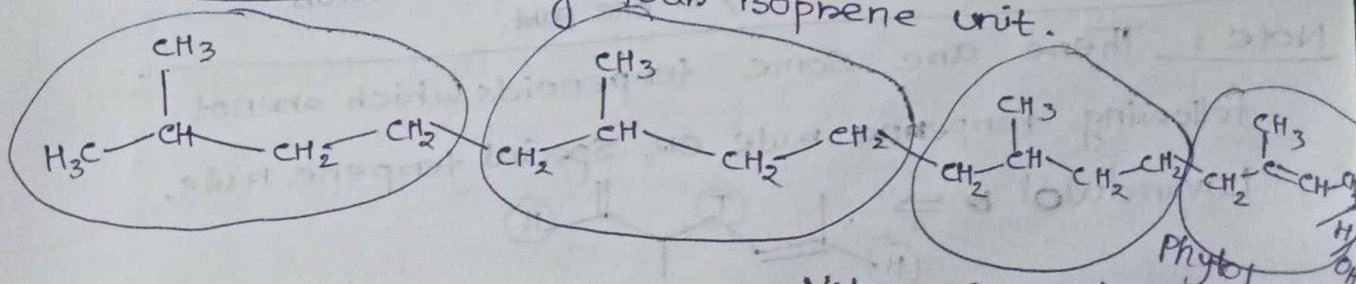
Example:

10

 β -pinene β -Myrcene

(5) C) Sesquiterpenes $\Rightarrow$ three isoprene units (15 carbon atoms)

(10) D) Diterpenes $\Rightarrow$ Having four isoprene unit.

Vitamin A $\rightarrow$ terpenoids

Phytol

E) Tristerpenes $\Rightarrow$ Having six isoprene units (C_{30})



Squalene

F) Tetraterpenes $\Rightarrow C_{40}$

M	10	Mahendra
S	15	Singh
D	20	Dhoni
S	25	Sachin
T	30	Tendulkar

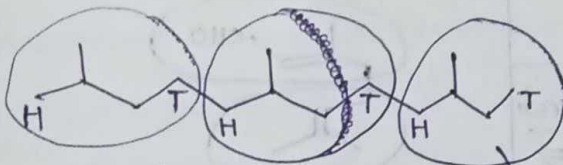
G) Polyterpenes $\Rightarrow$ Rubber (C_5H_8)_n, $n > 8$

Sesquiterpene - 25

Rules for combining repeating unit

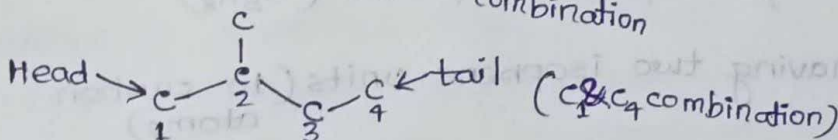
~~Head~~ Head-Tail combination stable.

Isoprene rule



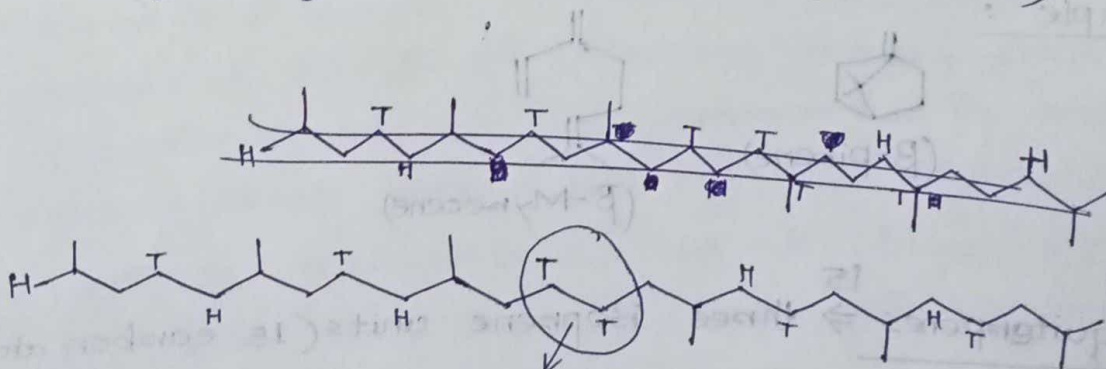
3-isoprene units

head-tail combination



Special Isoprene rule tail-tail combination only one position

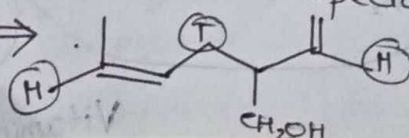
triterpenes 30 carbon atoms



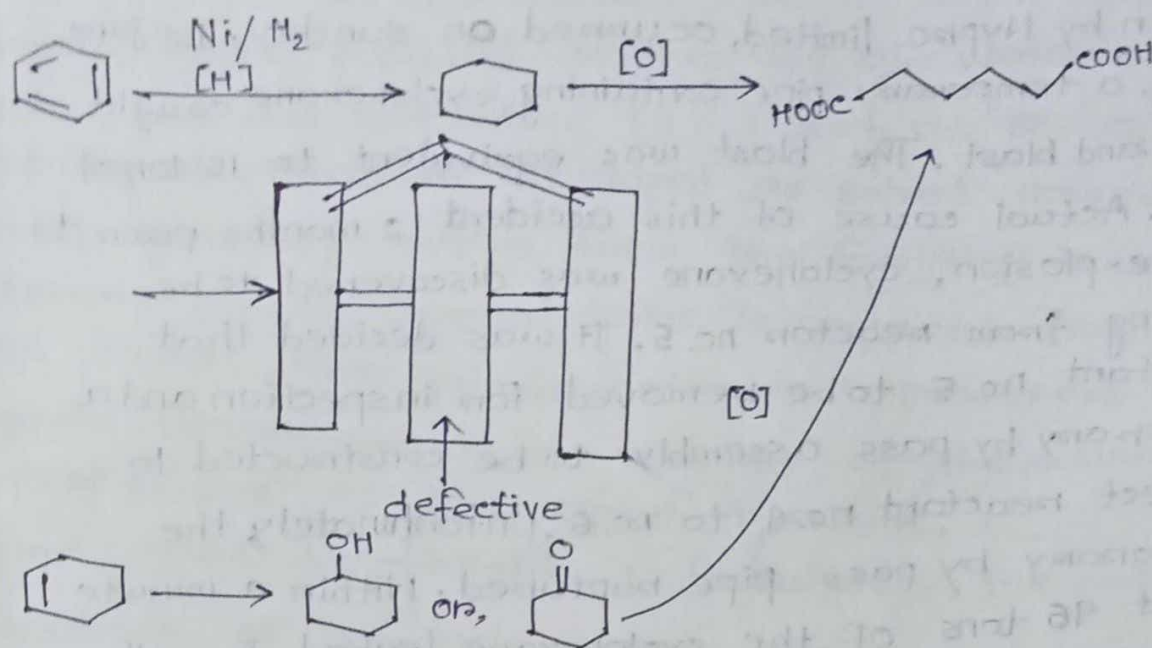
H-T combination does not occur only in one part

Note: There are some terpenoids which are not following terpene rule or, special terpene rule.

Lavandulol $\Rightarrow$



Inherent Safer Design (ISD) :



Q) What is ISD ?

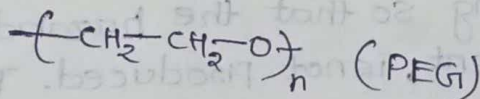
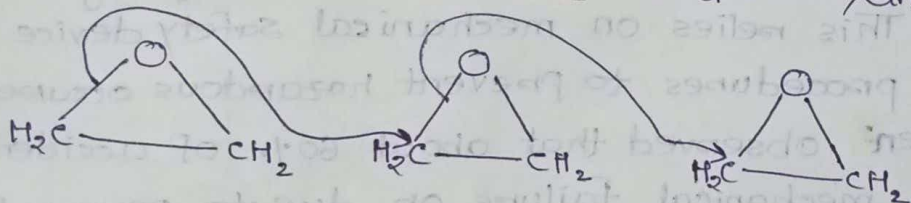
⇒ The principle is also inherently safer chemistry for accident prevention. ISD is defined as the design of chemical processes and produces with specific attention to eliminate hazards from the manufacturing process rather than relying on the control of their hazard. Hazard and operability studies are done before designing a chemical plant. This relies on mechanical safety device and well known procedures to prevent hazardous occurrences. It has been observed that about 60% of accident occurs due to mechanical failure or, due to personal, operational errors. This concept of ISD redesigns the process of manufacturing so that the hazardous product which is prone to accident, is not produced. The principle is "what you don't have cannot harm you".

Flixborough accident :

This disaster was an accident at a chemical plant, known by Nypro limited, occurred on Sunday, 1st June, 1974, a temporary pipe containing cyclohexane caught fire and blast. The blast was equivalent to 15 ton of TNT. Actual cause of this accident 2 months prior to the explosion, cyclohexane was discovered to be leaking from reactor no. 5. It was decided that reactor no. 5 to be removed for inspection and a temporary by pass assembly to be constructed to connect reactor no. 4 to no. 6. Unfortunately, the temporary by pass pipe ruptured. Within a minute about 46 tons of the cyclohexane leaked from the pipe and form a vapour cloud, that when coming on contact with an ignition source, exploded and completely destroyed the plant. The blast can be heard 30 miles away, 28 peoples were killed and 36 peoples were seriously ~~in~~ injured.

PEG as green solvent :

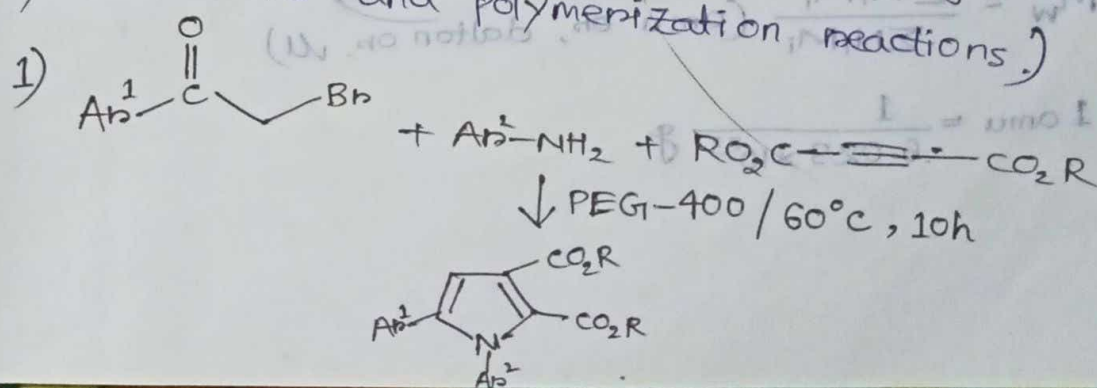
PEG $\equiv$ Polyethylene glycol

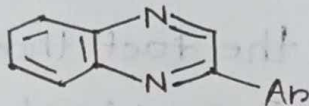
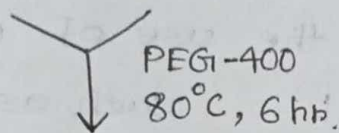
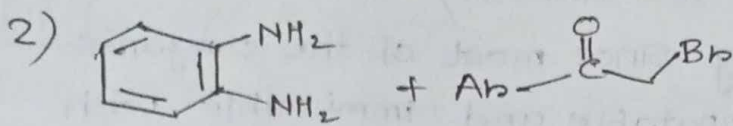


Organic reactions specially in large scale are carried out in solution phase. ~~Unfortunately~~ Unfortunately, most of the organic solvents used for this purpose are volatile organic compound (VOC) and these pose a serious environmental problem such as greenhouse effect, global warming, destruction of ozone layer, etc. To reduce this drawback as well as reaction cost, the concept of organic reactions in water ~~has~~ have

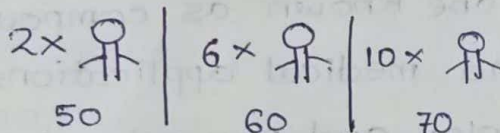
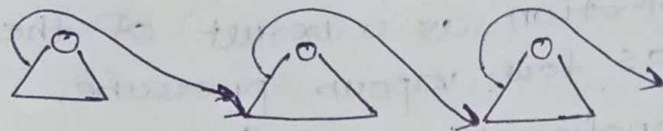
been developed. Despite remarkably achievement, this approach is slowly going since most of the organic substances are ~~low~~ incompatible and immiscible with aqueous media, parallel to the use of water as solvent, few less hazardous sc-CO_2 and ionic liquids have been developed as solvent. However, sc-CO_2 generally suffers from the fact that is under pressure system. Special device is required. Among these ionic liquids have gained noticeable improvement in organic transformation as a result of their unique properties such as low-vapour pressure, polarity and functionality. Unfortunately, the major drawback of use of ionic solvents are expensive and environmental safety as their toxicity are unknown.

Polyethylene glycols (PEG) are known as compounds with wide spread industrial and medical applications. PEGs are readily soluble in polar and non-polar solvent and insoluble in aliphatic hydrocarbons and sc-CO_2 . A very interesting aspect of these compounds is behind their application as solvent in organic reactions. Additionally, they are in expensive and significantly less-hazardous than other organic solvents. Moreover, PEGs are stable under ambient condition generates negligible vapour pressure and do not release VOCs. (They have good stability in both acidic and basic media and are suitable reaction media for oxidation, reduction, coupling, O-alkylation, S-arylation, S-allylation, multi-component reactions, asymmetric hydrogenations, cycloadditions and polymerization reactions.)





43
44
40
41



$$\text{Average} = \frac{2 \times 50 + 6 \times 60 + 10 \times 70}{2 + 6 + 10}$$

$$= \frac{N_1 M_1 + N_2 M_2 + N_3 M_3 + \dots}{N_1 + N_2 + N_3}$$

$$= \frac{\sum N_i M_i}{\sum N_i}$$

$$= 400$$

PEG-400

Number average
molecular weight
of polymer

Number of average molecular weight of polymer ($\bar{M}_N$)

Weight average molecular weight ($\bar{M}_W$)

$$\bar{M}_W = \frac{\sum N_i M_i^2}{\sum N_i M_i} \quad (\text{amu or, dalton or, } \mu)$$

$$1 \text{ amu} = \frac{1}{6.023 \times 10^{23}} \text{ g}$$

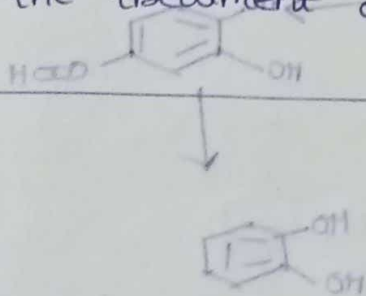
Available from an nomenclature :

PEG, PEO (polyethylene oxide) and POE (polyoxoethylene) referred to an ~~and oligomer~~ oligomer or, polymer of ethylene oxide. The three names are chemically ~~also~~ synonymous and ~~historically~~ historically PEG is preferred in biomedical field whereas POE is more appropriate in the field of polymer chemistry. Because different applications ^{polymer} required, ~~polymer~~ chain lengths, PEG has tended to refer oligomers or, polymers with a molecular mass below 20,000 gm/mole. PEO to polymer with molecular mass above 20,000 gm/mole and POE to a polymer of any molecular mass. PEG are commercially available over a wide range of molecular weight from 200 g/mole to 1000000 gm/mole. The number that are open included in the name of PEG indicate the average molecular weight i.e., a PEG when $n=9$, would have an average molecular weight approximately 400 daltons and would be labelled PEG-400.

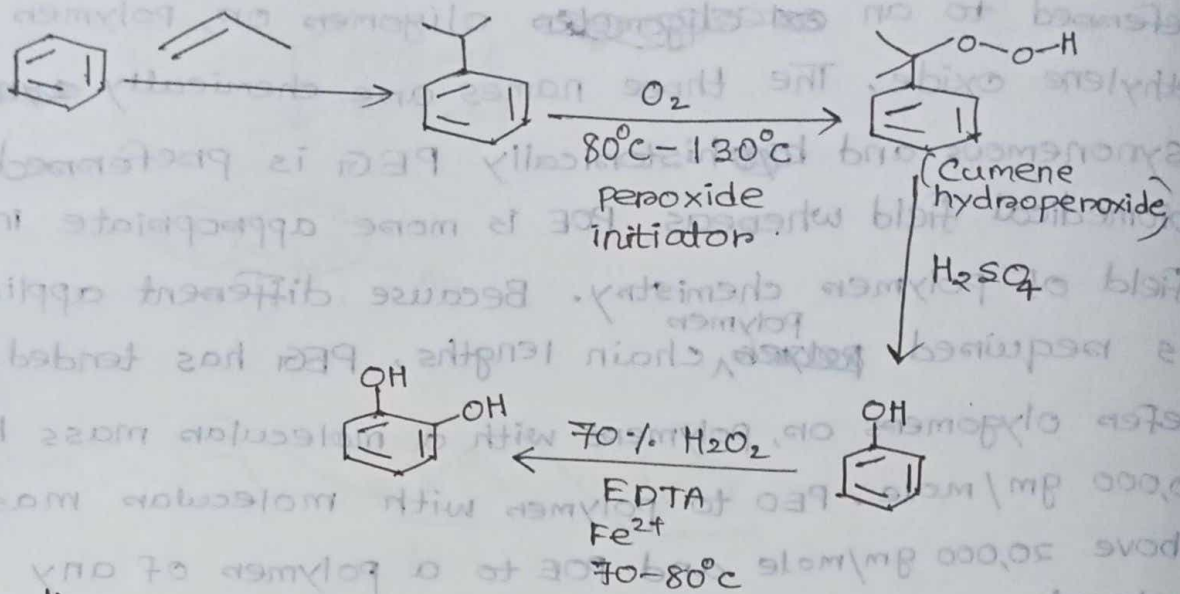
Green Synthesis of catechol:

Catechol and its derivatives are used as antioxidant, Polymerization inhibitors, photographic developen, etc.

The enzyme catechol O-methyltransferase catalysing O-methylation of ~~neurotransmitters~~ neurotransmitters is ~~used~~ used for the treatment of parkinson disease.



Previous or, ancient method of catechol synthesis:



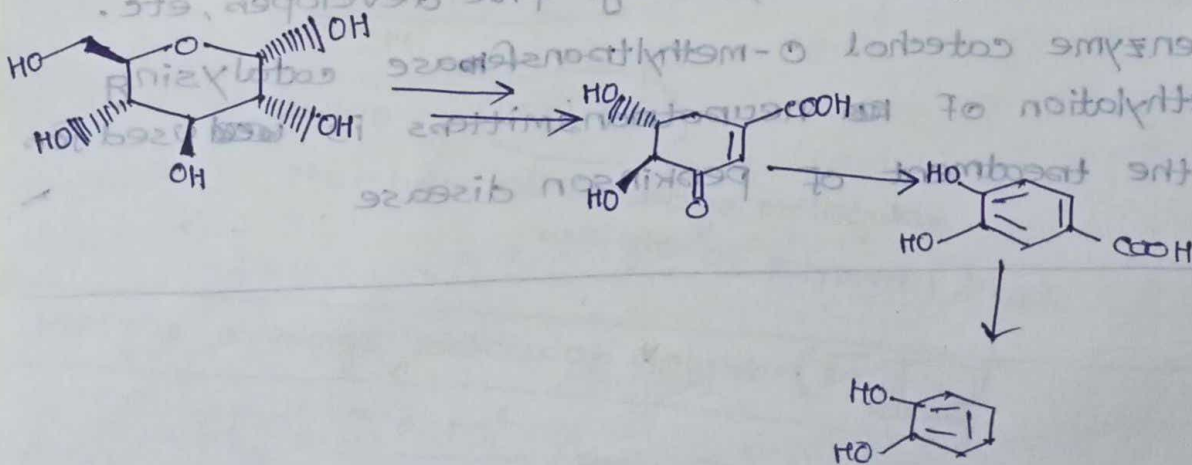
All the above methods are hazardous to environment.

Green synthesis of Catechol :

Bio-synthesis of Catechol (Bio-engineering) $\Rightarrow$

CU-22 Catechol can be synthesized from glucose by genetically modified micro-*escherichia coli*

(Tradename : AB-2834/b-P-KD 136/PKD-9.069 A as catalyst). This process converts 56 milimolar glucose $\times 18.5 \pm 2$ milimolar catechol.



19/4/23

Structure determination of terpenes and terpenoids:

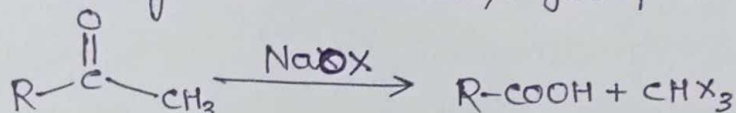
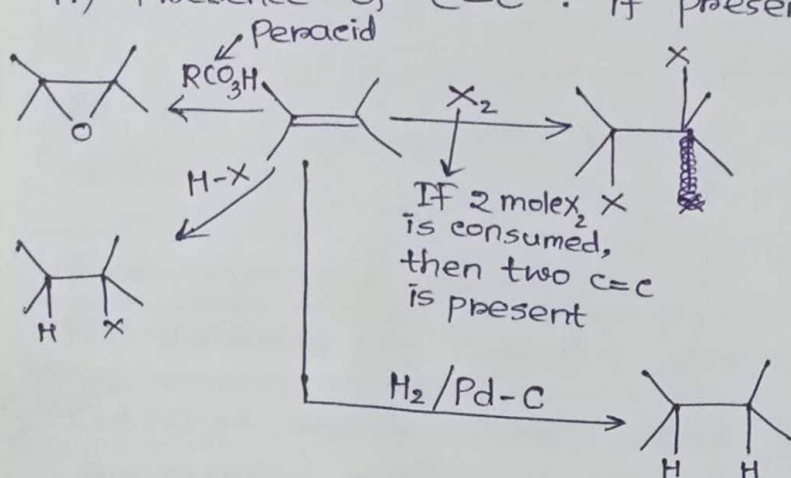
hydrocarbon

Oxygen contains

I) Molecular formula

II) Checking its optical activity; Is it optically active or, inactive

III) Finding out ketomethyl group is present or, not.

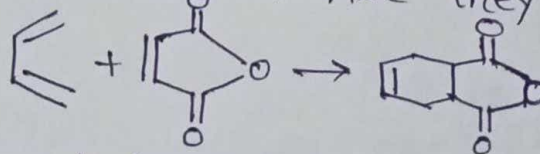
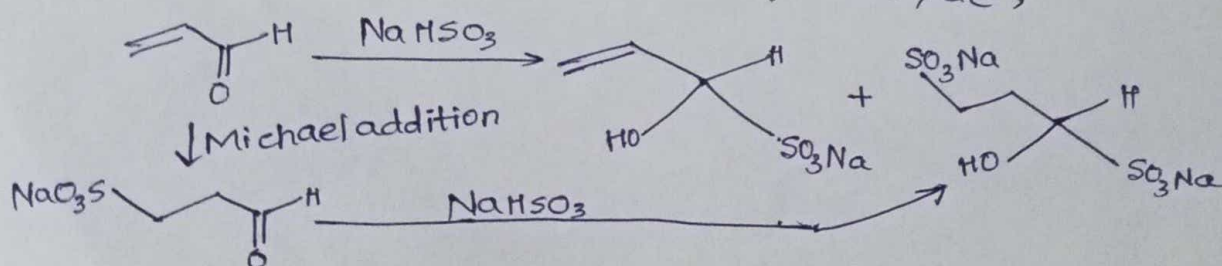
iv) Presence of $C=C$: if present how many?v) The molecule is cyclic or, acyclic. $\Rightarrow$ Say your unknown molecule has $DBE = 3$

Now by H_2 or, X_2 addition
tells $\text{present} = 2$

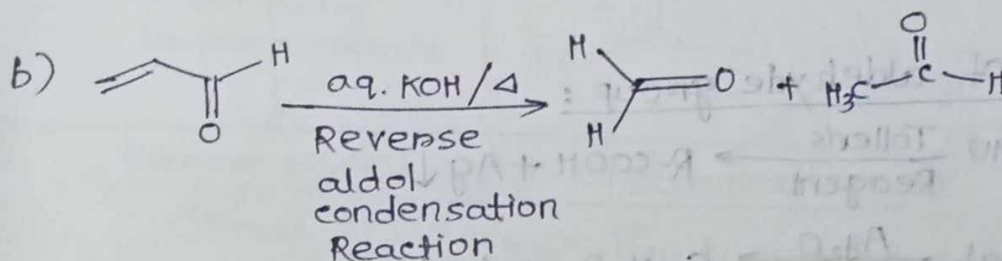
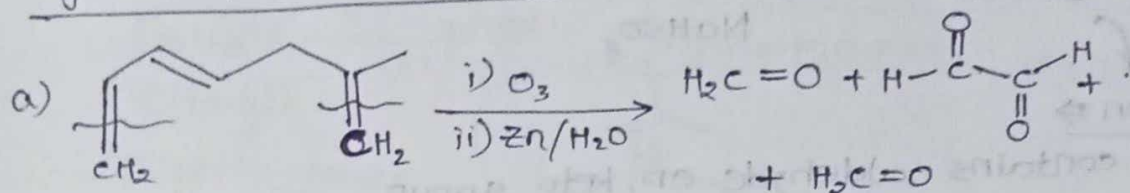
from molecular formula.

No aldehyde or, ketone is present.

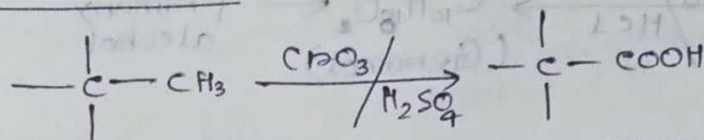
The molecule is cyclic one.

vi) Nature of double bond $\Rightarrow$ Are they conjugated double bond:or, α, β -unsaturated ketone/aldehyde,

VII) Degradation by simp of terpenes and terpenoids by to get simple compound :



c) Chromic acid $\Rightarrow$

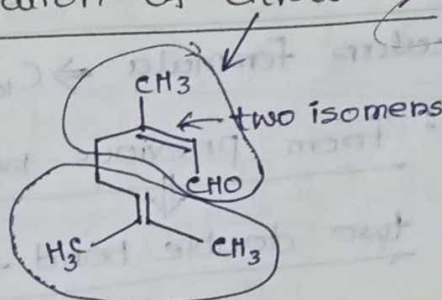
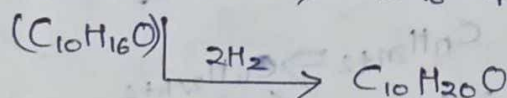
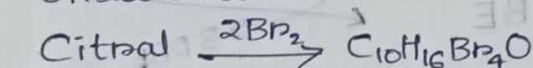


VIII) Spectroscopic study $\Rightarrow$ UV, IR & NMR

◆ Structure elucidation of citral $\Rightarrow$

1) Determination of molecular weight $\Rightarrow$
 $\text{C}_{10}\text{H}_{16}\text{O}$

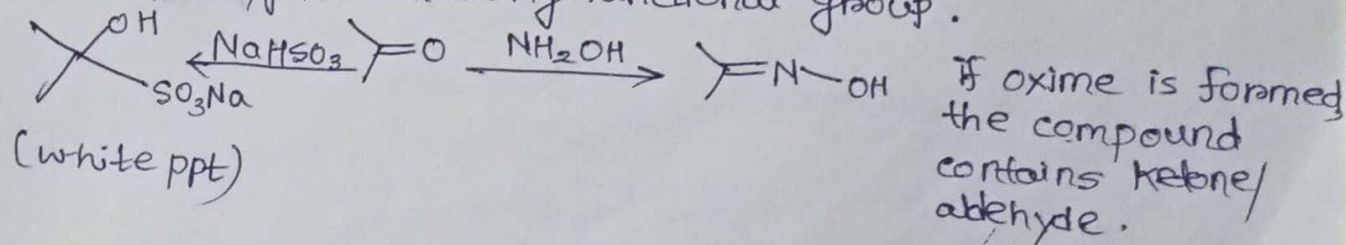
2) Detection of unsaturation



Conclusion : Presence of two double bonds.

3) Nature of oxygen atom : As in molecular formula contains one oxygen atom, thus we have to know the

Oxygen containing functional group.



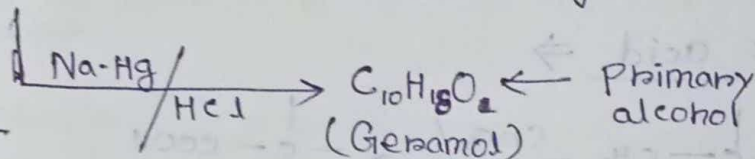
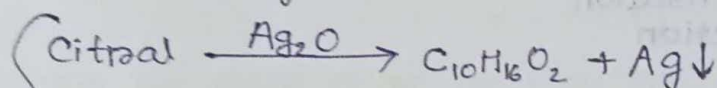
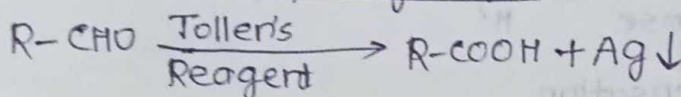
Citral $\longrightarrow$ it reacts with NH_2OH or, NaHSO_3

Conclusion $\Rightarrow$

Citral contains aldehyde or, keto group
ketone or, aldehyde $\rightarrow ?$

CV-22

● Presence of aldehyde group :



Conclusion: Citral contains aldehyde group.

4) Presence of open chain structure $\Rightarrow$

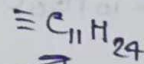
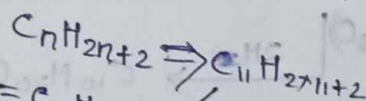
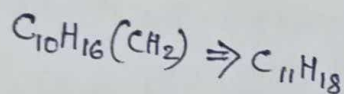
Molecular formula $\Rightarrow \text{C}_{10}\text{H}_{16}\text{O}$

Conclusion: From previous reactions

$\downarrow$
two double bond + one aldehyde

DBE

3 DBE



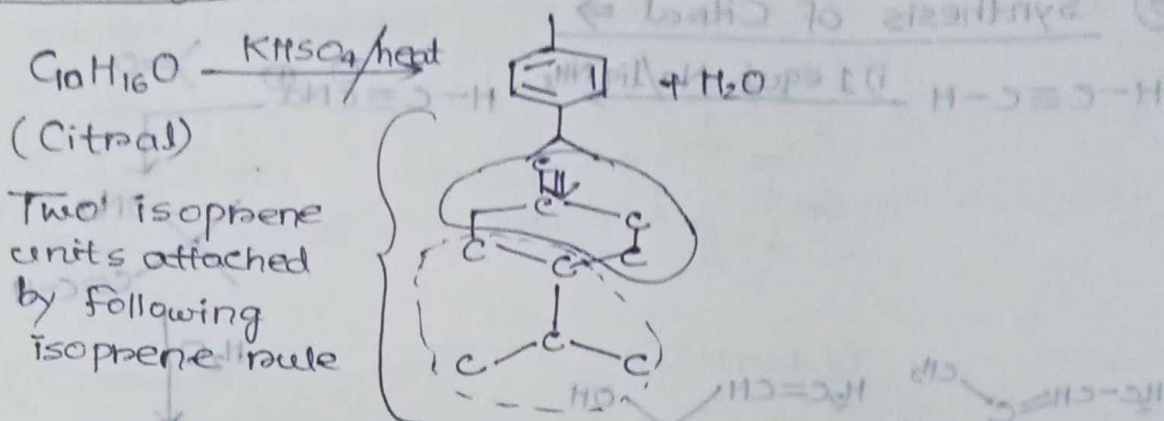
6'H' short

DBE = 3

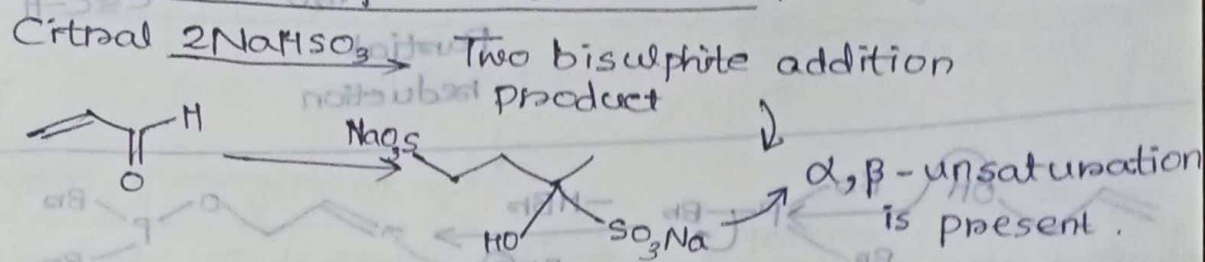
~~Thus final conclusion~~

Thus final conclusion: The molecule is acyclic.

5) Dehydrogenation : Determination of carbon skeleton

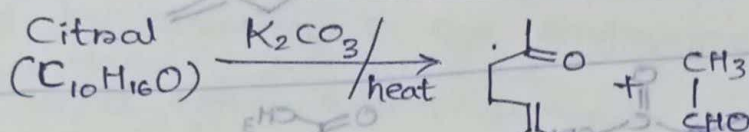


6) Presence of α, β -unsaturation $\Rightarrow$



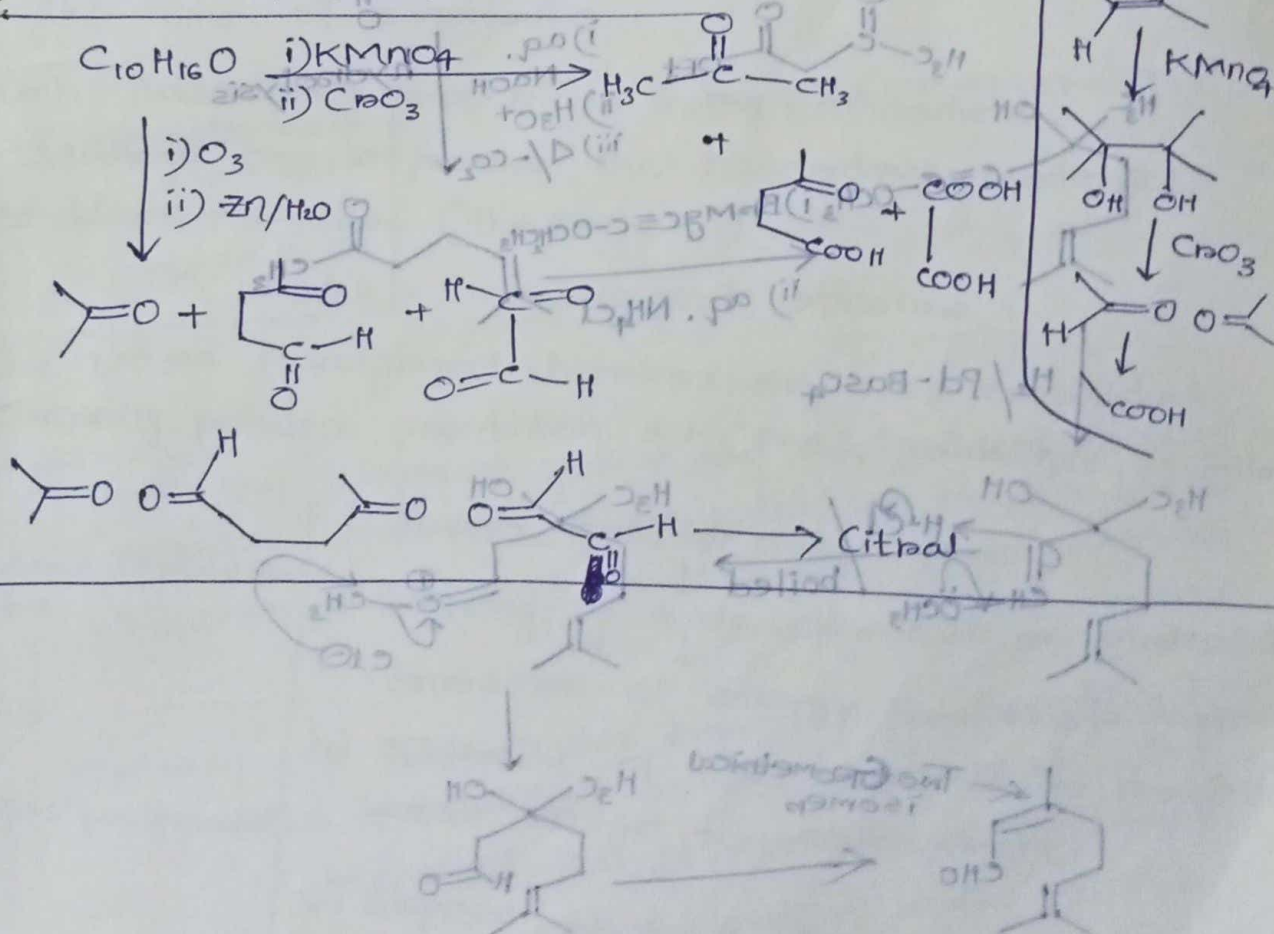
7) By reverse aldol condensation $\Rightarrow$

CJ-22

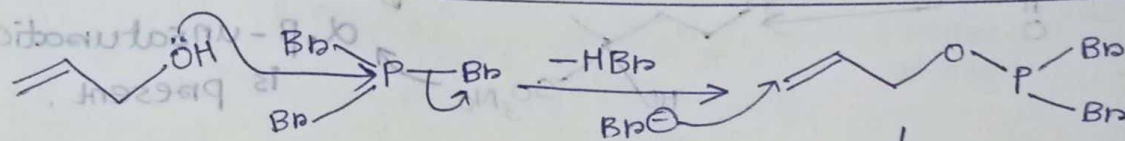
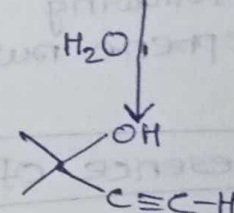
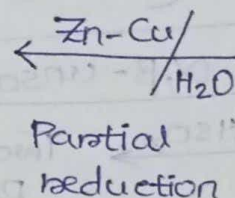
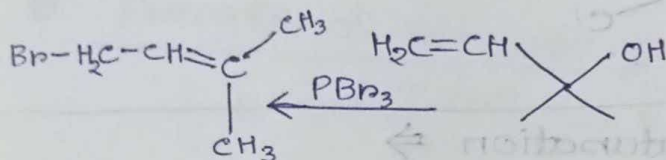
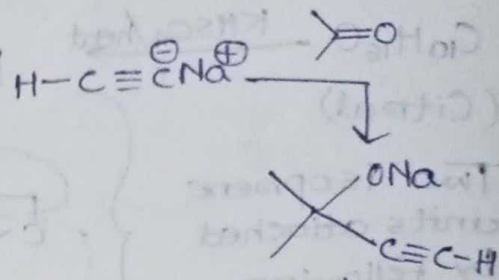
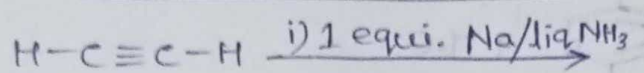


8) CJ-22

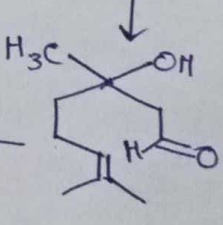
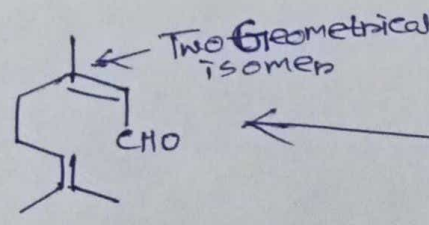
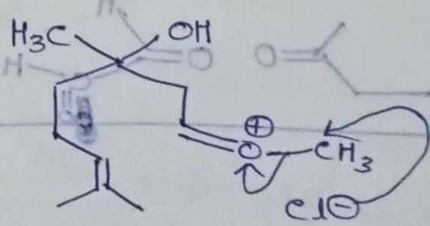
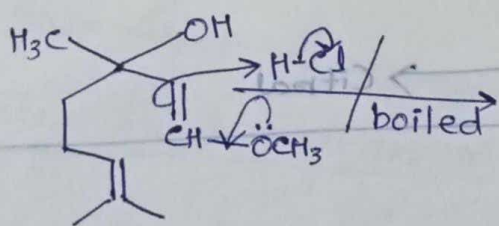
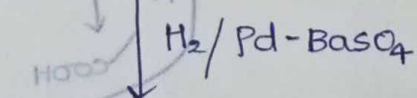
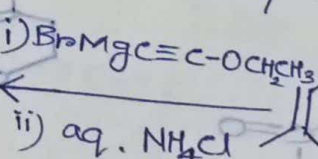
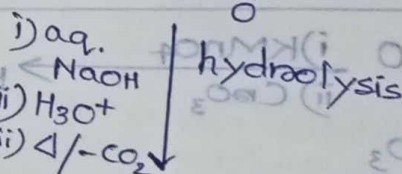
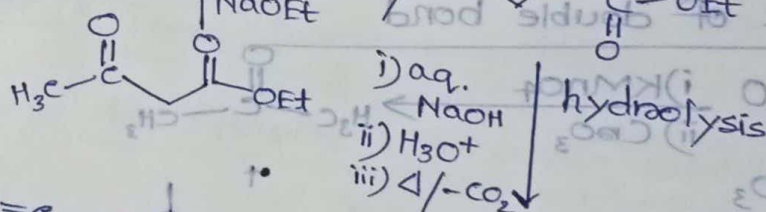
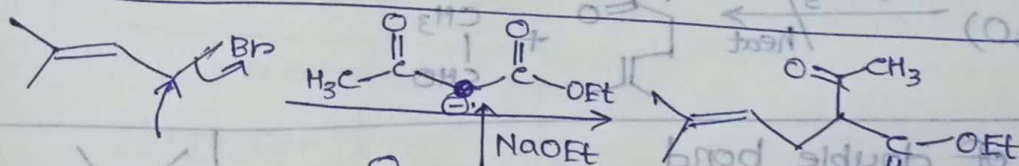
Position of double bond



⑨ Synthesis of Citral $\Rightarrow$

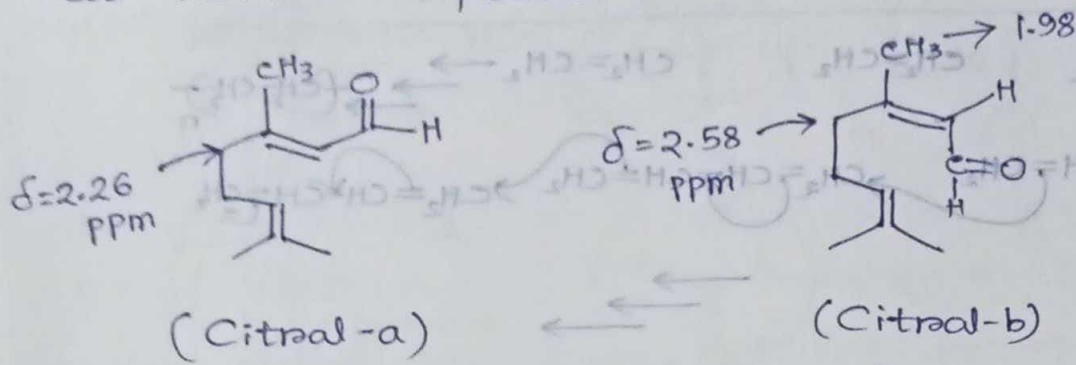


By reverse aldol condensation $\Rightarrow$



Two Geometrical isomers

The spectroscopy ($^1\text{H NMR}$) tells that which Geometrical isomer is present.



Offline
26/4/23

The waste management $\Rightarrow$

The purpose of preparing different policies, acts regulations related to green environment movement is to eliminate or, minimize the hazards, and diminish the risk caused by chemicals in the environment.

Risk is a term which depends on two factors —

- (i) Potential of the material to do hazard and
- (ii) Time of exposure

Such hazardous materials in the environment.

$\rightarrow$ Without any exposure the hazardous material could do no harm (the risk '0')

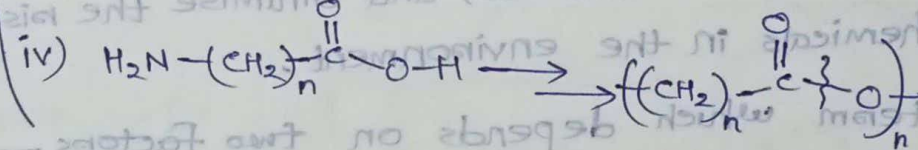
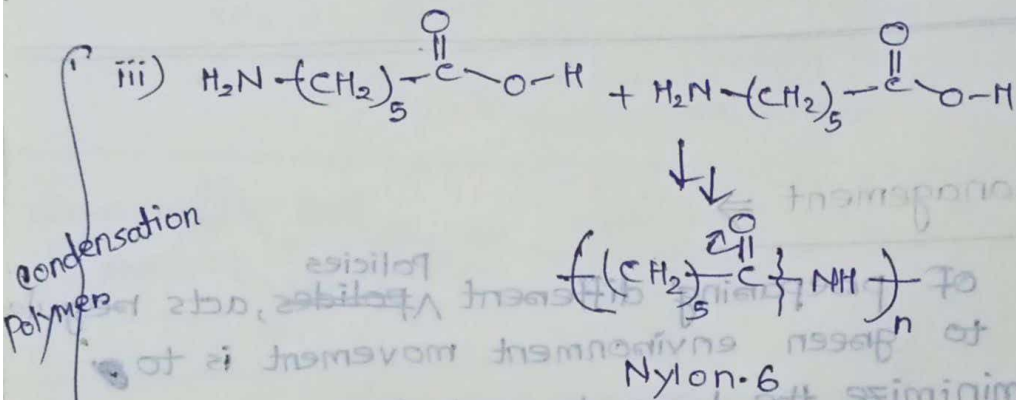
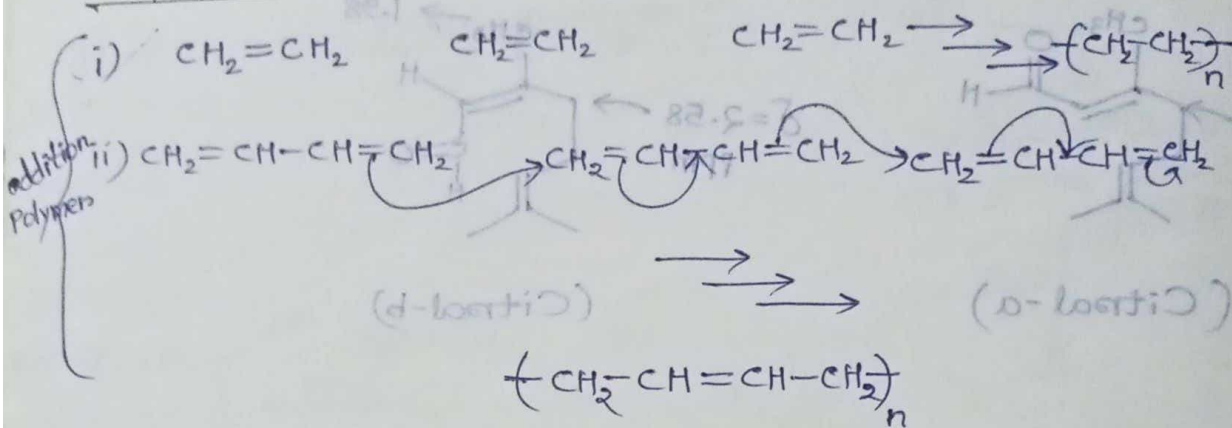
So, $\text{risk} = \text{hazards and exposure}$

the waste management hierarchy was established obeying pollution prevention act (PPA), guidelines as follows —

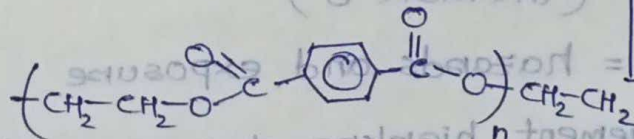
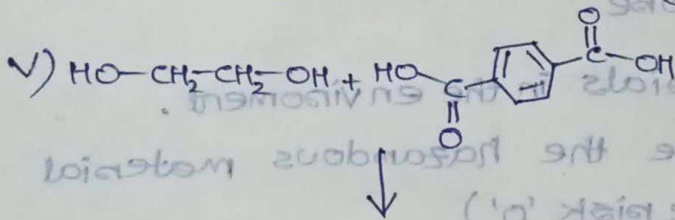
- | | |
|--|--|
| More preferable

less preferable | i) Prevent pollution of source
$\downarrow$ |
| | ii) Recycling of toxic chemicals or, materials
$\downarrow$ |
| | iii) Generation of energy from waste material
$\downarrow$ |
| | iv) Treatment of toxic chemicals to make the waste benign for environment.
$\downarrow$ |
| | v) disposal of waste toxic chemicals to the environment. |

Polylactic acid (PLA - A biodegradable polymer)



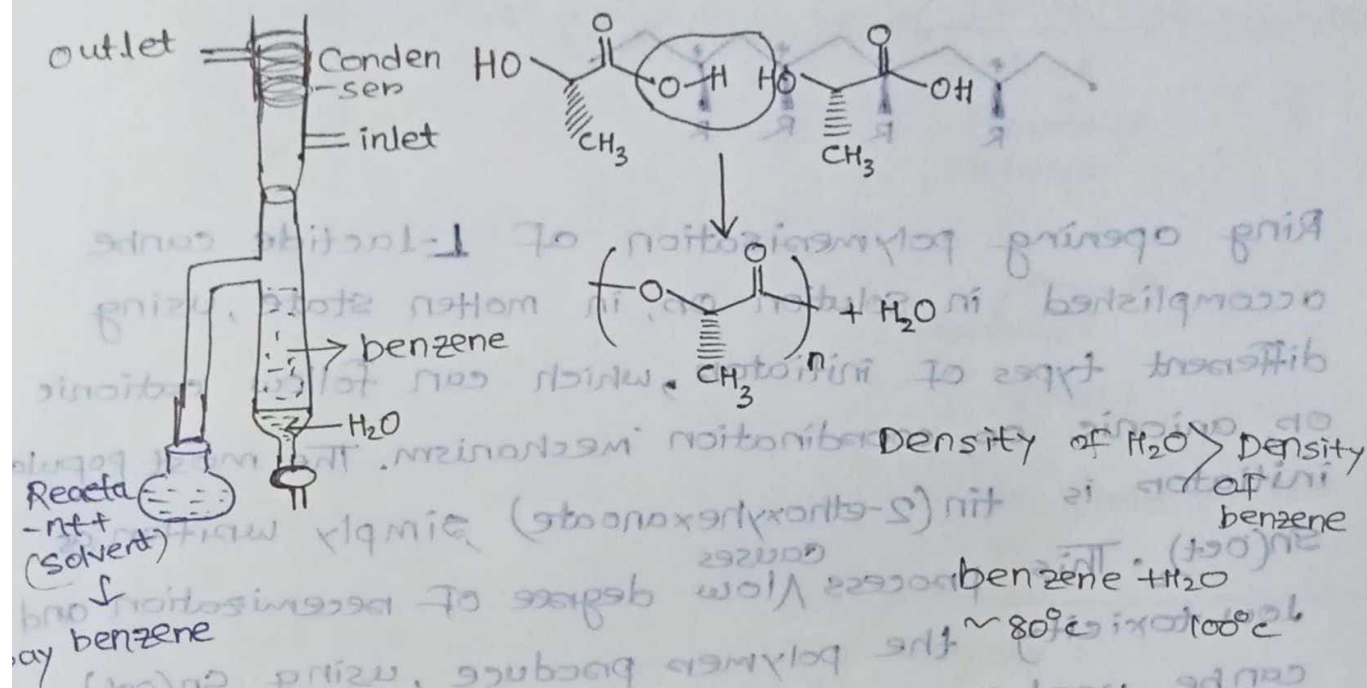
biodegradable role of (ester) amide



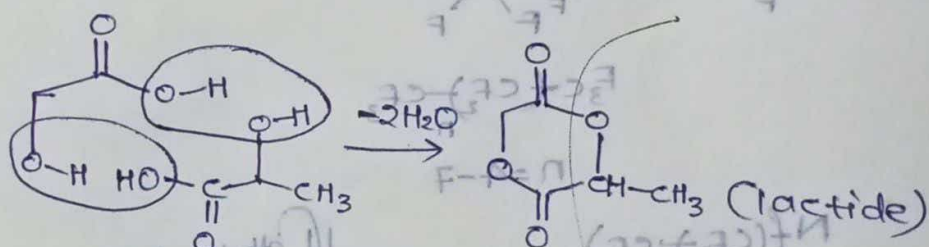
amide bond stronger than ester hence hydrolysed in a slower rate.

- Packaging industries are trying to replace petrochemical based polymer by biodegradable polymer to decrease environmental pollution and also due to the safety reason towards human health.

- Biodegradable polymer means that the polymer will degrade itself in nature by action of light, water and air, in the increase or of any other natural species.



- B. It gives high molecular weight PLA which are generally used in packaging industry.
- C. Polymerization through lactide formation is the most popular method industrially.



Three isomers stereoisomers can be formed.

Lactide is a cyclic dimer of lactic acid formed by elimination of 2 molecules of water. A mixture of d- and l-lactic acid on heating produces 3-stereoisomers of lactide. (i) R,R-lactide or, d-lactide (ii) S,S-lactide or, l-lactide (iii) R,S-lactide or, meso lactide.

Based on stereochemistry of lactides, three classes of PLA can be considered, such as poly(L-lactide) or, (PLLA), poly(D-lactide) or, (PDLA), poly(D,L-lactide) or, (PDLLA). Optically active polymers (PLLA and PDLA) are isotactic polymer, and are crystalline whereas optically inactive polymer (PDLLA) is relatively

atactic polymer & amorphous in nature.



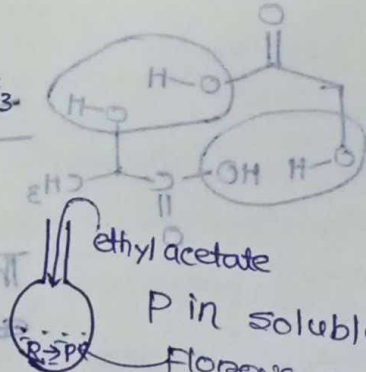
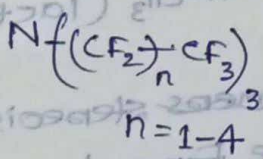
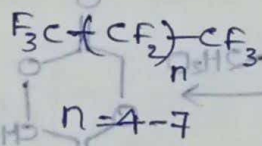
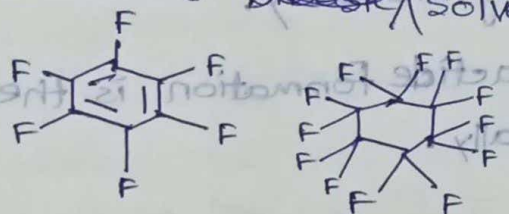
Ring opening polymerisation of L-lactide can be accomplished in solution or, in molten state, using different types of initiator, which can follow cationic or, anionic or, coordination mechanism. The most popular initiator is tin(2-ethoxyhexanoate) simply written as $\text{Sn}(\text{oct})_2$. This process ^{causes} low degree of racemization and low toxicity the polymer produce, using $\text{Sn}(\text{oct})_2$ can be used in food industry.

~~Mesoporous~~

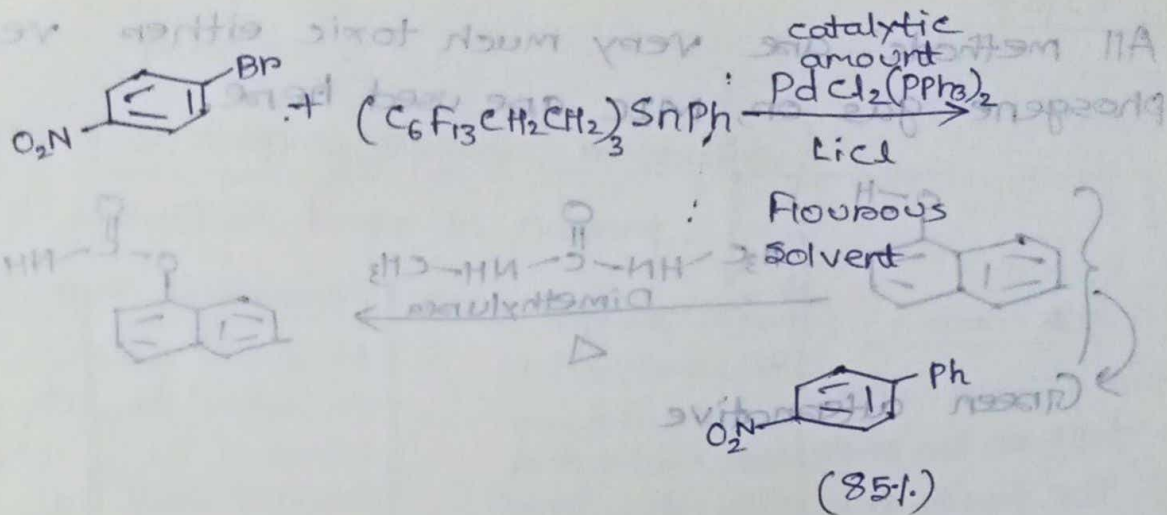
Fluorous

biphasic

Solvent ← Green solvent

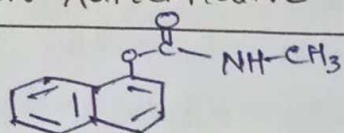


Characteristic feature of fluorous solvents is that they mix with neither common organic solvents nor water at room temperature, thus forming biphasic system & they dissolve fluorine rich compound well. Solvents containing fluorine with a relatively large component in molecules are called fluorous solvents. Most fluorous solvents have high thermal stability & ^{chemo-}stability and are low in toxicity. As example,



N.B : Fluorous solvent gives maximum yield of the process.

Green ^{inner} Alternative of bhopal gas tragedy :

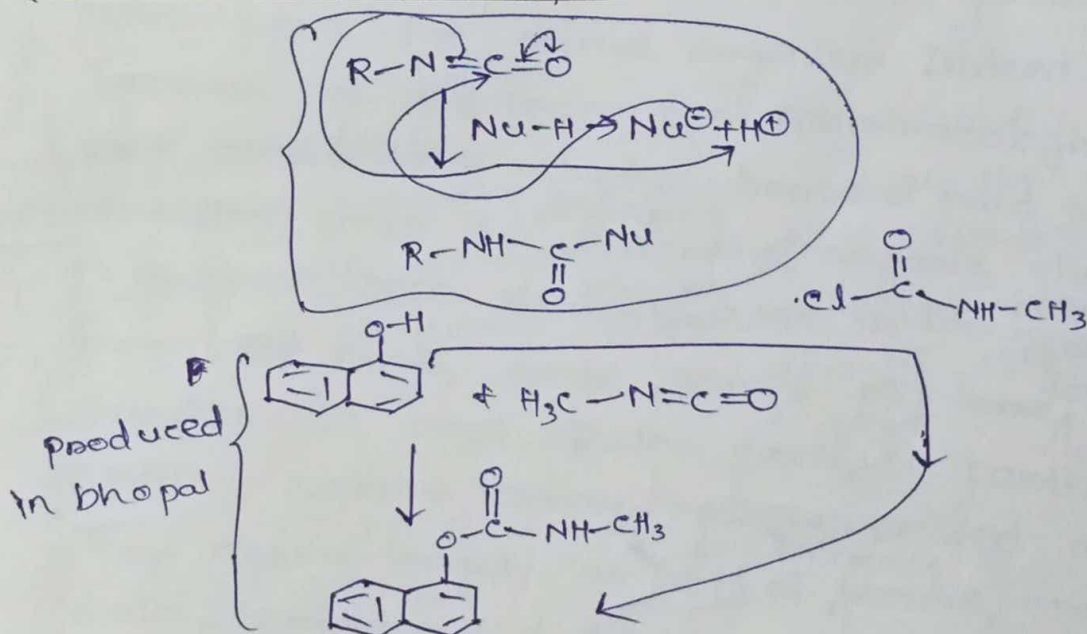


(Carbaryl)
Sevin

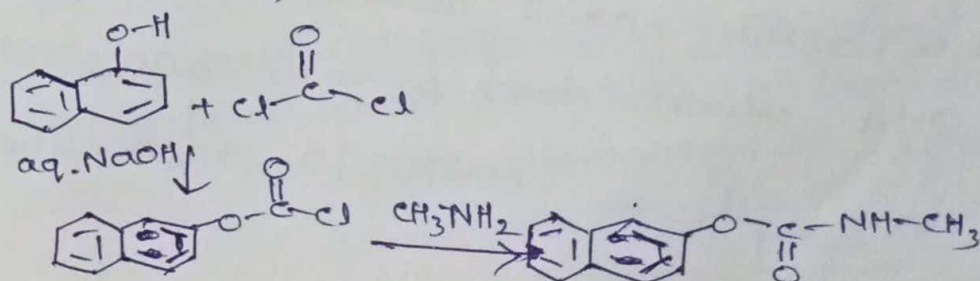
IUPAC Name: 1-Naphthyl-Methyl-carbamate

This is insecticide

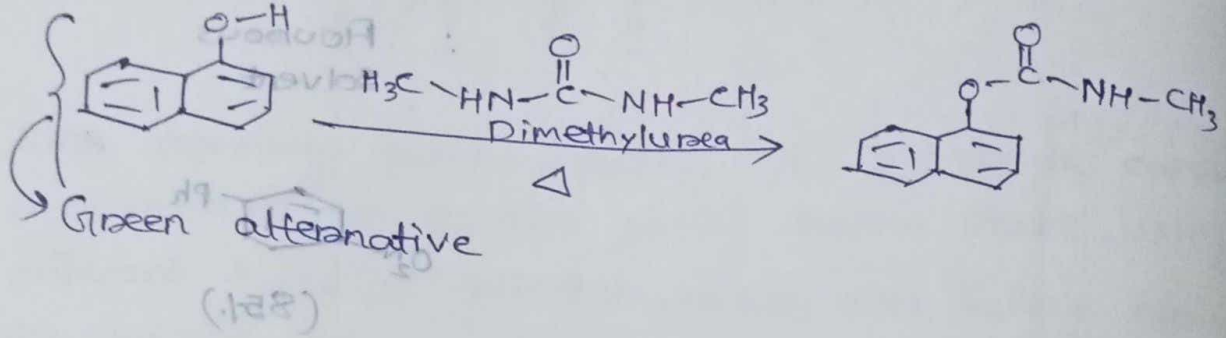
Reaction used in bhopal :



Other alternatives,

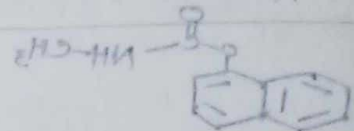


All methods are very much toxic either phosgene gas or, MIC are used here. very toxic



N.B.: Phosgene solvent gives maximum yield of the process.

Green Alternative of phosgene toxicity:

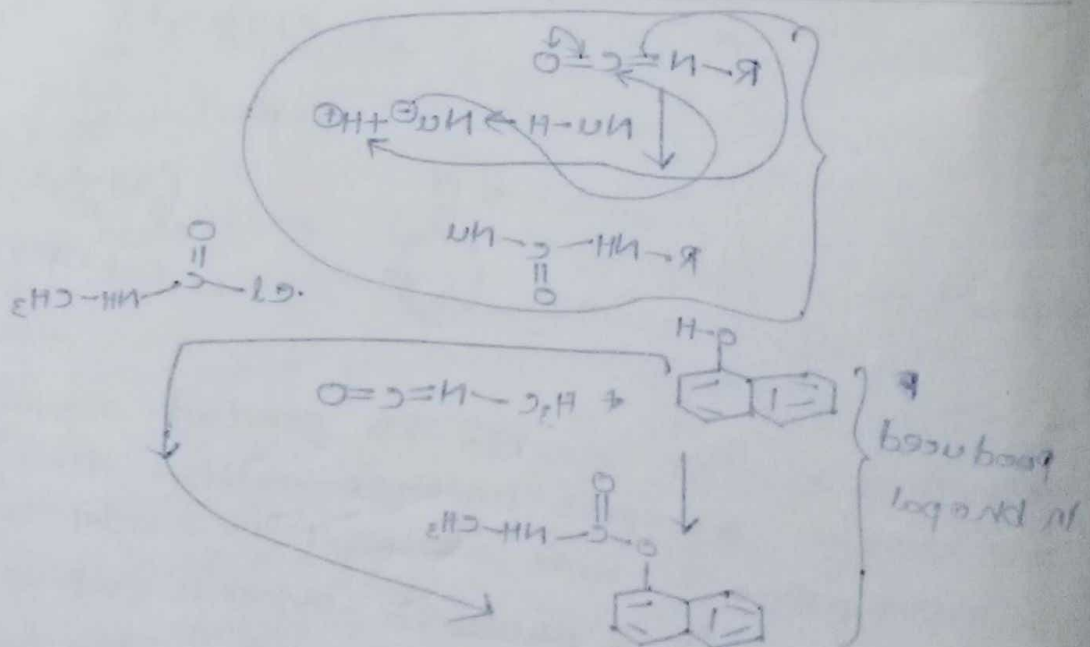


(carbamyl)
sevin

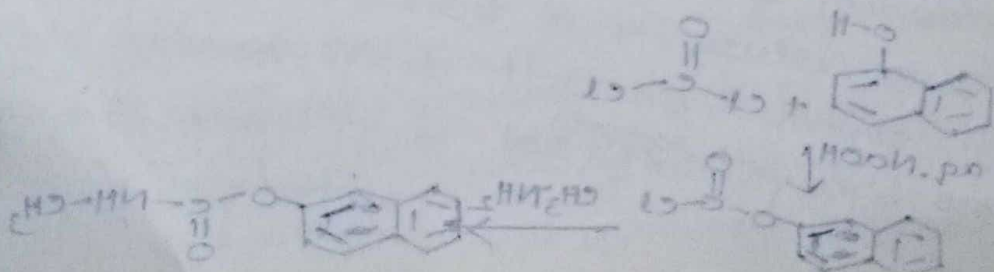
IUPAC Name: 1-Naphthyl-Methyl-Carbamate

This is insecticide

Reaction used in phosgene:



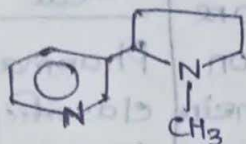
Other alternatives:



6/5/23

Alkaloids

- ① Nitrogen containing organic molecules
- ② They should be basic in nature.
- ③ They are naturally occurring.



(Nicotine)

Q What does it mean by alkaloids?

⇒ Alkaloids are basic, nitrogen containing compounds, that occur in the plants. We may define alkaloids as compounds obtained from plants having a basic character & containing at least one 'N' atom in a heterocyclic ring. Generally, speaking, they have complex molecular structures & display characteristic physiological actions either curative or, toxic upon the animal organism. Indeed, it is because of this pronounced pharmacological property that considerable attention has been paid to their chemistry, since the beginning of systematic organic chemistry, more than 2000 alkaloids have so far been isolated from the roots, seeds, leaves of some forty families. In most of the cases, a particular plant portion contains several closely related alkaloids. They occur largely as salt of ^{acetic} ~~acidic~~, malic, tartaric and citric acids. The term, alkaloid was ^{coined} ~~put~~ by German scientist Carl F.W. Meissner & in 1819, and derived from Arabic Al-Qualja : Means ashes of plants.

Classification of alkaloids :

① Based on taxonomic :

This classification is done on the basis of the family of alkaloids. As for example, the alkaloids are described as, Solanaceous & Papilionaceus without reference of their family chemical type.

② Biosynthesis

This method is most fundamental method of classification of alkaloids. It is done depending on the type of precursor used by plant to synthesis the complex structure. Example, Morphine, Nicotine comes under biosynthesis. They can be obtained from phenylalanine.

③ Chemicals

Alkaloids are classified on basis of their chemical structure. For example, alkaloids that contain a ring system which is called indole are referred to as indole-alkaloids.

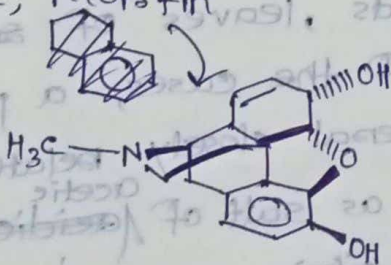
④ Pharmacological

Pharmacological classification listed alkaloids according to their use or physiological effect. As for example, Analgesic alkaloids, cardioactive alkaloids.

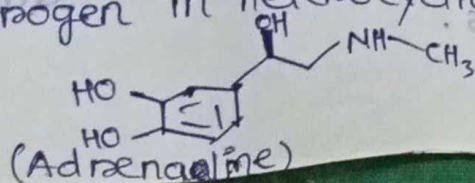
■ Classification of alkaloids, following primary groups :

① True alkaloids : The alkaloids, which are called true alkaloids, contain the nitrogen content in the heterocyclic & it originates from amino acid. The characteristic ^{example} of alkaloids are :

Nicotine, Morfin



② Proto-alkaloids : Proto-alkaloids are those alkaloids, which are derived from amino acid but do not have nitrogen in heterocyclic ring.

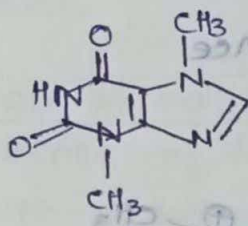


③ Polyamine alkaloids :

The derivatives of spermidine, spermine and putrescine -e. Examples: cyclopeptide and peptide alkaloids.

④ Pseudo alkaloids :

The alkaloid like compound that do not originate from amino acid. These groups are steroids like, terpene like alkaloids, purine like alkaloids as well as, ~~exa~~ example, theobromine, theophylline



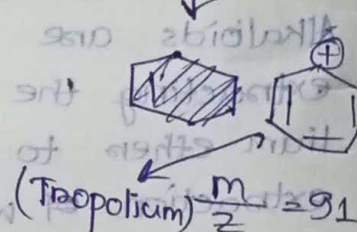
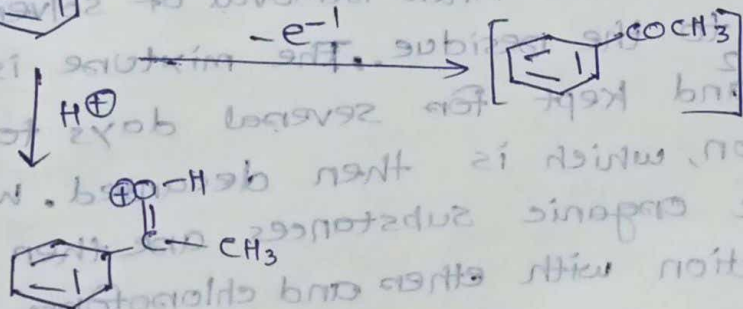
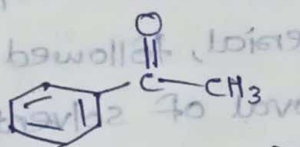
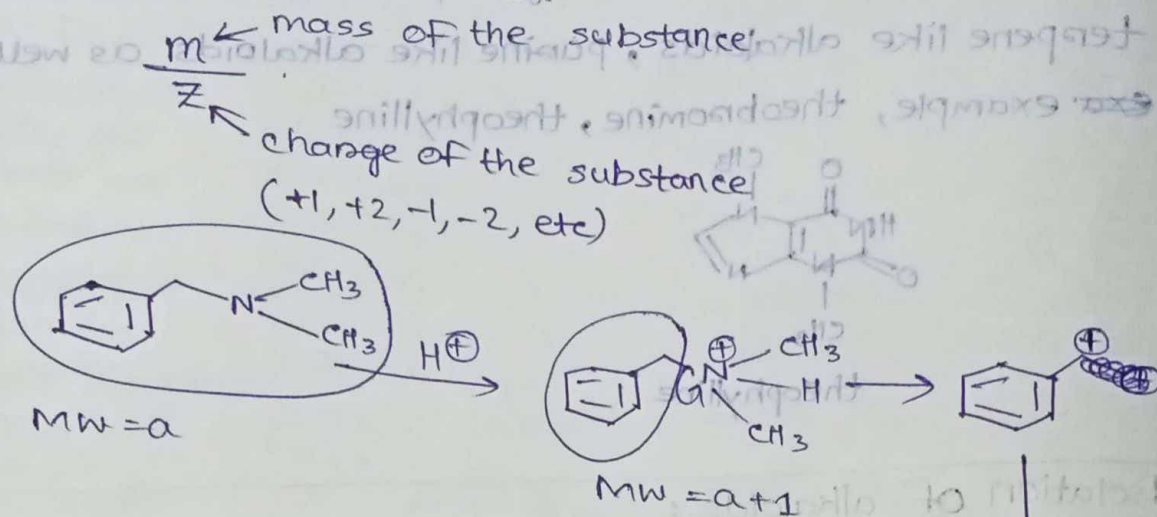
theophylline

Isolation of alkaloids :

Alkaloids are generally isolated from plants by first extracting the air dried powdered material with petroleum ether to remove the fatty material, followed by extraction of with ethanol. After removal of solvent, water is added to the residue. The mixture is acidified to $\text{pH } 2$ and kept for several days to obtain a clear solution, which is then decanted. Water soluble non-basic organic substances are then separated by extraction with ether and chloroform. The solution is then basified by addition of sodium carbonate or, ammonia & successively ~~ex~~ extracted to ether or, ethanol, to extract free bases. The removal of solvent, yields a mixture of alkaloids which are then separated into the individual components, either by fractional distillation or, more frequently by column chromatography.

Determination of molecular structure:

The molecular formula of an alkaloid is ascertained by elemental analysis, and determination of molecular weight. A more accurate method is high resolution mass spectroscopy which not only tells the exact molecular weight but also reveals the elemental composition of alkaloids.



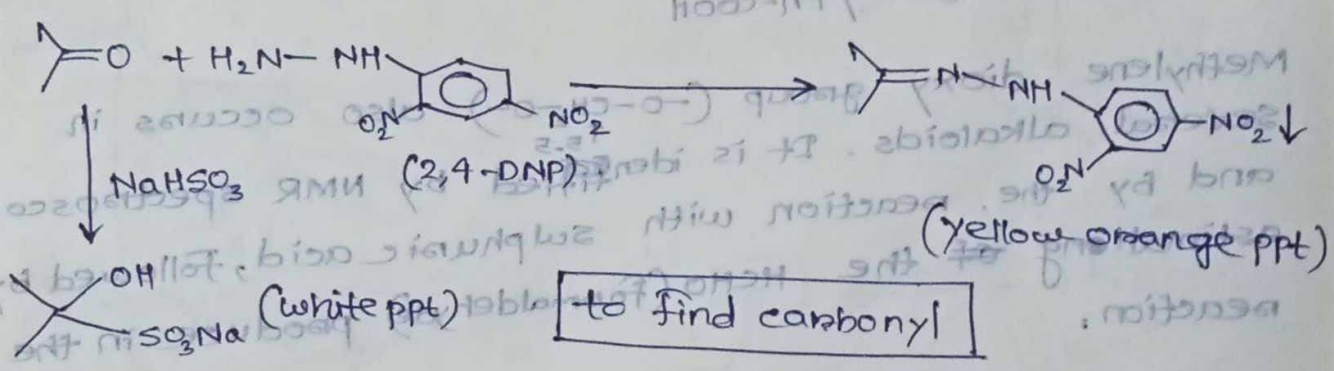
Invariably, the alkaloids contain carbon, H, N, and quite often 'O'. The nature of these last two elements is ascertained by a combination of several chemical and physical methods. Oxygen is usually present in the form of hydroxy (-OH), acetoxy (O-C(=O)CH₃), benzoxyloxy (O-C(=O)Ph), methoxy (OCH₃) groups.

Infrared spectroscopy ^{provide} a very ~~in~~ convenient technique ^{for characterising} of all these functional groups except the methoxy groups. A phenolic group is recognised by a colour with FeCl_3 , acylation to an ester and by alkali solubility whereas an alcoholic group is usually identified by acylation rxn, action of dehydrating agent, and by oxidation. Carboxy groups are verified by solubility in weak bases and by esterification.

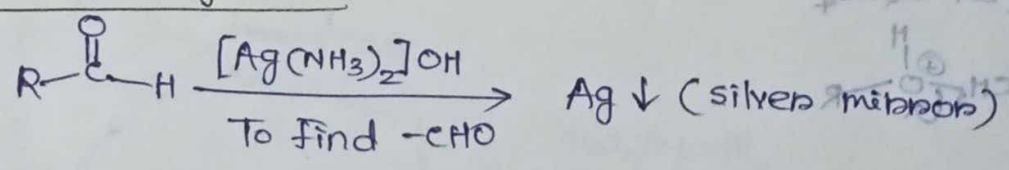
Determination of molecular structure :

9/5/23

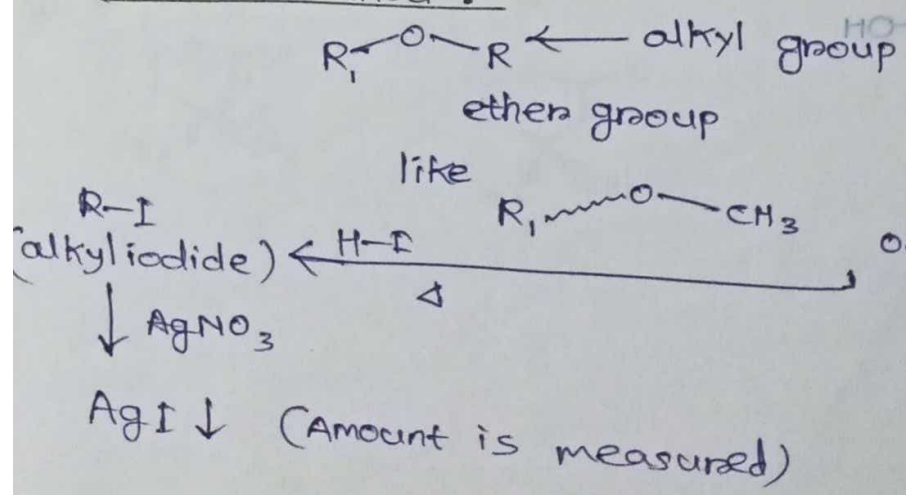
The presence of ketonic function is ascertained by reaction with standard carbonyl reagents (2,4-DNP test) $\rightarrow$ {yellow orange ppt} or, sodium hydrogen sulphide (NaHSO_3) $\rightarrow$ {white ppt}



Tollen's reagent :



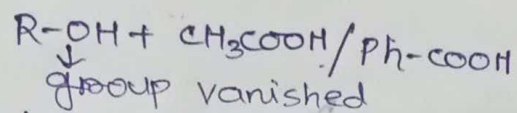
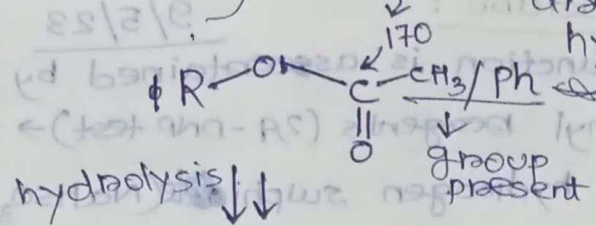
Zeise's method :



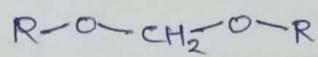
Zeise's method, which consist of boiling the ~~absor~~ substance with H-I, and estimating the quantity of methyl iodide or, alkyl by its conversion to silver iodide, provides a ~~quantity~~ quantitative method for the determination of methoxyl group or, alkoxy group, this group is found ~~in~~ in many alkaloids, and is easily identified by ¹H. NMR spectroscopy in which it appears as a sharp s-proton singlet for methyl group at about 3.7 ppm.

(3.5-3.7 ppm normally) ¹³C NMR

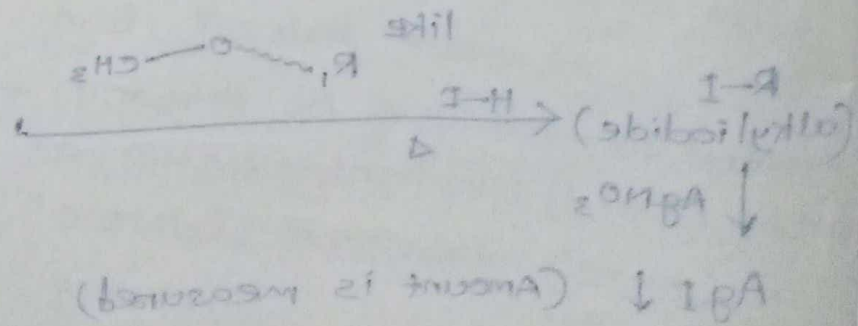
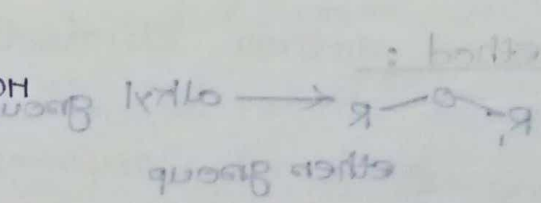
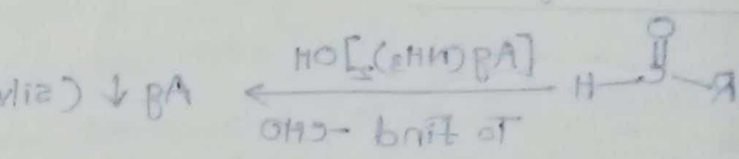
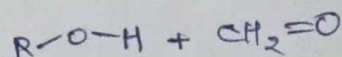
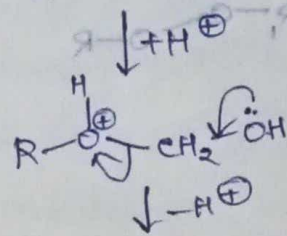
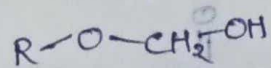
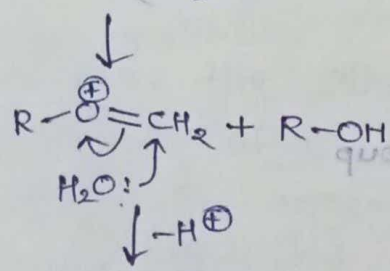
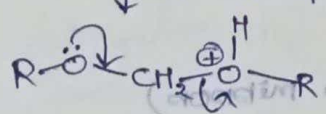
Acetoxy and benzoxy groups are usually identified by readily hydrolysis and by a combination of infrared (IR) and NMR spectroscopy.



Methylene dioxy group ($-\text{O}-\text{CH}_2-\text{O}-$) also occurs in several alkaloids. It is identified by NMR spectroscopy and by the reaction with sulphuric acid, followed by estimation of the HCHO (Formaldehyde) produce in the reaction.

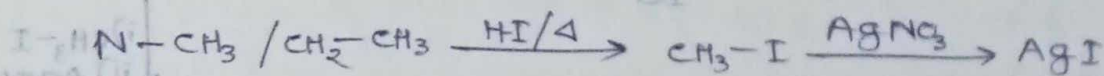


$\downarrow$ dil. H_2SO_4



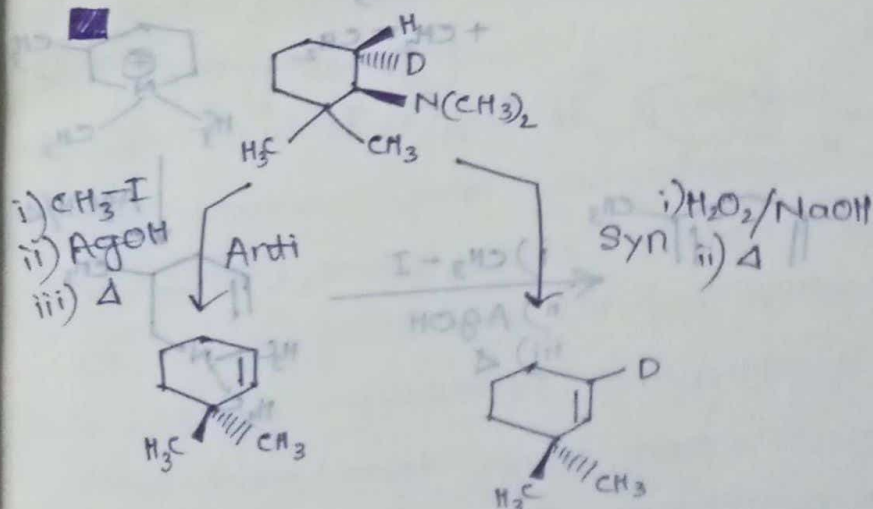
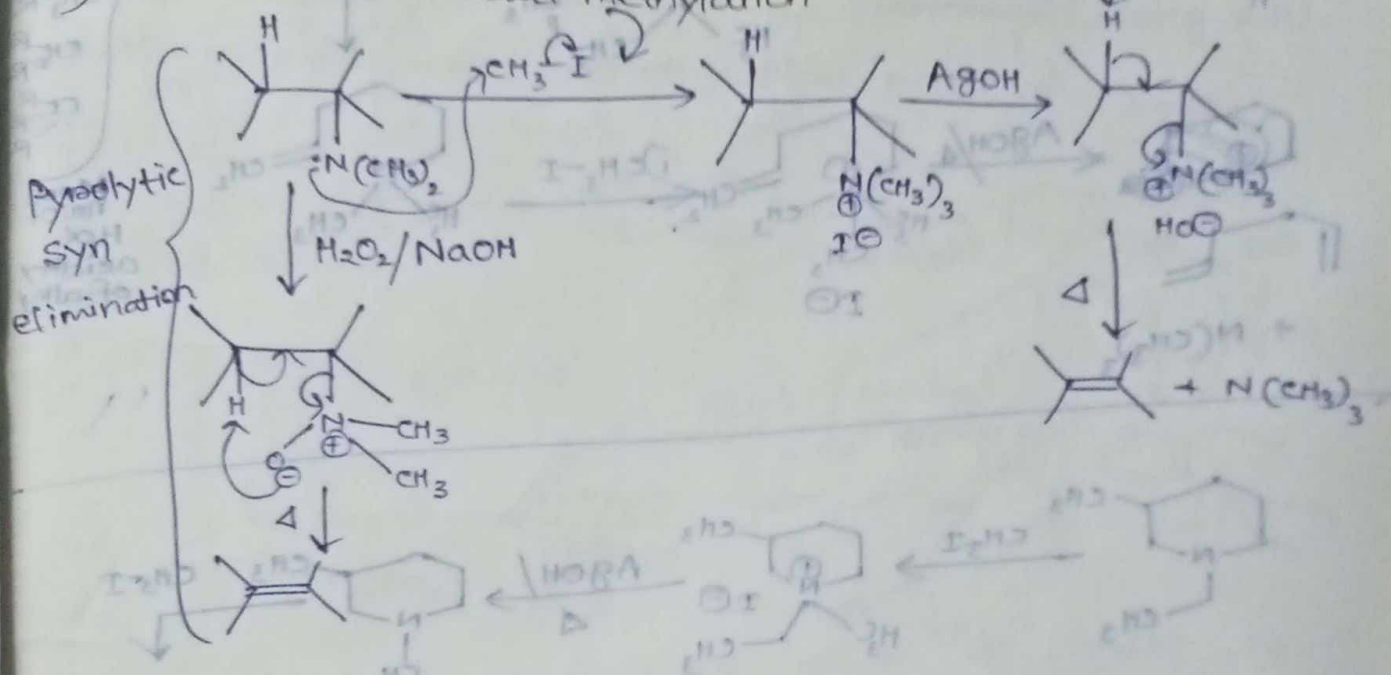
Alkyl groups, located on 'N' atom ($-N-CH_3/-CH_2-CH_3$) are identified by NMR spectroscopy and by Herzig-Mayer method.

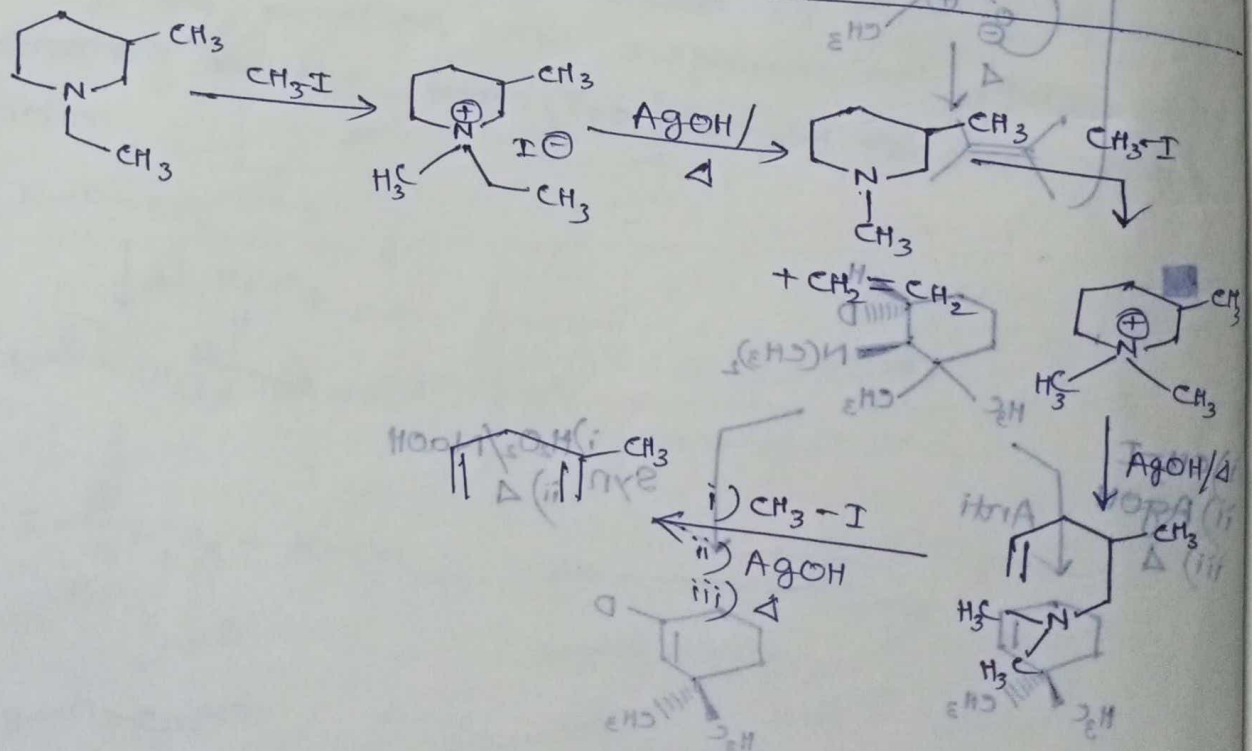
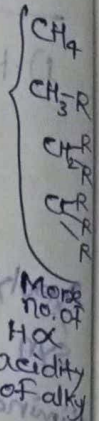
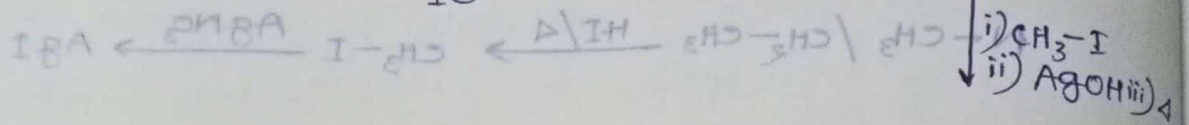
Herzig-Mayer method:



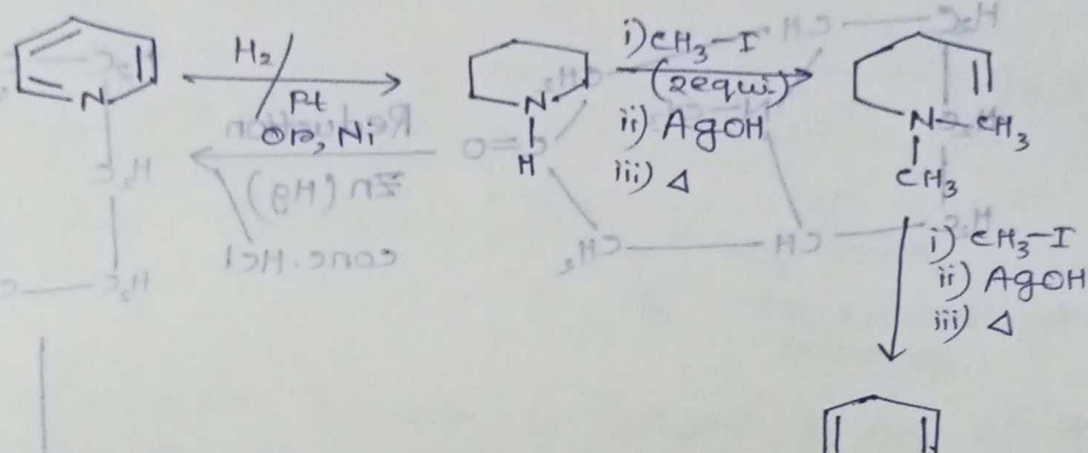
Most important methods for structure determination of alkaloids are Hofmann Degradation and Emde modification:

1) Hofmann exhausted methylation

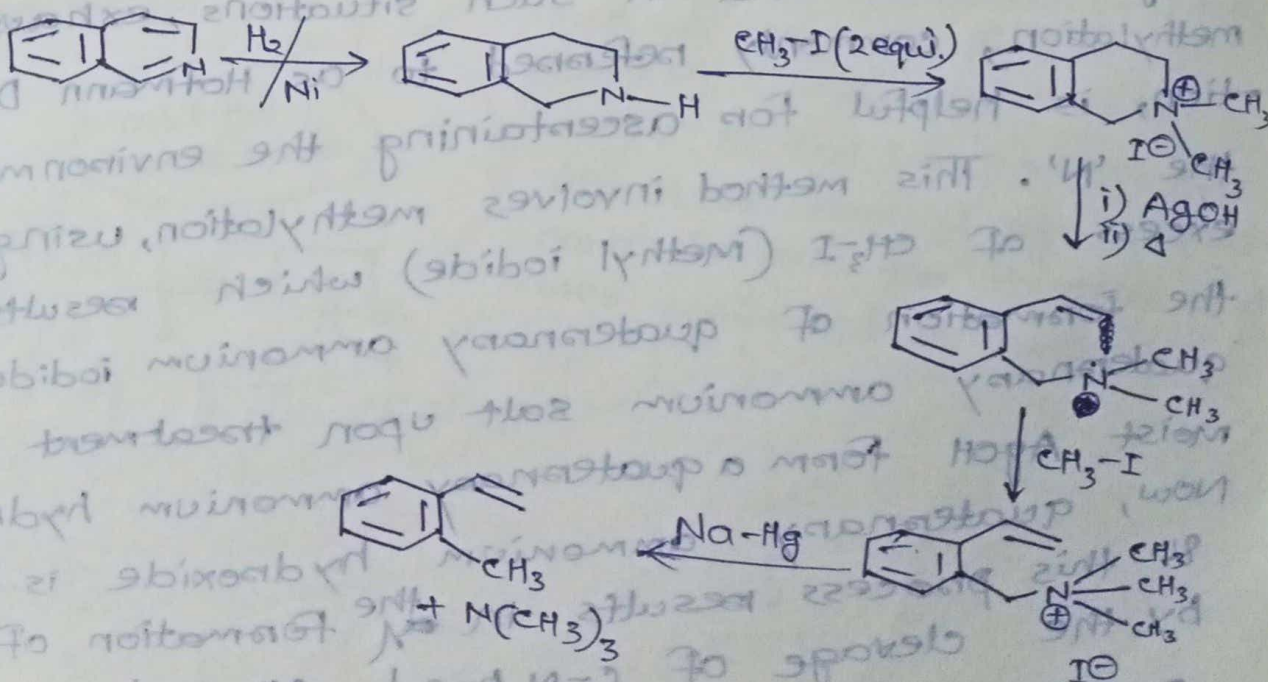
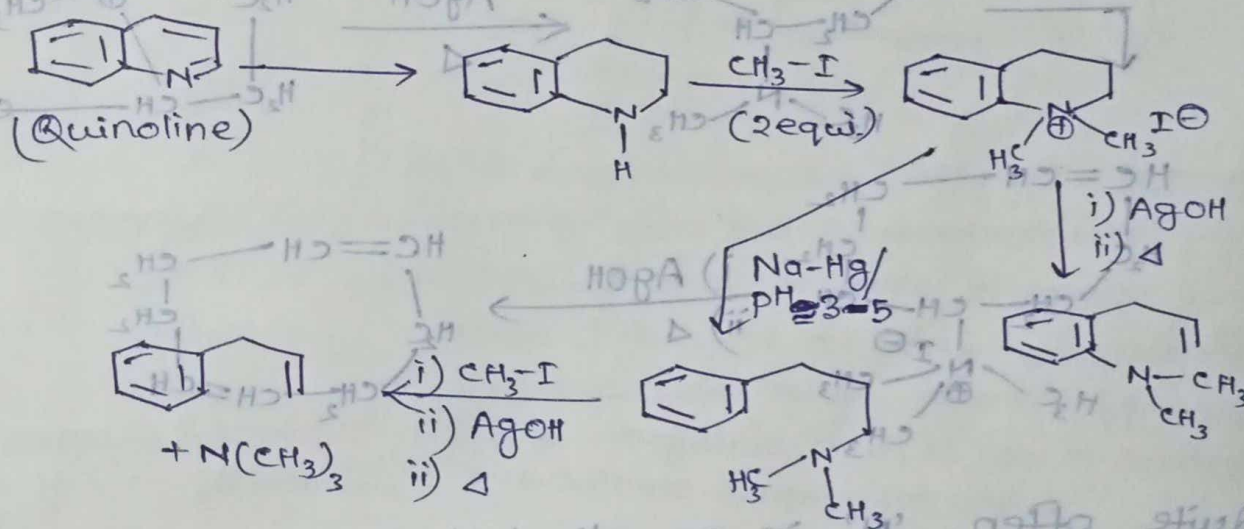




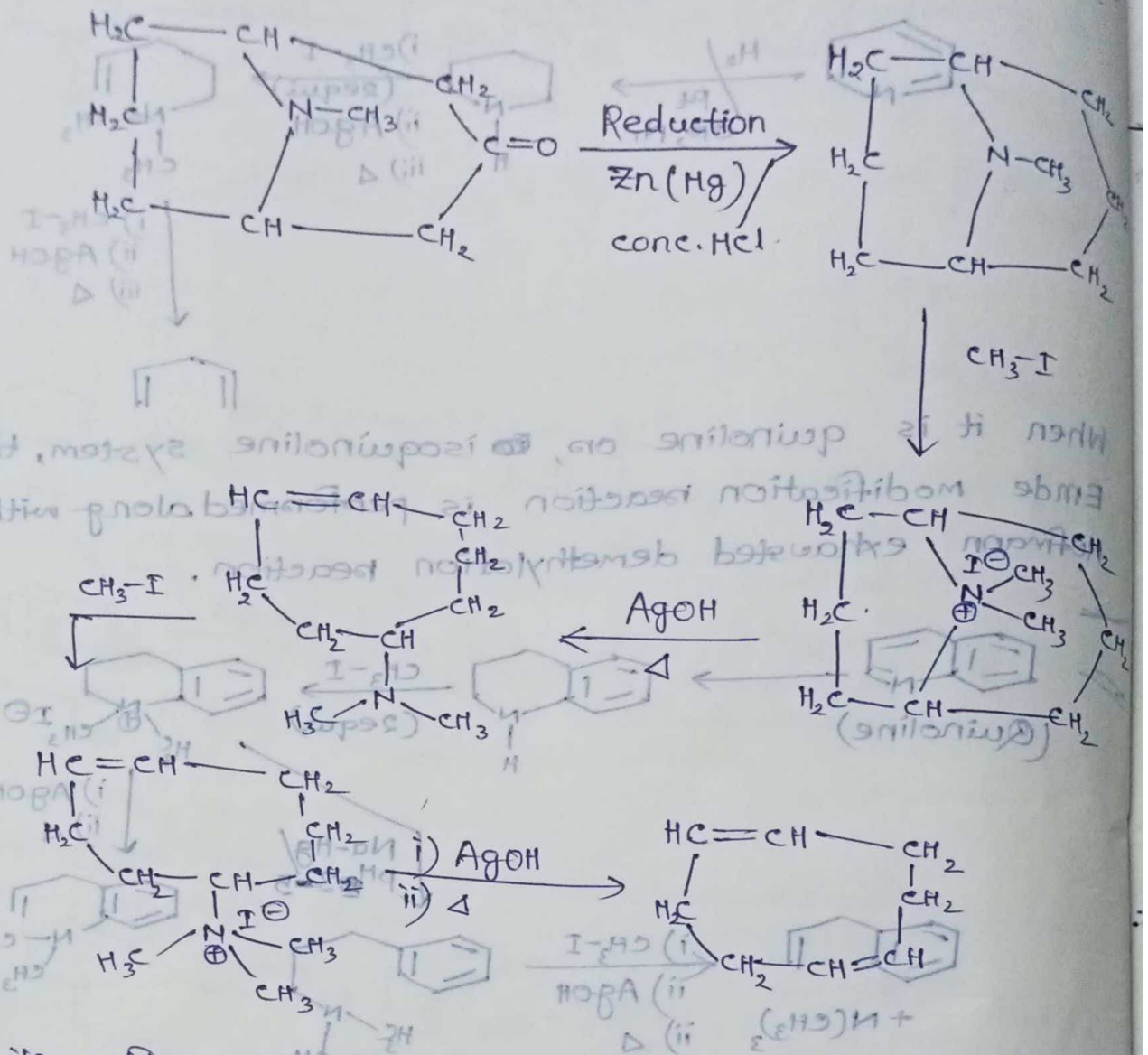
■ Hofmann exhausted methylation reaction of pyridine system :



When it is quinoline or isoquinoline system, then Emde modification reaction is performed along with Hofmann exhausted demethylation reaction.



Hofmann Degradation of pseudo pelletierine:



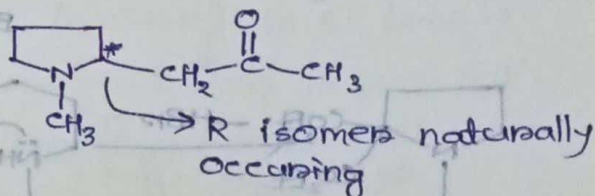
Quite often, 'N' in an alkaloid is involved in a ring structure and in such situations, exhaustive methylation, commonly referred to as Hofmann Degradation, is helpful for ascertaining the environment of the 'N'. This method involves methylation, using an excess of CH_3I (methyl iodide) which results in the formation of quaternary ammonium iodide. This quaternary ammonium salt upon treatment with moist AgOH form a quaternary ammonium hydroxide. Now, quaternary ammonium hydroxide is heated & this process results in the formation of alkene by the cleavage of C-N bond. Alkaloids containing pyridine or, quinoline or, isoquinoline nucleus are hydrogenated

before applying the decomposition. Sometimes, Emde modification is required before or, after Hofmann Degradation reaction.

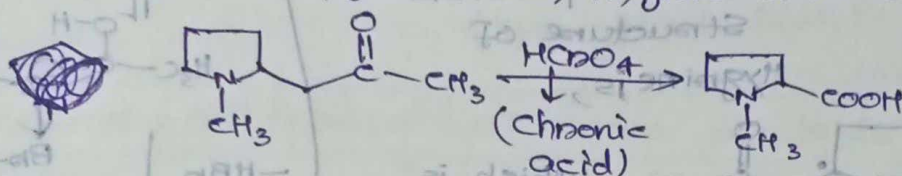
13/5/23

Synthesis of Hygrine :

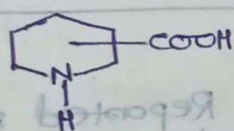
Structure of Hygrine $\rightarrow$



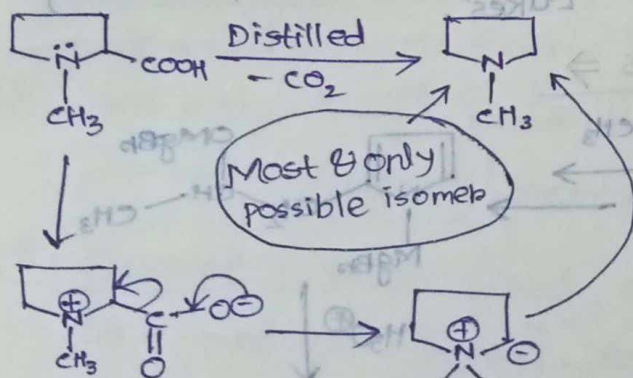
Hygrine molecule formula is $C_8H_{15}NO$, is one of the coca-alkaloids. Its reactions show the presence of keto group & tertiary 'N' atom, when oxidised with chromic acid, Hygrinic or, Hygric acid is formed.



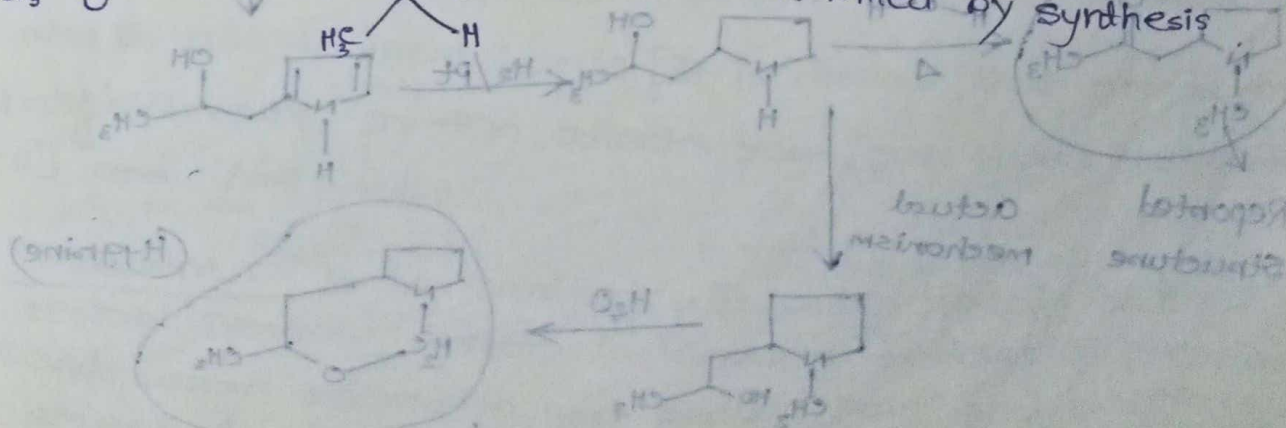
Hygric acid was first believed to be a π -pyridine π -pyridine carboxylic acid, but comparison with 3-pyridine acid, showed that it was incorrect.



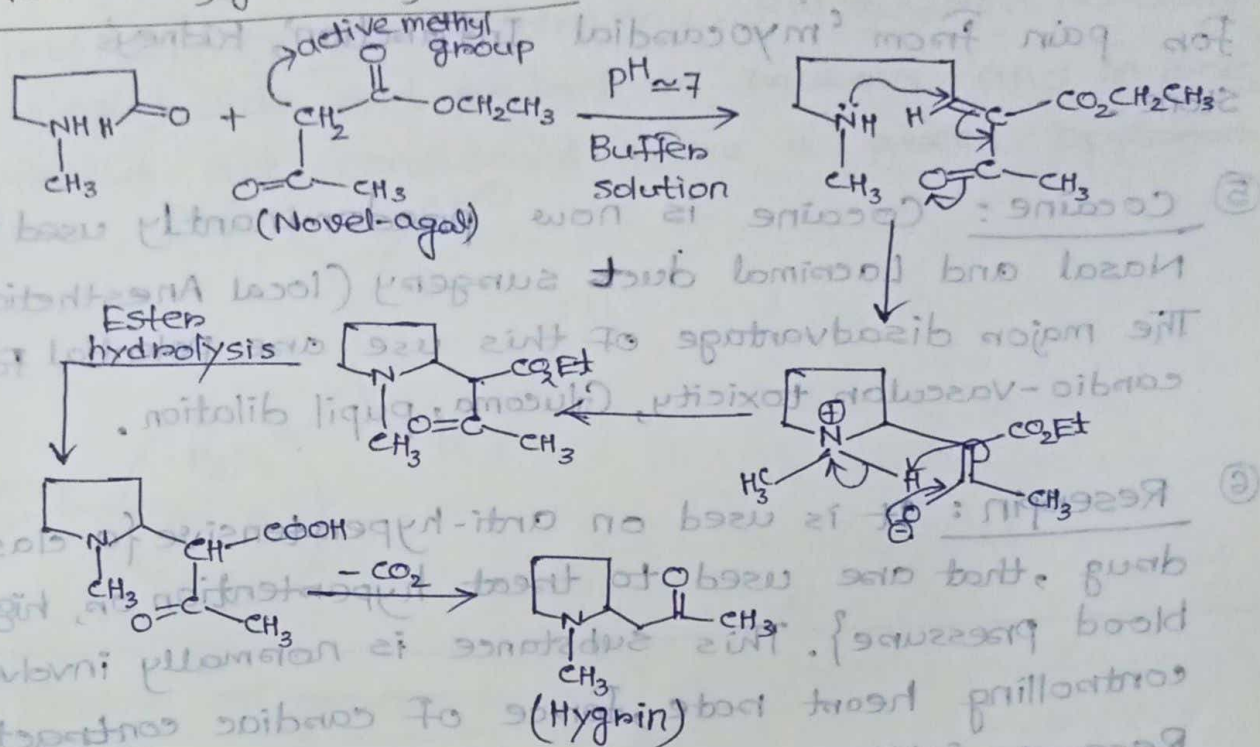
When subjected to dry distillation, Hygrinic acid gives N-methylpyrrolidine. Here Hygrinic acid is an N-methylpyrrolidine carboxylic acid.



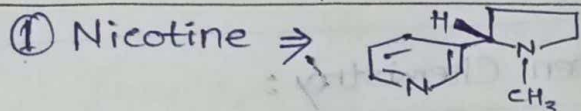
Further more decarboxylation occurs very rapidly, the carboxylic acid was assumed to be in the two position. This structure 1-methylpyrrolidine-2-carboxylic acid for Hygrinic acid was confirmed by synthesis



Actual hygrine synthesis:



Medicinal importance of some alkaloids:



Stimulant, Nicotine acetylcholine receptor, Against, Control levels of Nicotine are given to patients through gums, lozenges, inhalers, for Nasal sprays through wear them of their dependent.

② Hygrine: The drug is broadly as a sedative {Promoting calm or, inducing sleep}, hypotic-laxative {a sleep inducing drug}, laxative {tending to stimulate one}, diuretic {causing increased passing of urine}.

③ Quinine: It is used as anti-pyretic [used to prevent or, reduce fever]. Anti-malaria medicine, quinine is also use to treat Lupus [It is disease, that occurs when body's immune system attacks ~~your~~ its own tissues & organism-s] and Arthritis.

④ Morphine: ^{CU-22} It is analgesic. It acts directly on the central nervous system. To increase feelings of pleasure, and warm relaxation and reduce pain, and is often abused for this purpose. It can be taken for both acute

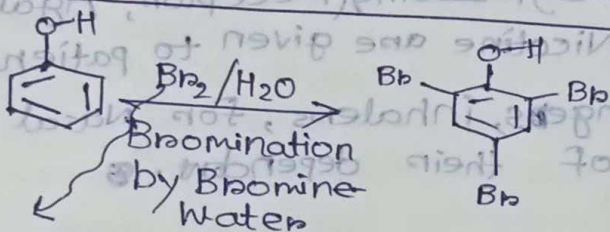
pain and chronic pain and is frequently used for pain from 'myocardial Infarction', kidneys stone.

⑤ Cocaine: Cocaine is now predominantly used for Nasal and Lacrimal duct surgery (local Anesthetic). The major disadvantage of this use are potential for cardio-vascular toxicity, Glucoma, pupil dilation.

⑥ Reserpin: It is used on anti-hypertensive {a class of drug, that are used to treat hypertension or, high blood pressure}. This substance is normally involved in controlling heart rate, force of cardiac contraction. Reserpin inhibits the form of biofillos.

Future trends in Green Chemistry:

Use of green oxidant & catalyst



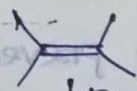
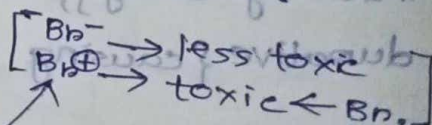
molecular bromine

↓
highly toxic

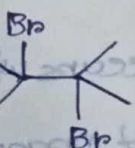
↓
high corrosion

activity → {should not used}

The molecular Bromine when reacts with any species, it is acting as electrophile.

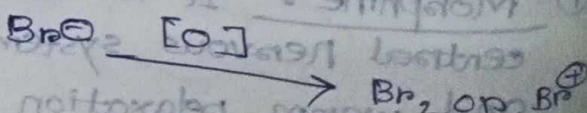


Defect in vocal cord

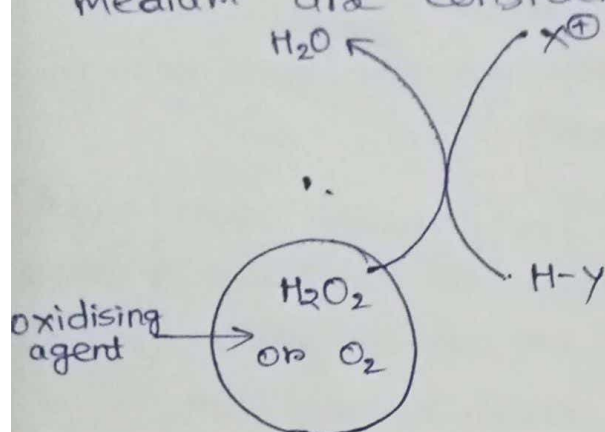


Br acts as electrophile (+ve)

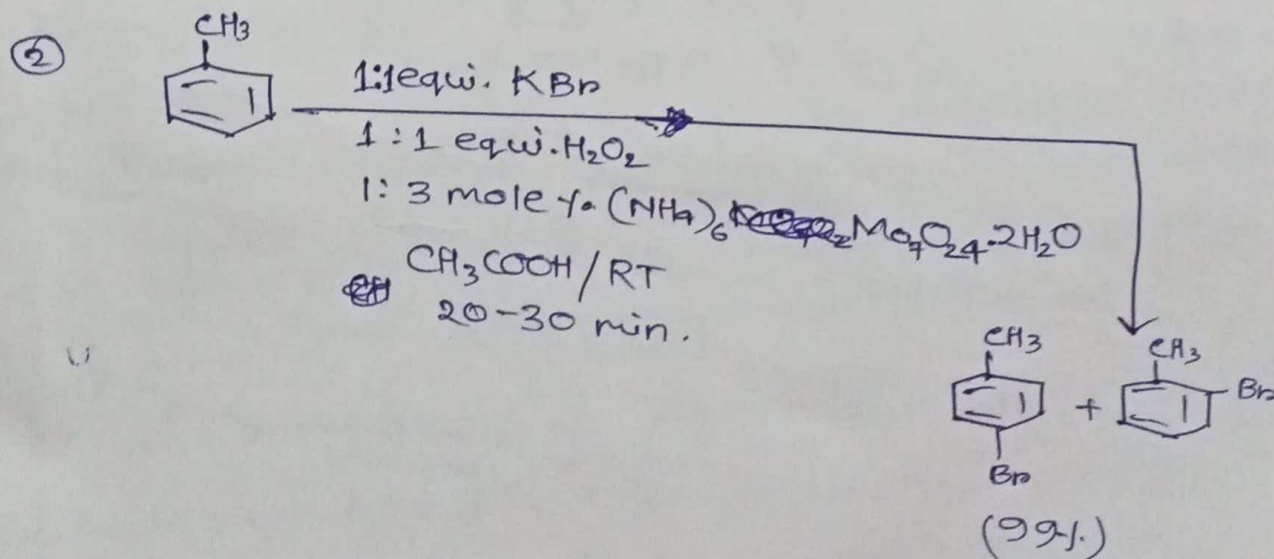
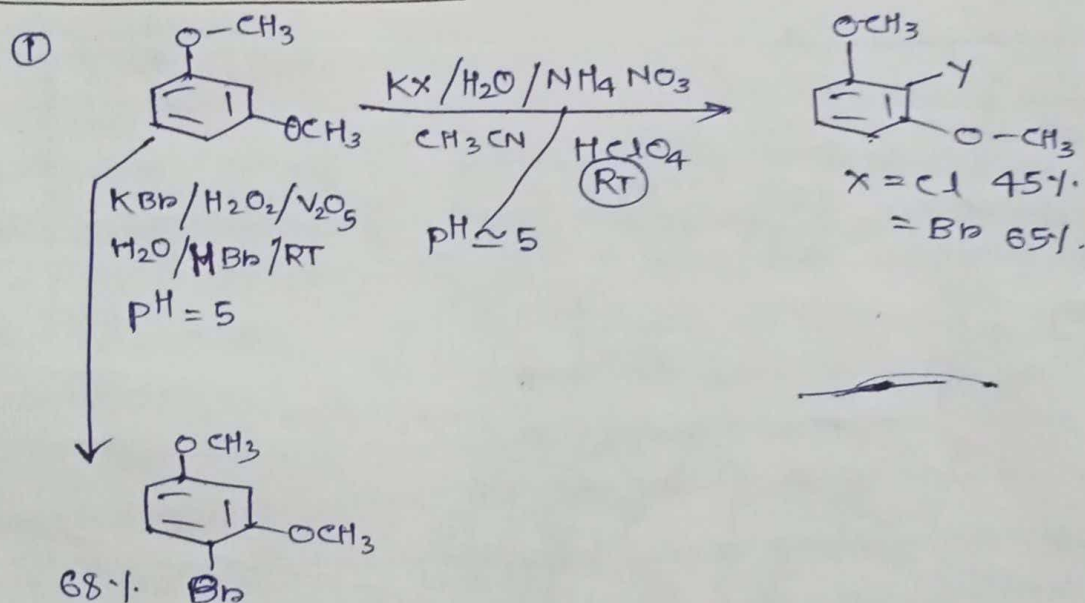
Here we cannot use BrO , but we can prepare it Br_2 from BrO .



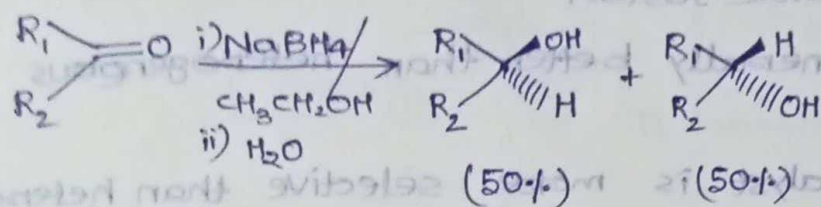
Halogenation is an important ~~reaction~~ reaction in the field of pyrogean chemistry. Halogenation reactions using halide and oxidant in aqueous and in ionic medium are considered to be a green approach.



Example of reaction :

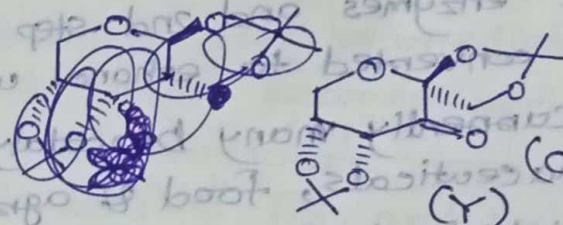
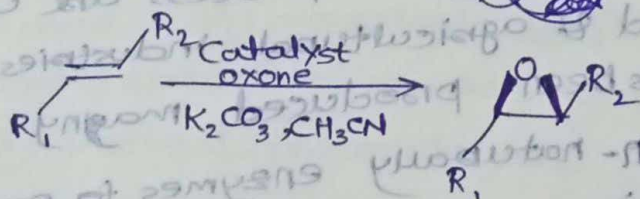
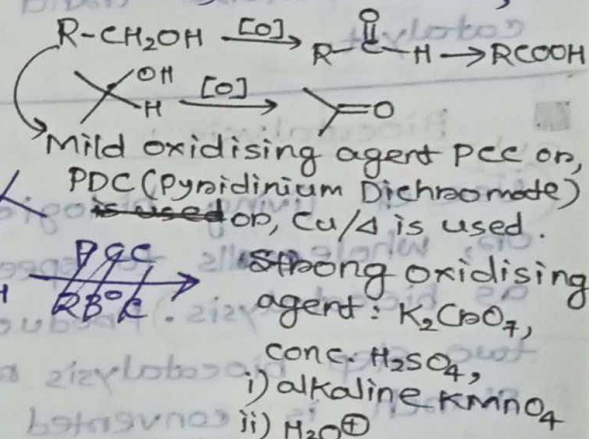
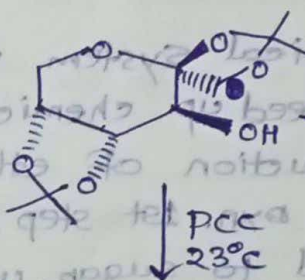
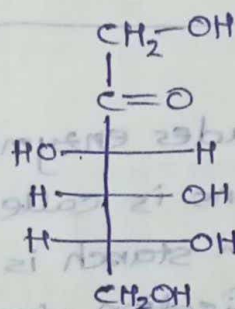


Future trend of asymmetric catalysis in green chemistry

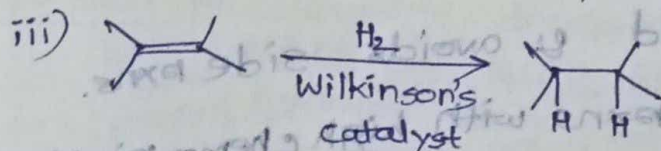
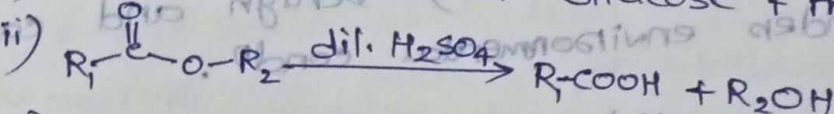
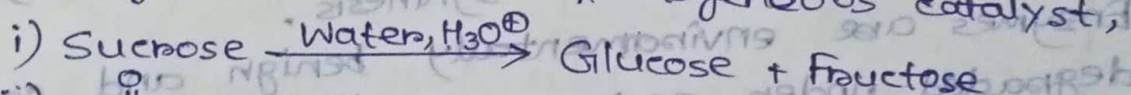


(Not specific and not selective reaction)

Asymmetric epoxidation of substituted alkene can be accomplished in the presence of an asymmetric catalyst (Y) by using oxone as oxidising agent at a pH 10.5. Oxone is a mixture of $KHSO_5 : KHSO_4 : K_2SO_4$ in the ratio 2:1:1. This organocatalyzed reaction is popularly known as, Shi-epoxidation.

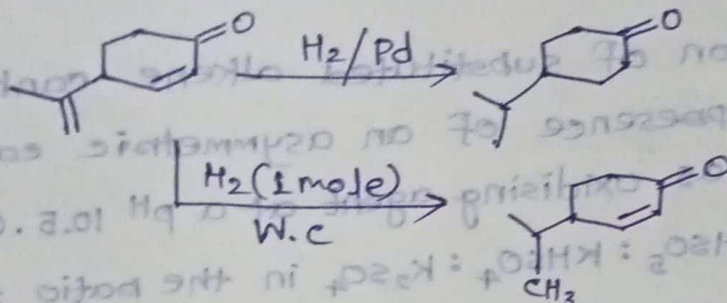


Use of Asymmetric Homogeneous catalyst: example of An/homogeneous catalyst,



Importance, of Homogeneous catalysts:

- 1) Reaction rates are faster.
- 2) % of yield is generally better than heterogeneous catalyst.
- 3) Homogeneous catalyst is more selective than heterogeneous catalyst.



So, the future trend is developed by homogeneous catalyst.

■ Biocatalysis:

Use of living biological system that includes enzymes or, whole cells to speed up chemical reactions is called as biocatalysis. Production of ethanol from starch is a two step biocatalysis rxn. 1st step is saccharification where, starch is converted to sugar, using glucoamylase and α -amylase enzymes and 2nd step is fermentation, where sugar is converted to ethanol using, *Saccharomyces cerevisiae*. Currently many biocatalytic process are used in pharmaceuticals, food & agricultural industries. Modern biotechnology has been produced many modified enzymes & non-naturally enzymes to enable many organic transformation. There are very many advantages of chemoenzymatic synthesis.

- a) Enzymes are environmentally benign and can be degraded under environmental condn.
- b) Rxn condns are mild & avoids side rxns.
- c) Enzymes undergo rxns with high chemo, rigid and stereoselective.

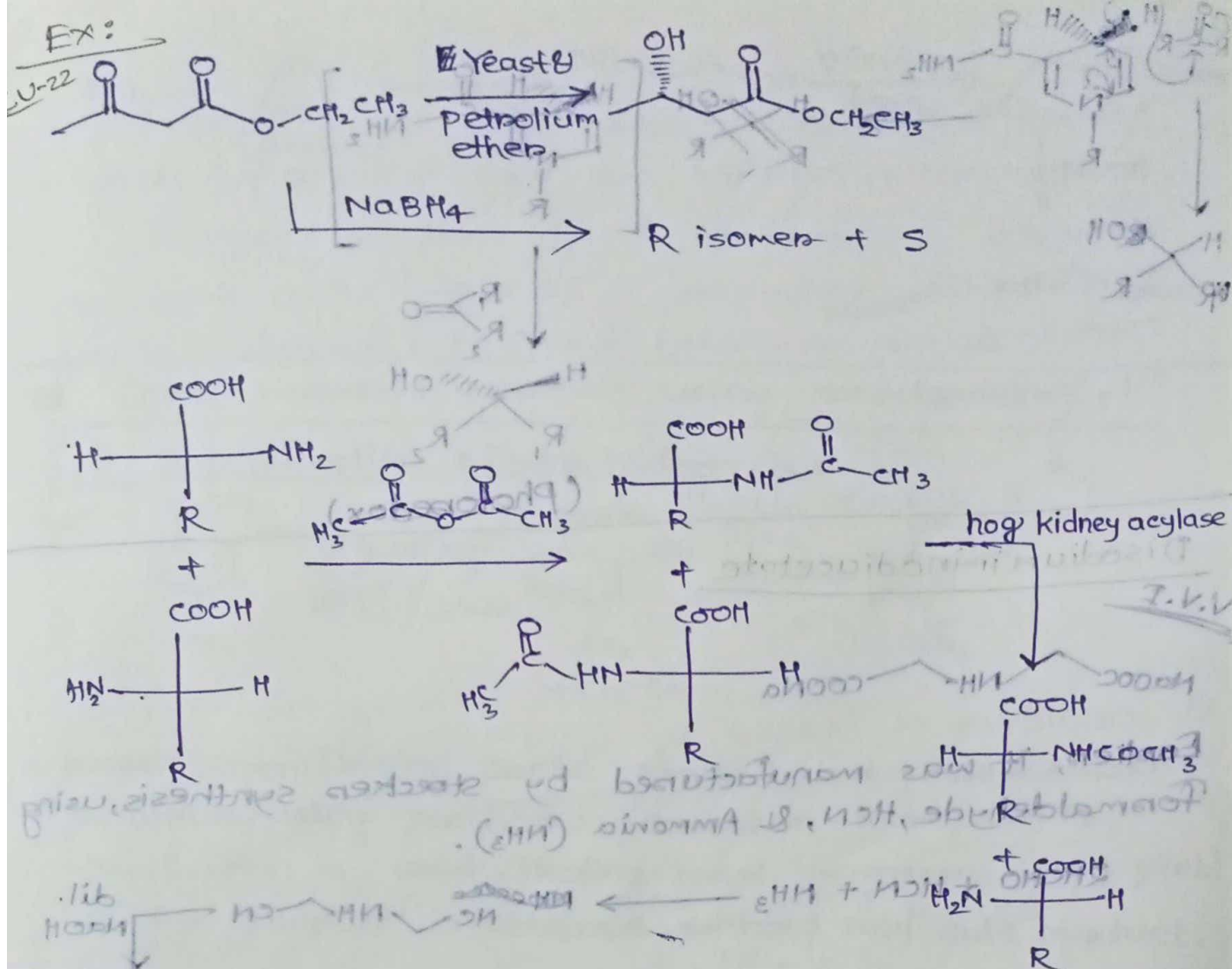
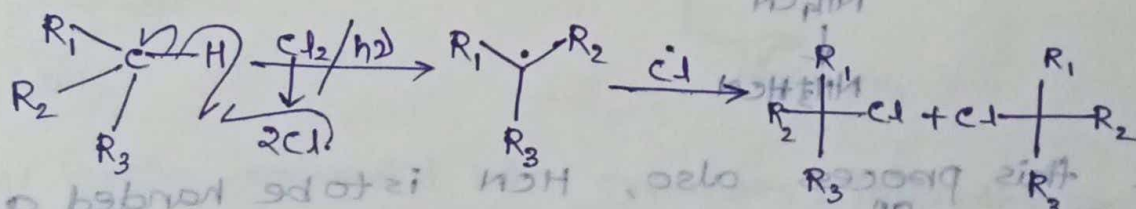


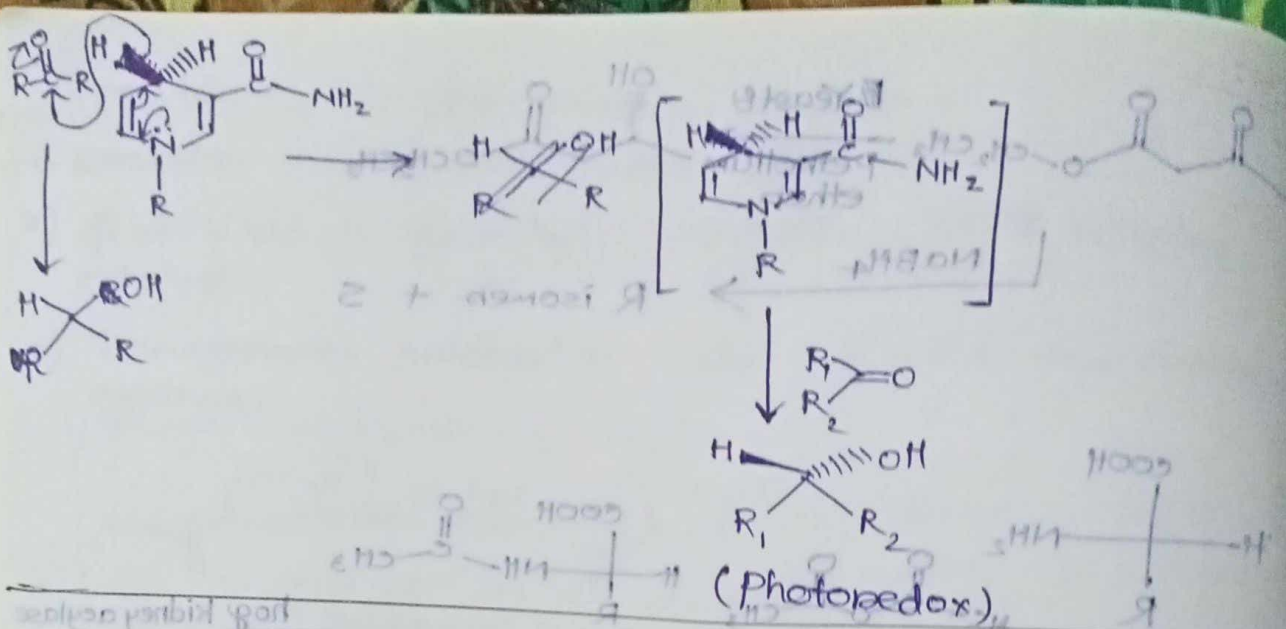
Photo redox enable biocatalysis :

Light induced rxns are generally passed through radical mechanism. As the radical intermediates are achiral, the products formed becomes racemic. In the presence of enzyme, the enantiotopic phases of radical become diastereotopic in the T.S. and leads to enantioselective synthesis. Coenzyme & Co-factors acts as internal photocatalysis.



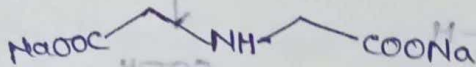
Example: Nicotinamide dependent ketoreductase

i) NADH or, NADPH is commonly considered as hydride donor & weak single electron donor but in presence of light, it becomes a potent single electron reductant which is reflected in their redox potential.

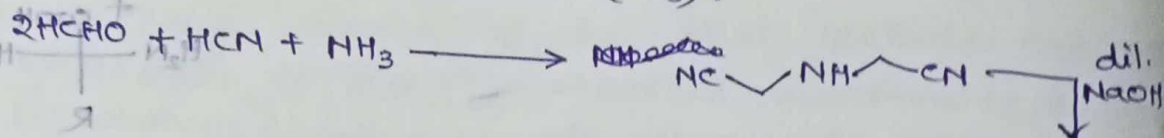


Disodium iminodiacetate

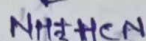
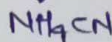
V.V.F



Earlier, it was manufactured by strecker synthesis, using formaldehyde, HCN, & Ammonia (NH₃).

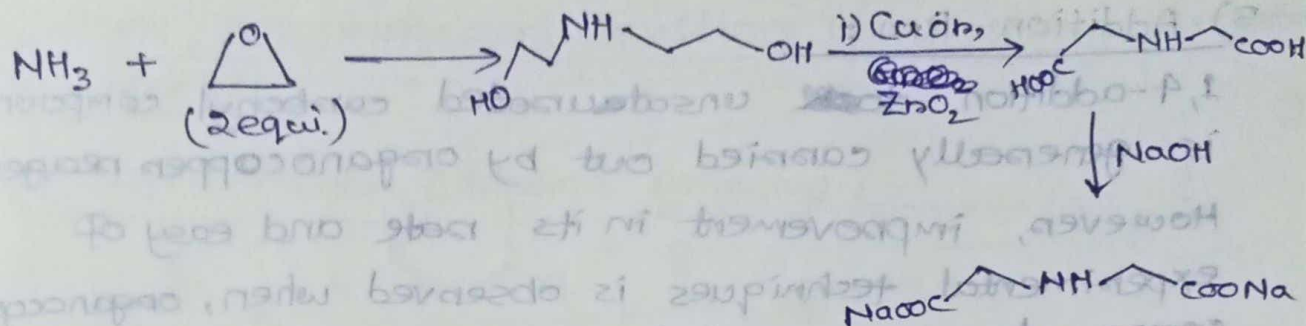


Relatively convenient method is to use NH₄Cl & NaCN with formaldehyde. In single step, to get iminodiacetonitrile which on subsequent hydrolysis produces IDA. The mixture of NH₄Cl and NaCN produces NH₃ & HCN, via the formation of NH₄CN, via the formation.



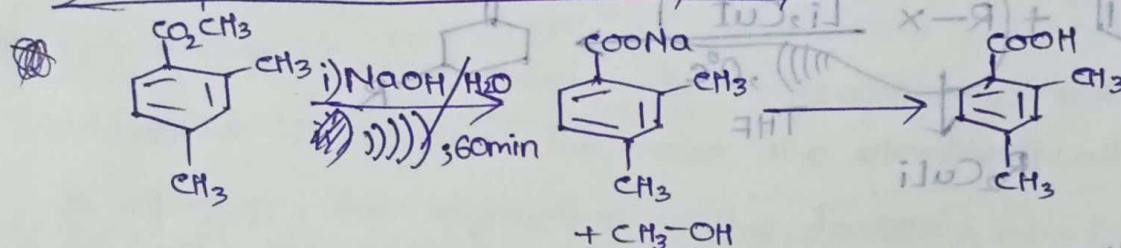
In this process also, HCN is to be handled as a reactant or an intermediate to overcome this hazard an alternative green synthesis of IDA is required. Diethanolamine was oxidized using Cu or ZnO₂ catalyst to iminodiacetic acid which on treatment with alkali produces disodium salt of IDA. This process

Advantage: low production cost, simple operation process, little pollution, high yield with high purity of the product.



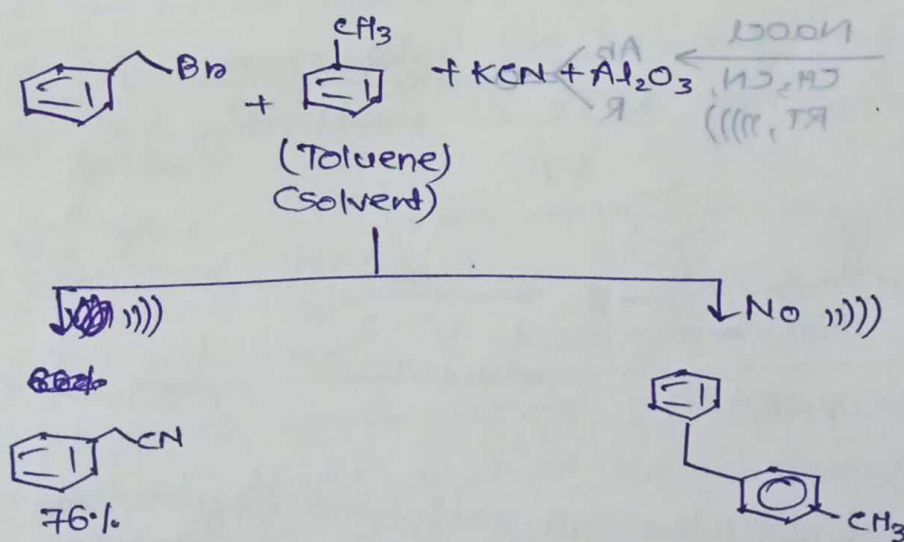
Some important reaction using sonochemistry:

1) Saponification : Ester hydrolysis:



~~Saponification~~ Saponification can be carried out under milder condition, using sonification / sonication. Here, 20 kHz sonification is used. Heating is not necessary. 94% yield of the product is obtained without any side product.

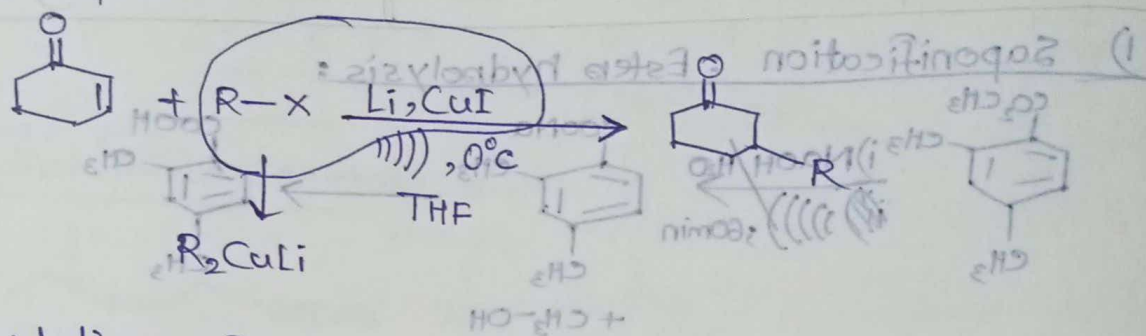
2) Substitution reaction:



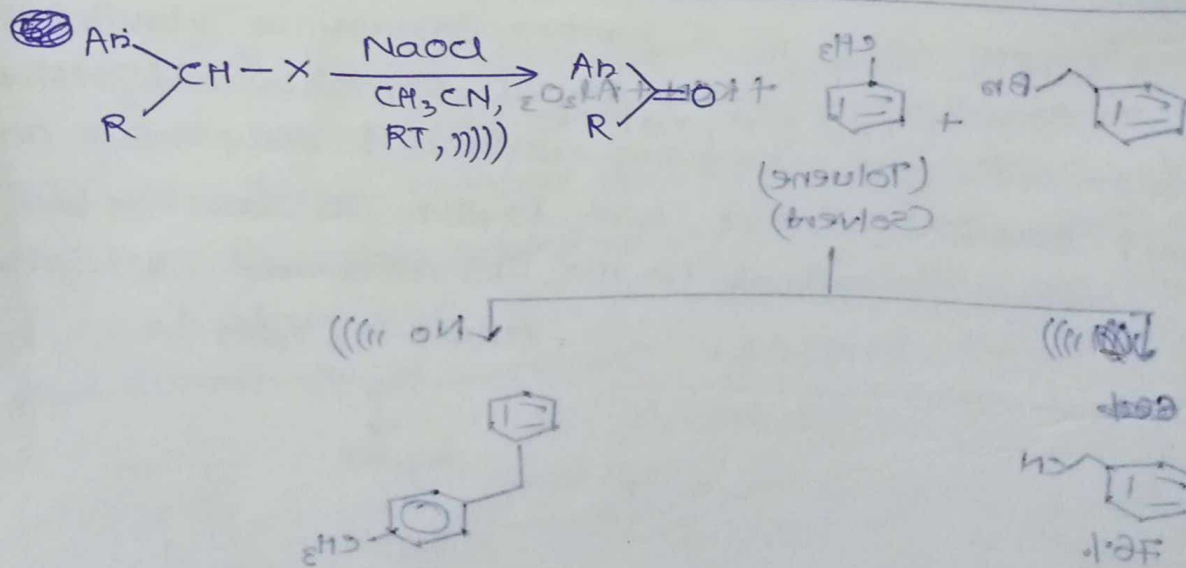
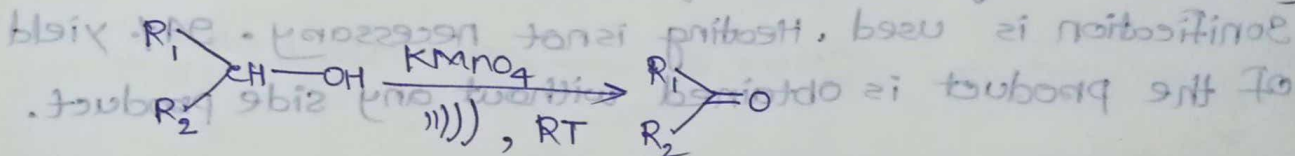
Halides can be converted into cyanides. Thus, the rxn of benzyl bromide in toluene with KCN, catalysed by Al_2O_3 on sonication gives benzyl cyanide in 76% yield. The absence of ultrasound, alkylation is the preferred pathway. The difference is because ultrasound forces cyanide to the surface of Al_2O_3 , enhancing cyanide nucleophilicity & reducing the Lewis acid character.

3) Addition Rxn:

1,4-addition to unsaturated carbonyl compound is generally carried out by organocopper reagents. However, improvement in its rate and ease of experimental techniques is observed when, organocopper compounds are generated insitu by sonication of copper-1-compound.



4) Oxidation of alcohol by solid potassium permanganate in hexane or benzene is enhanced considerably by sonication.

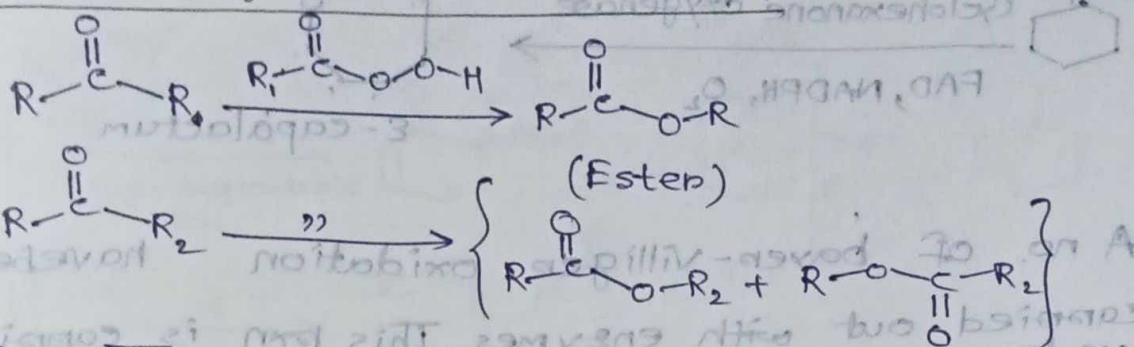


Halides can be converted into oxides. Thus, the reaction of benzyl chloride in toluene, catalyzed by Al_2O_3 , gives benzyl chloride in 40% yield. The absence of oxides, alkylates in the presence of Al_2O_3 is because of the formation of a complex between the oxide and the alkyl halide.

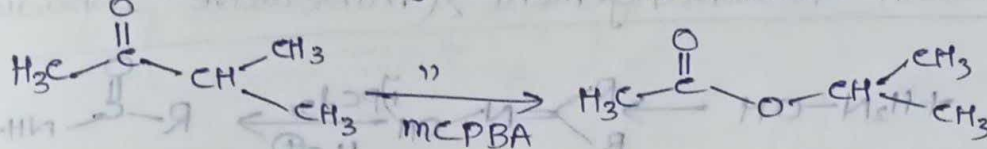
Some rearrangement reactions using green chemistry

Principle :

1) Bayer-Villiger Oxidation Reaction :

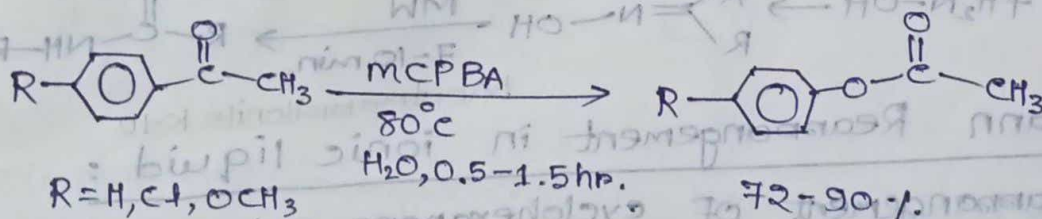
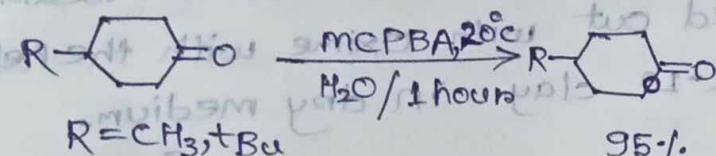


N.B: The alkyl group is migrating to electronically deficient 'O' centre. The more the electronically rich of R group, the migration will be faster.

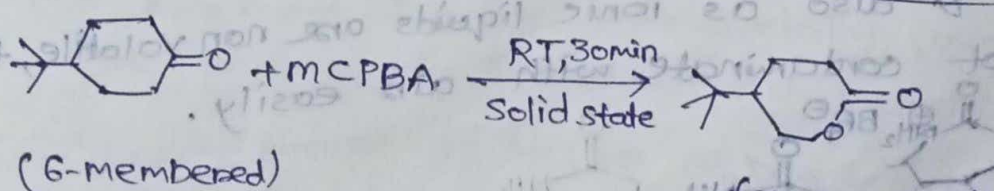


Green part of Bayer-Villiger oxidation reaction:

① Bayer-Villiger oxidation can be carried out in aqueous phase.

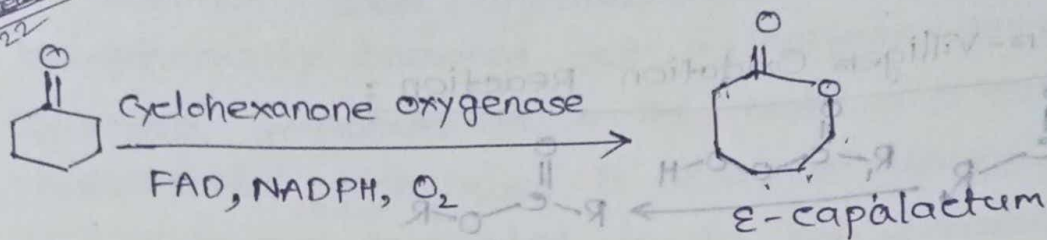


② Bayer villiger oxidation in solid state :



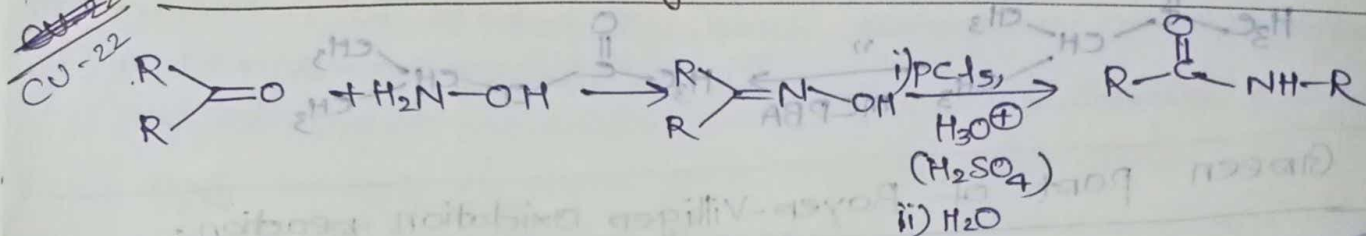
A mixture of powder ketone & 2 more equivalent of MCPBA is kept at room temperature to give the p.dts. The main importance of the reaction is that it is solvent-free.

③ Enzymatic Bayer Villiger oxidation:

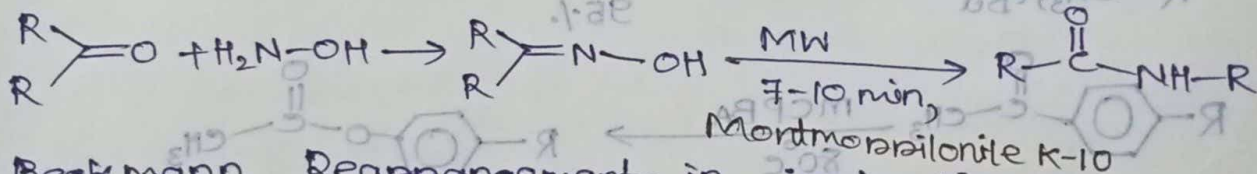


A no. of bayer-villiger oxidation have been carried out with enzymes. This rxn is carried out under ambient condition and with biological environment.

④ Beckmann Rearrangement under Microwave Irradiation:

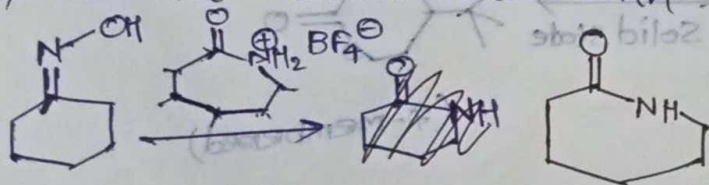


A solid state microwave assisted beckmann rearrangement has been carried out with oxime with the help of Montmorillonite K-10 clay in dry medium.



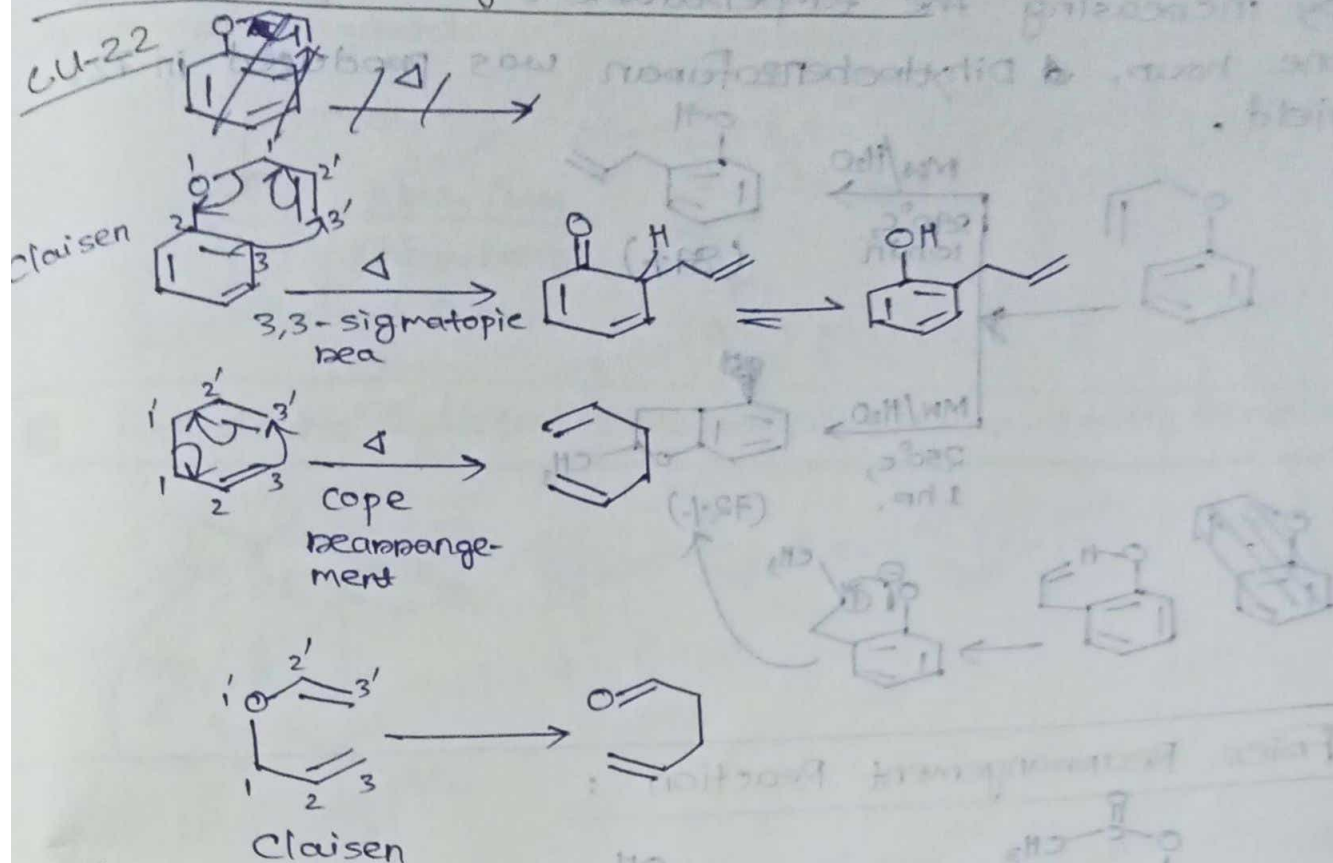
● Beckmann Rearrangement in ionic liquid:

This rearrangement of cyclohexanone oxime to caprolactam can be carried out in ionic liquid. The ionic liq. to be used here, serve the dual role of catalyst & reaction medium & also as ionic liquids are non volatile, they are not contaminate with air easily.



(Caprolactum)

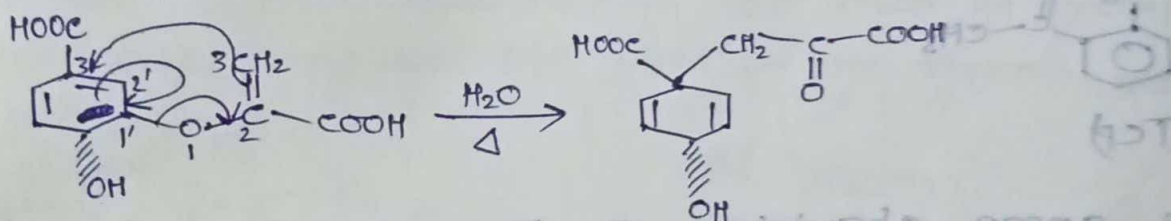
Claisen Rearrangement Reaction :



Claisen Rearrangement in green solvent :

1) In Aqueous media

CU-22 The use of water in promoting claisen rearrangement was first recorded in 1970.

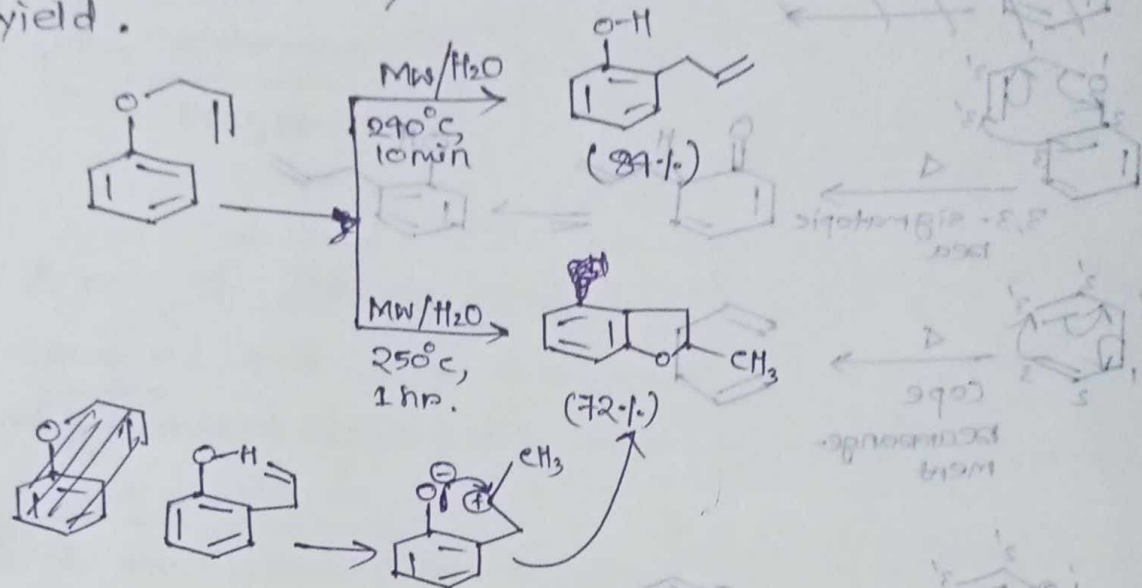


Claisen rearrangement in near critical water :

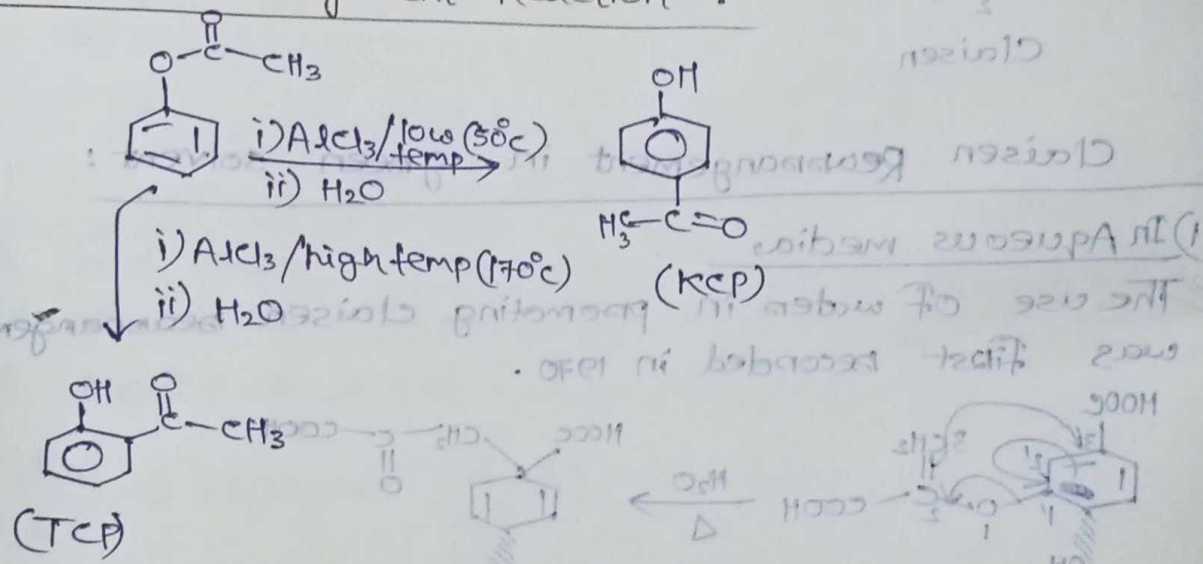
Reactions, conducted in microwave oven in water, above 200°C, exist due to the pressure limit about 20 bar for most of the commercially available microwave instrument. Pure water reaches an autogenic pressure of 50 bar at 250°C. This condition is called near-critical water region between 20°C & 300°C.

The Claisen rearrangement of allyl phenyl ether was successfully performed at 240°C. However, at 200°C

only 10% conversion was achieved. It was found that by increasing the temperature & time to 250°C at one hour, Dihydrobenzofuran was produced in 72% yield.



Fries Rearrangement Reaction :



The green chemistry of Fries-Rearrangement Reaction

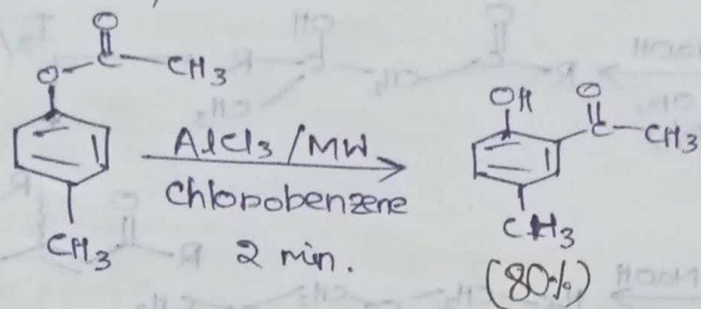
1) Photo-Fries Rearrangement :

Photolysis of enolic ester gives a mixture of ortho & para acetyl phenol. Unlike the normal Fries Rearrangement, photo-Fries Rearrangement does not need a catalyst and predominantly and ~~internal~~ intramolecular free radical process.

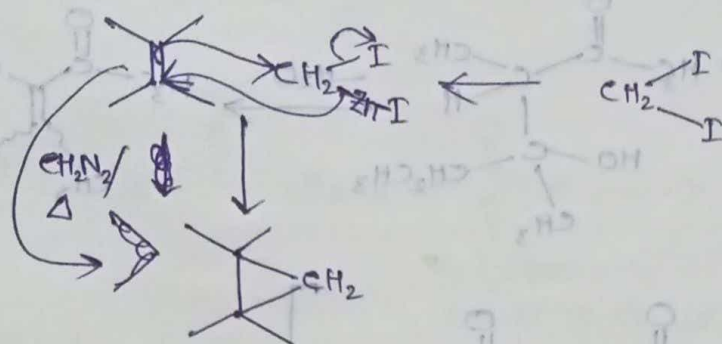
2) Fries Rearrangement under Microwave Irradiation

There is considerable rate enhancement of Fries rearrangement by commercial microwave ovens over conventional method. Thus a mixture of p-cresyl

acetate & anhydrous AlCl_3 are heated in chlorobenzene in a seal tube in a microwave oven for 2 min. to give 80% yield.

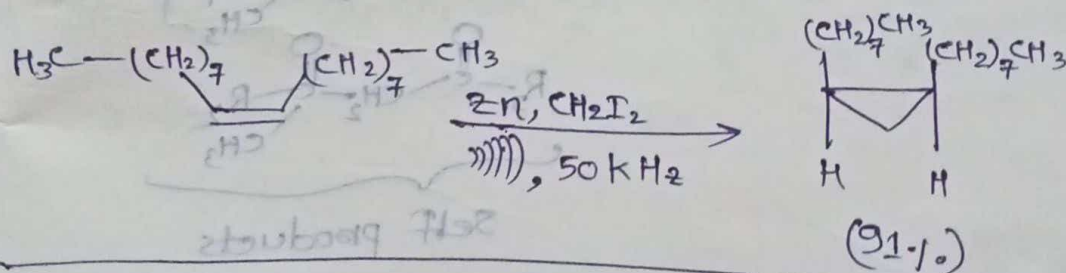


■ Ultrasound assisted ~~Simon-Smi~~ Simon-Smith Reaction:



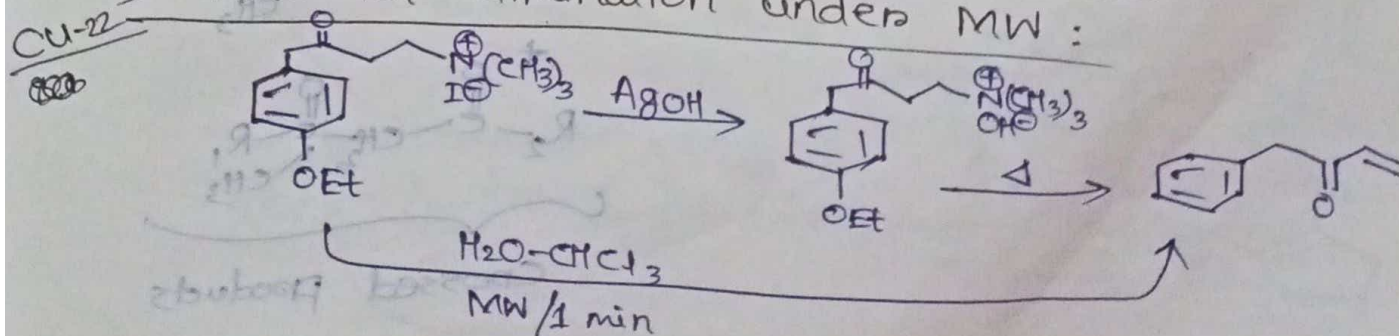
● ~~Simon~~ Simon-Smith under ~~some~~ MW:

In the procedure, sonochemically activated Zn & methylene iodide are used. The generated carbene adds to the ~~olefinic~~ ^{Olefinic} bond to give 91% yield of cyclopropane derivative, compared 51% yield by the normal ~~best~~ ^{route}.

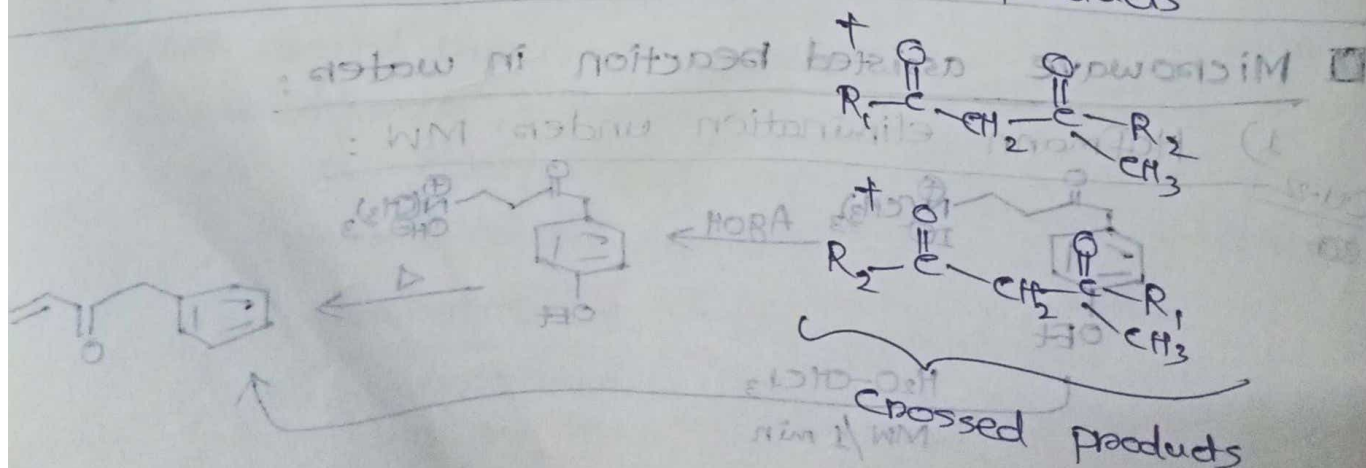
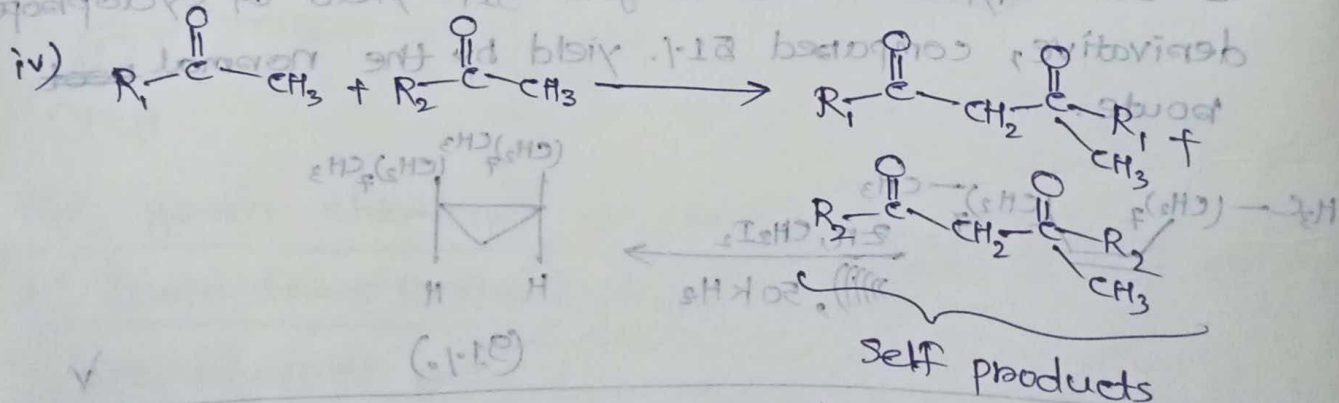
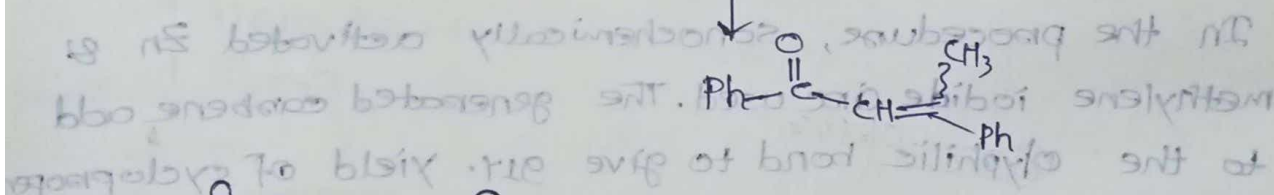
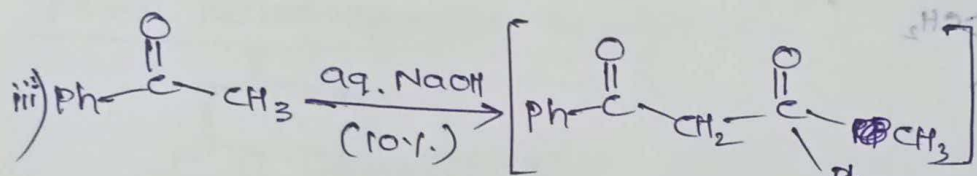
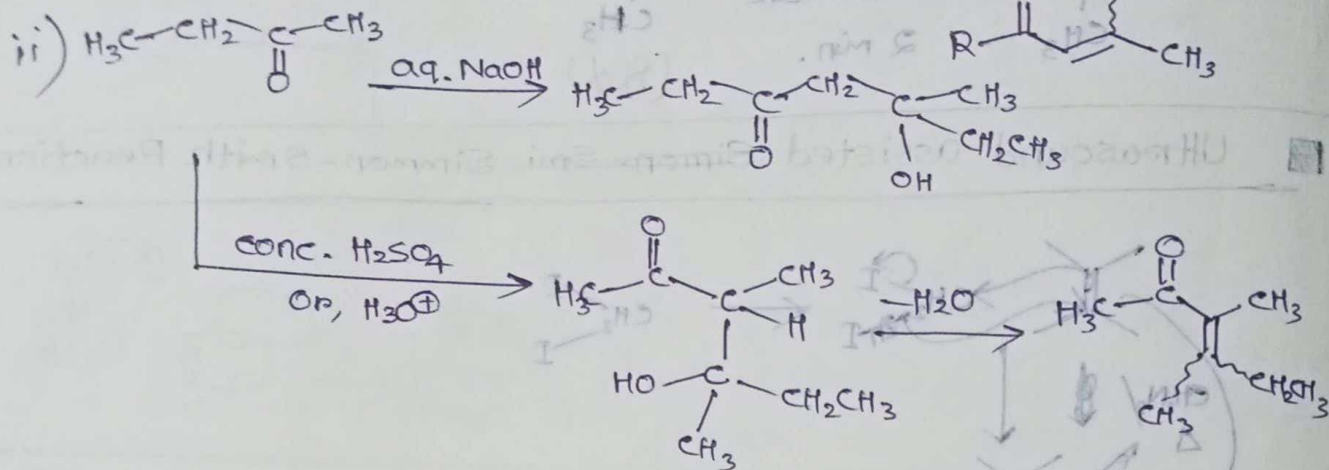
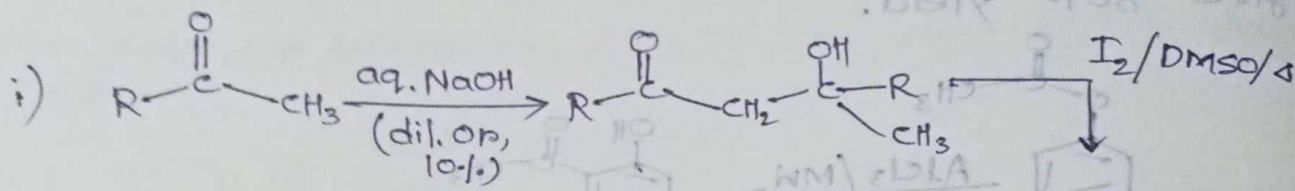


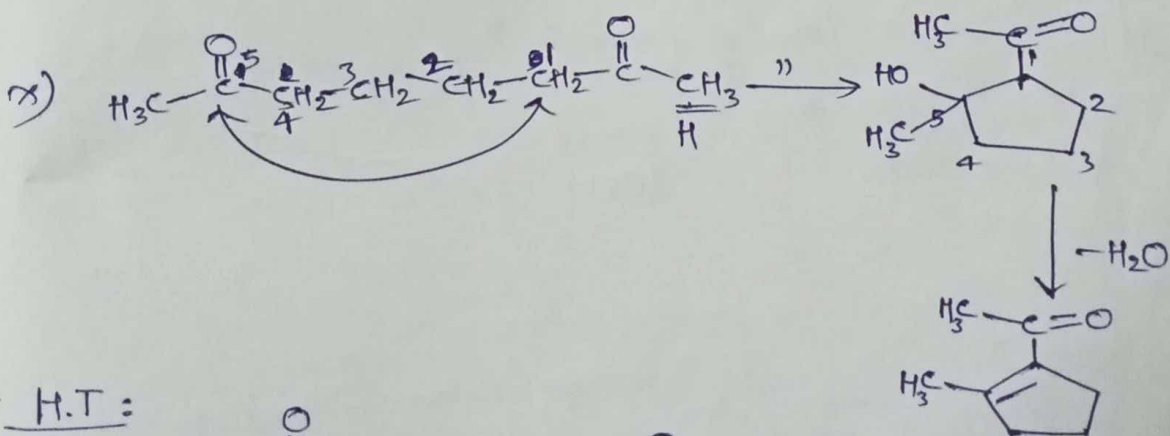
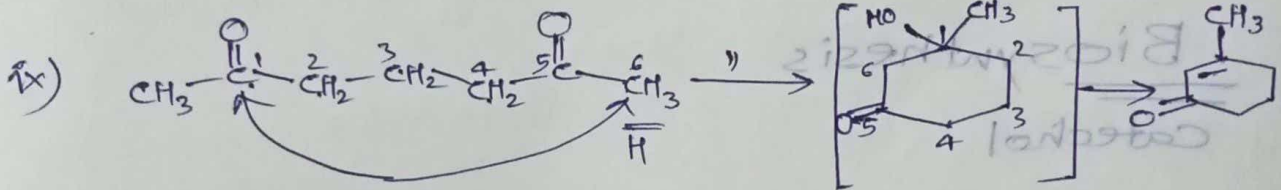
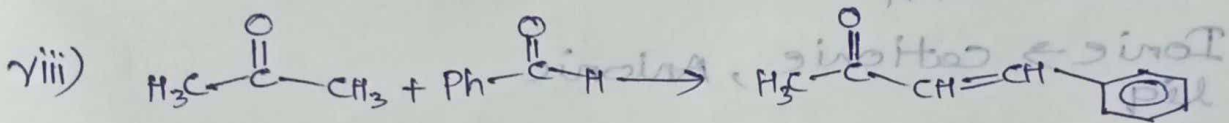
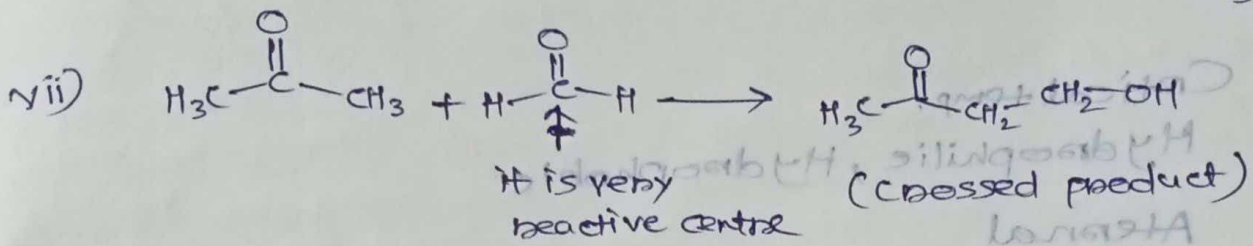
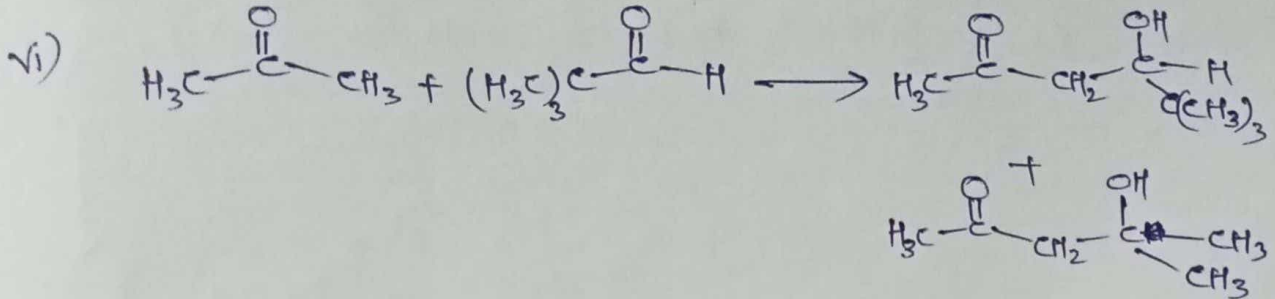
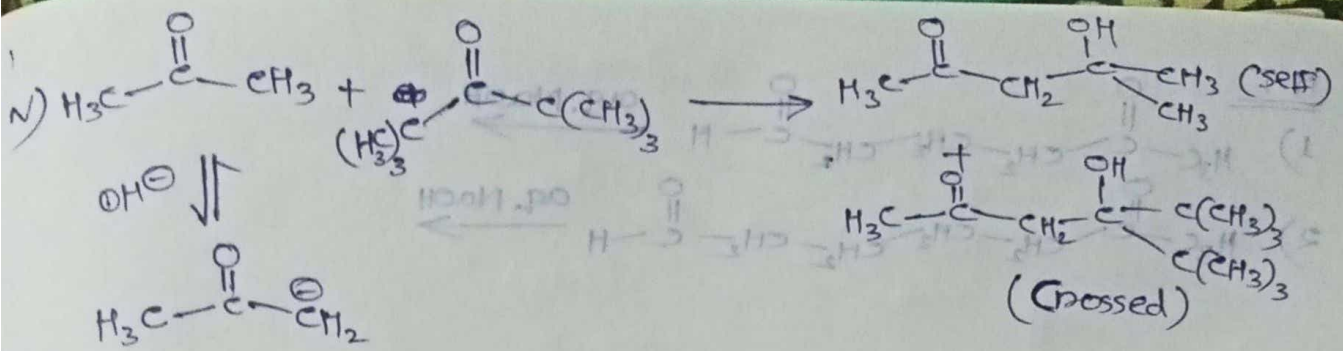
■ Microwave assisted reaction in water:

1) Hofmann elimination under MW:

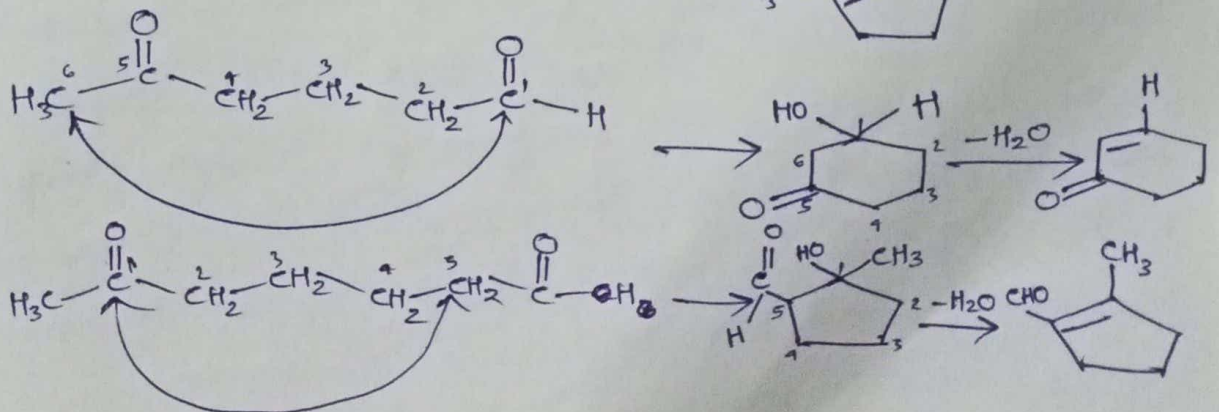


2) Aldol-Condensation Reaction :

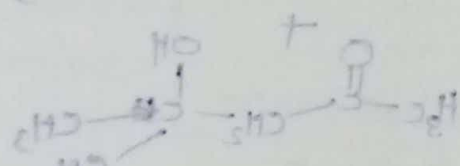
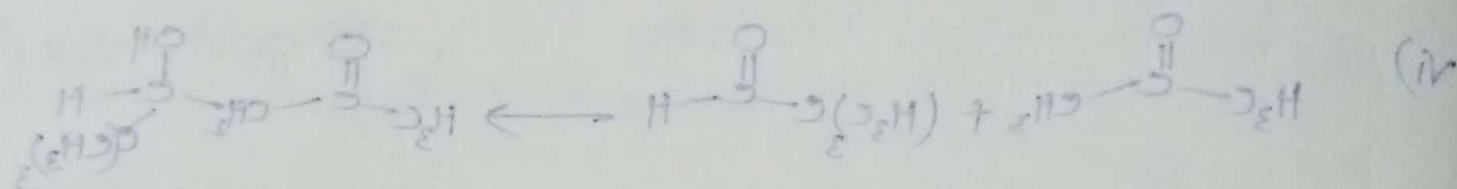
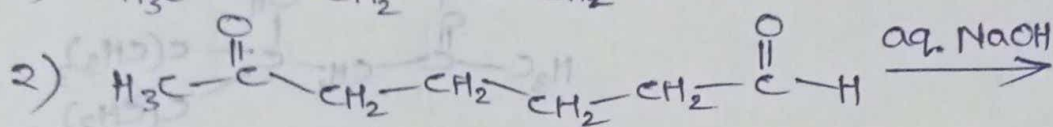
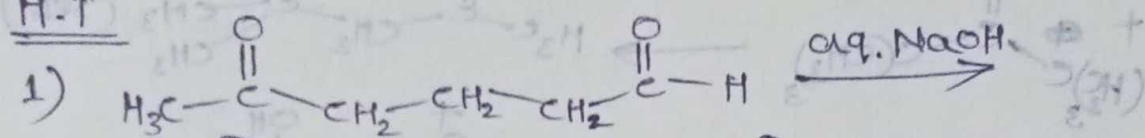




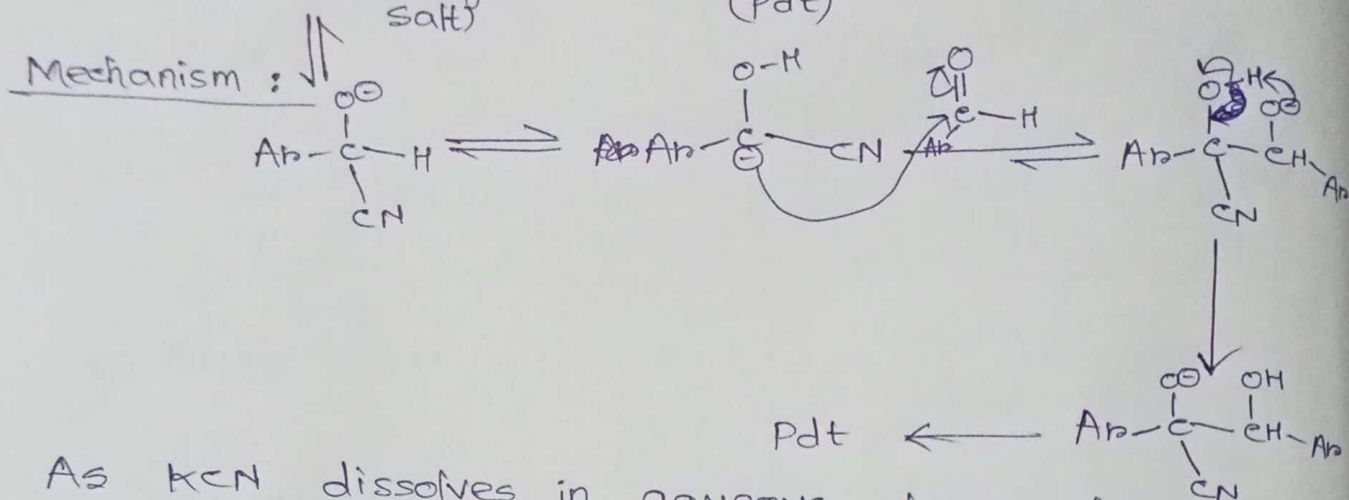
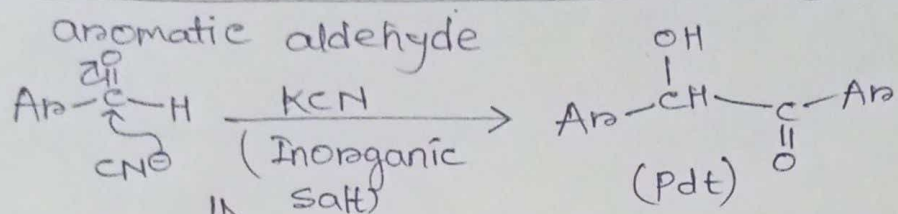
H.T.:



H.T

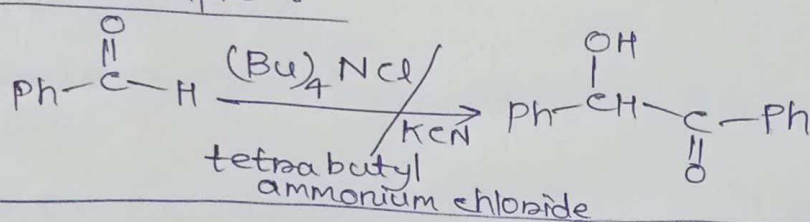


Benzoin Condensation under catalytic condition:

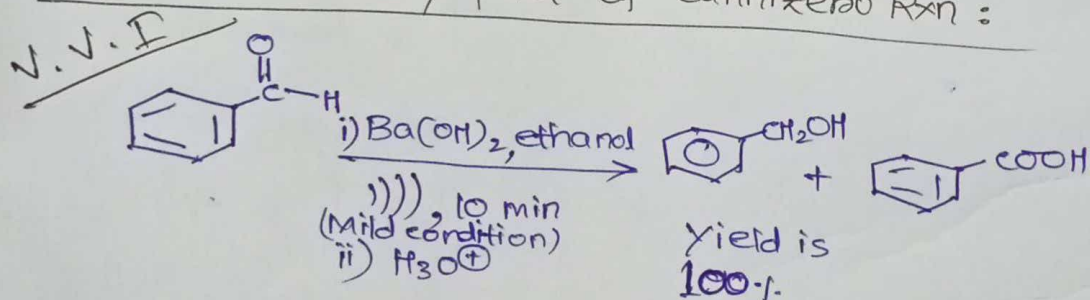


As KCN dissolves in aqueous phase whereas aromatic aldehyde dissolve in organic phase. So, there will be a problem of mixing of two reagents that is why phase transfer catalyst is used here.

As for example:



Green Chemistry part of Cannizzaro Rxn:



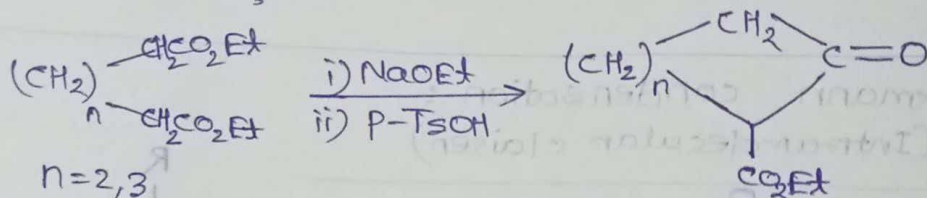
Cannizzaro Reaction in solid state:

It has been found that the Cannizzaro reaction proceed rapidly on $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$ surface which demonstrate the first application of reagent in solvent free cross Cannizzaro Rxn. A mixture of benzaldehyde & para-formaldehyde on mixing with barium hydroxide octahydrate & then irradiated in a microwave oven gives mainly a crossed product.

Green Chemistry in Dieckmann Cyclisation

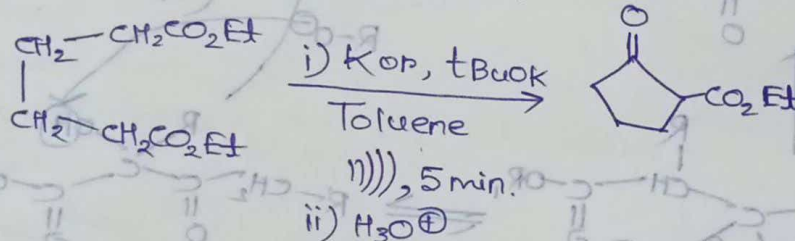
1) Solid state reaction :

Dieckmann condensation of diester has been carried out in solid state in absence of any solvent. The product is obtained by direct distillation of the powdered reaction mixture which was neutralized with p-TsOH (CH_3).

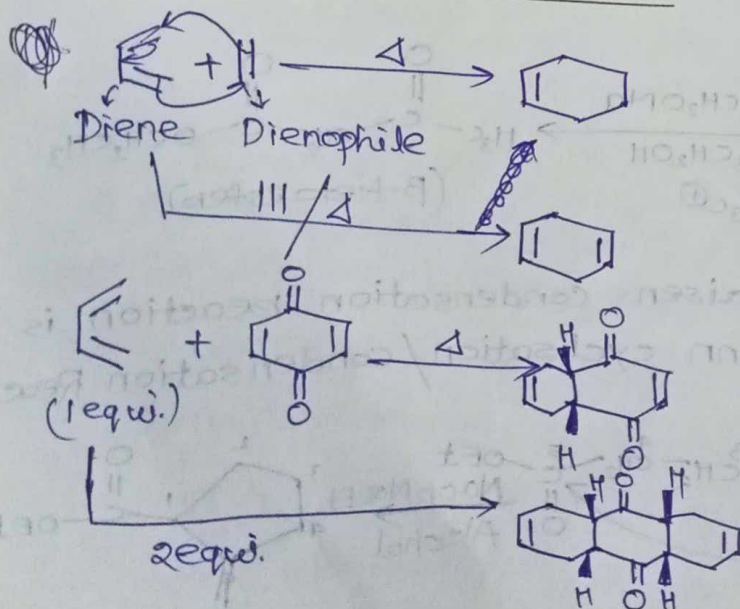


2) Under Sonication :

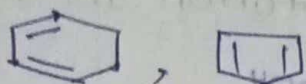
Dieckmann condensation proceeded very well on sonication in a short time. On sonication, potassium tertbutoxide (tBuOK) is easily transformed to a silver blue suspension in toluene. The ultrasonically is extremely helpful in this cyclisation Reaction.



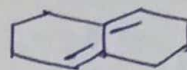
Diels-Alder Reaction :



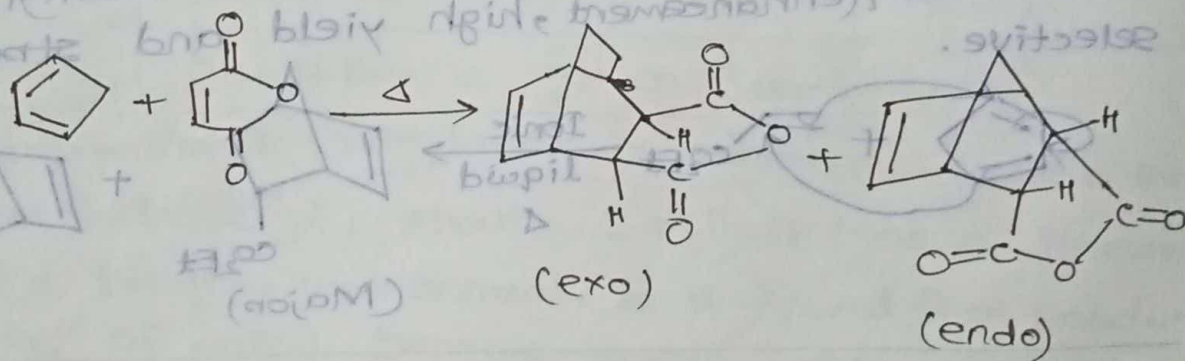
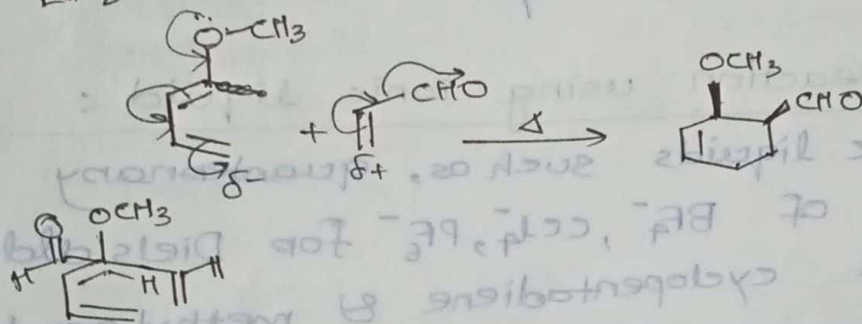
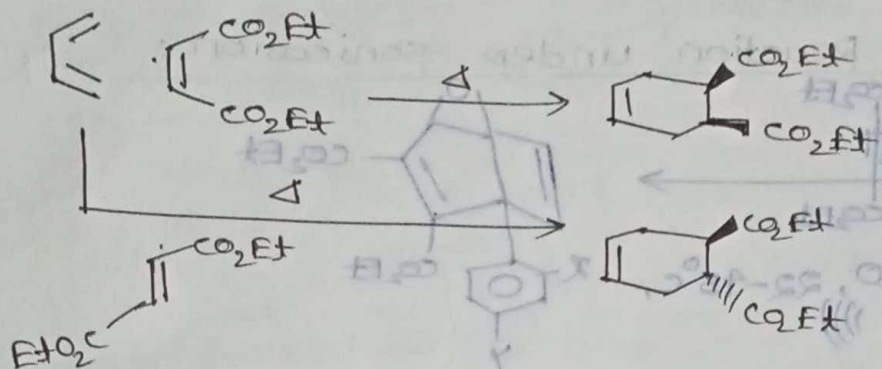
~~S-cis~~ S-cis form of diene actually reacts with dienophile. Thus, the compounds, which are locked in S-cis form reacts rapidly.



II. But there are some compound, locked in s-trans form, cannot act as diene;

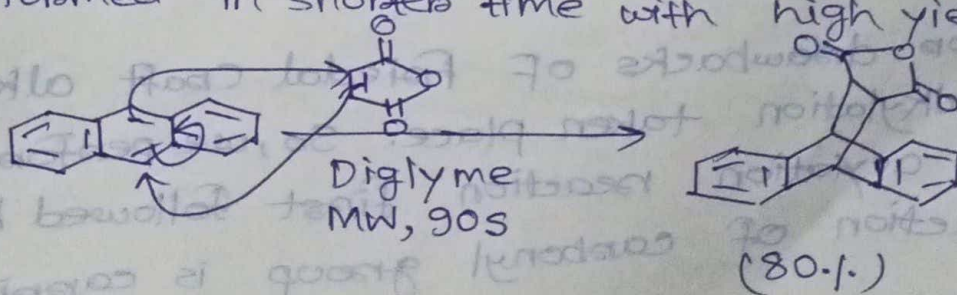


Example :

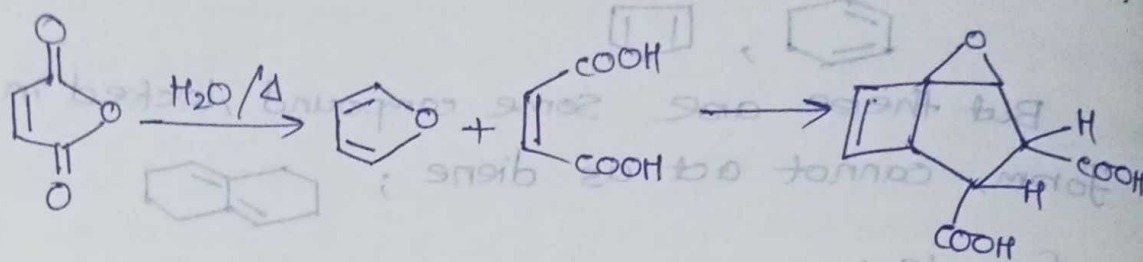


Green Chemistry in Diels Alder:

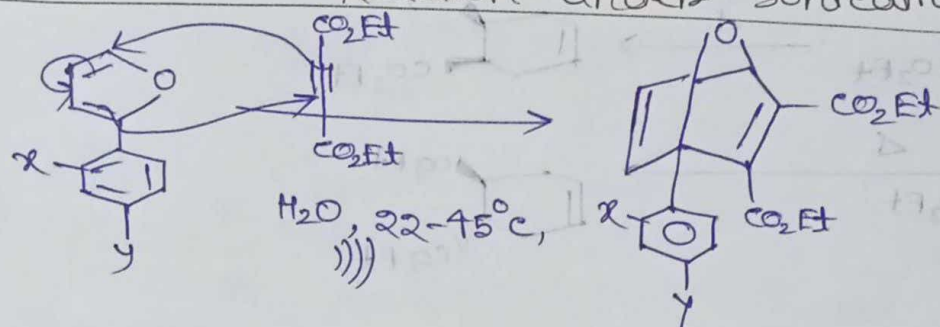
Diels Alder reaction is conventionally carried out under microwave irradiation. The reaction is performed in shorter time with high yield.



Diels alden Reaction in aqueous phase was
carried out first in 90th century where Malic anhydride is treated with Furan in hot water.

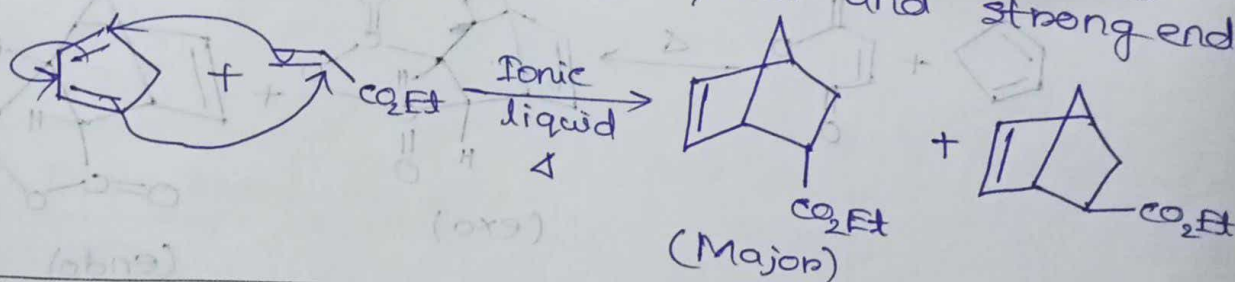


Diels alden Reaction under sonication:

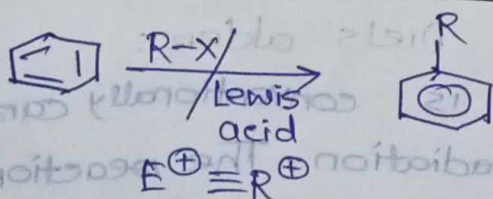


Diels alden Reaction using ionic liquid:

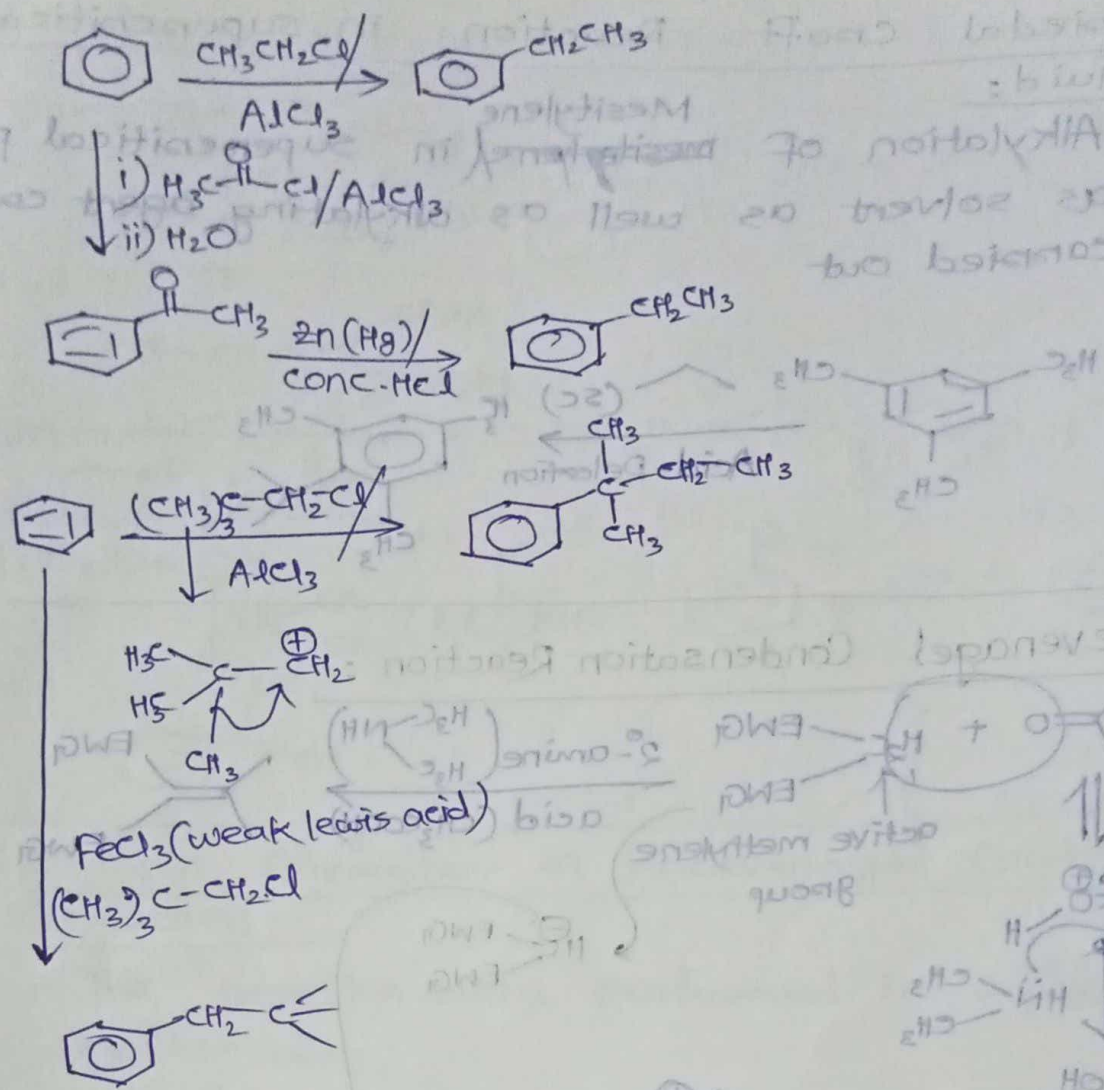
The use of ionic liquids such as, quaternary ammonium salt of BF_4^- , CCl_4^- , PF_6^- for Diels alden reaction between cyclopentadiene & methyl acrylate results in rate enhancement, high yield and strong endo selective.



■ Friedal - Craft alkylation reaction:

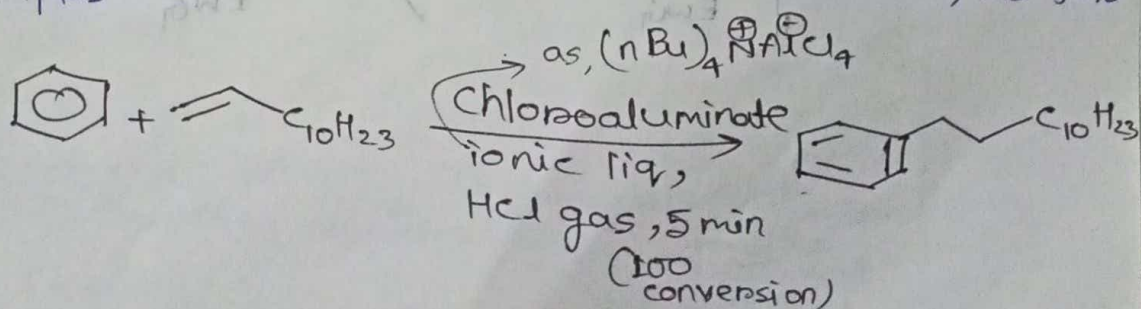


Major drawbacks of Friedal craft alkylation is poly alkylation taken place. So, we perform Friedal craft acylation reaction first followed by fuel reduction of carbonyl group is carried out.



CU-22 Friedal Craft Rxn in green chemistry :

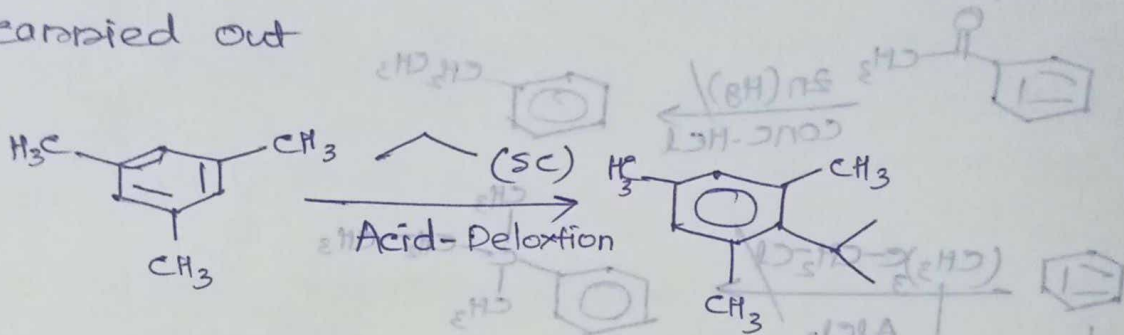
Friedal-Craft alkylation is ~~adverse~~^{key} step in the manufacture of about 3 million tons of linear alkyl benzene per annual. It is found that production of alkyl benzene using chloroaluminate ionic liquids as solvent and catalyst, system offers huge benefits. This include reduced consumption hazardous catalyst & solvents, As for examples —



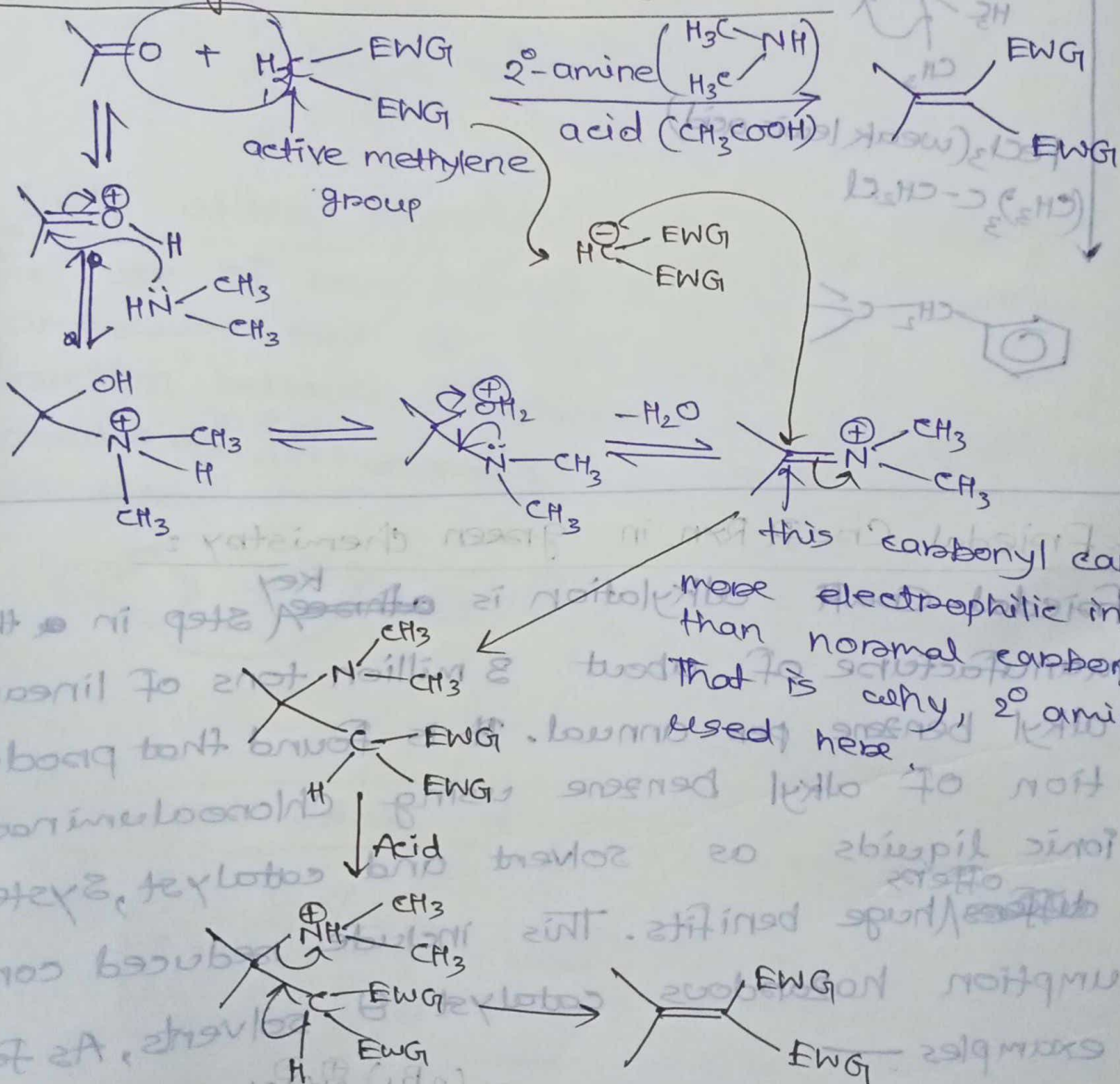
Friedel Craft Reaction in supercritical

Fluid:

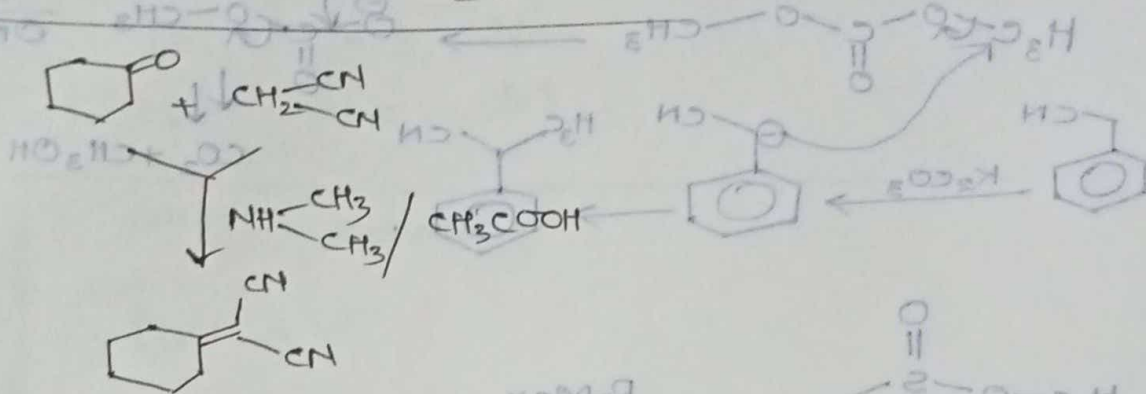
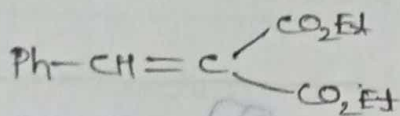
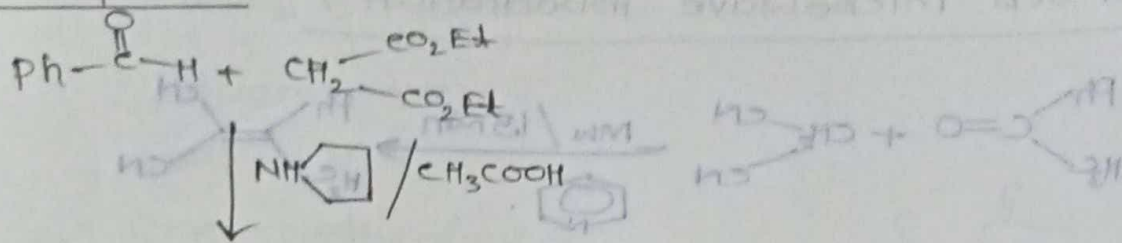
Alkylation of ~~mesitylene~~ Mesitylene in supercritical propane as solvent as well as alkylating agent can be carried out



■ Knoevenagel Condensation Reaction :

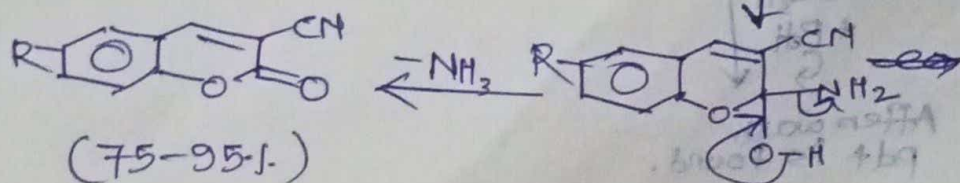
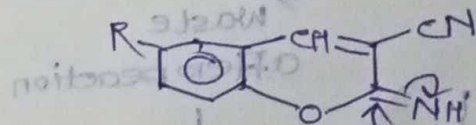
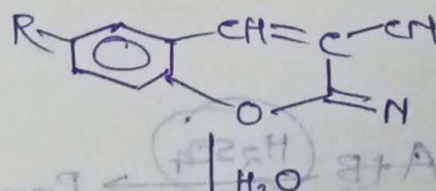
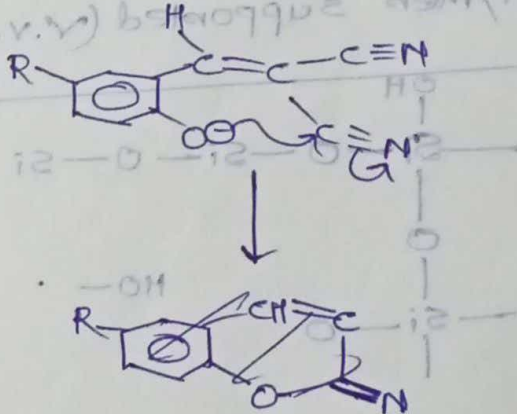
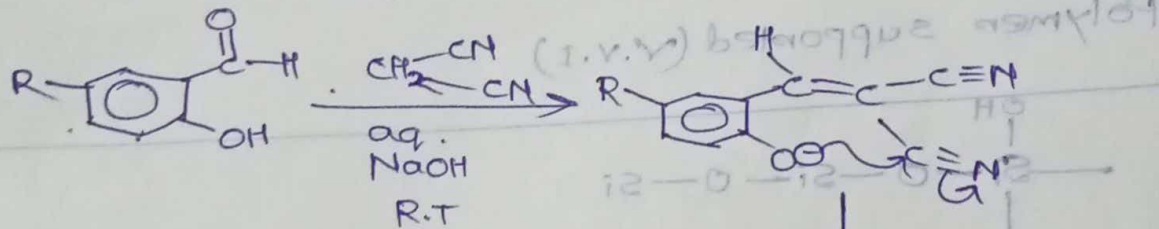


Example :

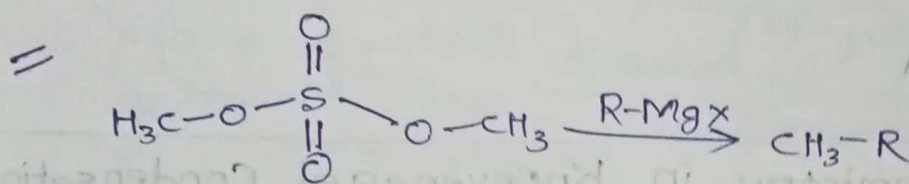
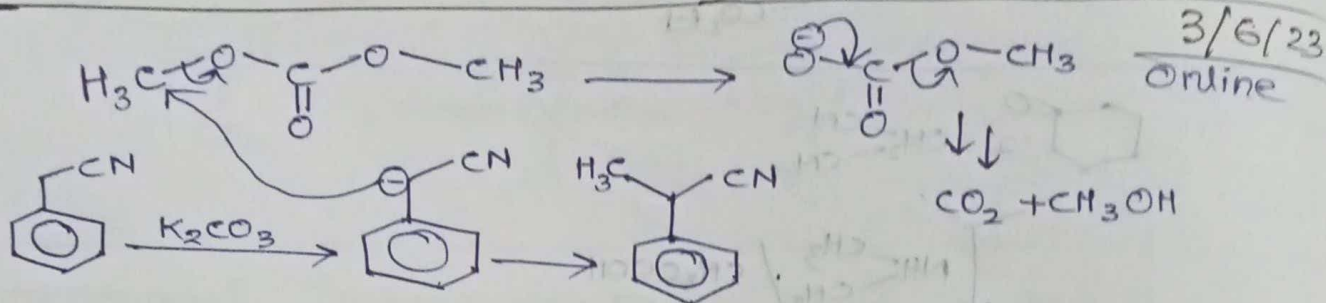
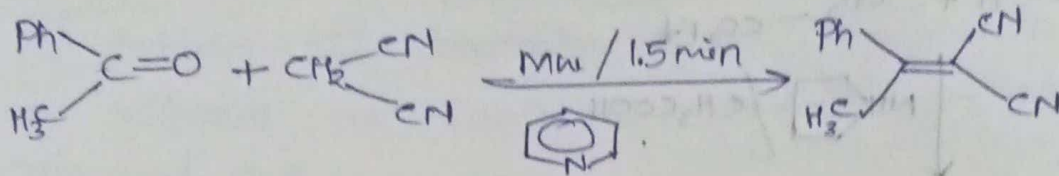


Green Chemistry in Knoevenagel Condensation reaction :

The reaction can be performed in aqueous medium also.



Under Microwave irradiation :



~~Acid catalyst~~

Polymer supported (v.v.i)

