Green Synthesis

Designing a Green synthesis :→

In any synthesis of a target molecule, the starting materials that are made to react with a reagent under appropriate conditions.

- Before coming to a final decision, consider all the possible methods that can gives the desired product.
- By modifying the conditions same product should be obtained.
- Do not use toxic starting material (eliminate by-products & wastes.

There are some following important considerations :—

(1) Choice of Starting Materials :→

- It is very important to choose the appropriate starting materials.
- synthetic work will depend on this
- Now a day we use petrochemicals (made from petroleum), (Fossils) for most of synthesis. which are non-renewable.
- Petroleum refining also require considerable amounts of energy. It is therefore important to reduce the use of petrochemicals by using alternative starting materials which may be of agricultural / biological origin.

eg. → Agricultural product → such as corn, potatoes, soya & molasses are transformed through a variety of processes into products like textiles, Nylon etc.

(thick, black brown ← juice obtained from raw sugar during the refining process).

Biological origin → Materials → Butadiene, pentane, pentene benzene, toluene, xylene, aldehydes, acetic acid, resorcinol, glucose (sugars)

(2) Choice of Reagents :→

Selection of the right reagent for a rxn is made on the basis of efficiency, availability & it effects on environment.

- Selection of a particular (right reagent) can effect the nature of by-product, % yield etc.

(3) Choice of Catalyst :→

- In the presence of catalyst, certain rxn's proceed much faster at a lower temp.
- Heavy metal catalysts should be avoided as they cause environm problem and are toxic (Highdensity) in nature.
  Heavy metals like (Hg, Cd, As, Cr, Tl, Pb)

(4) Choice of Solvents :→

- Most of the common solvent generally used cause severe hazards.
- Benzene → ↑cancer (cause) in humans and other animals.
  Toluene → Brain damage (have adverse effect on speech, vision and Balance)
  (Aromatic hydrocarbs) cause liver and kidney problems.
  All these solvents are widely used becoz of their excellent solvency properties.
- commonly used halogenated solvents, like CH_3Cl, $CHCl_3$, CCl_4 have been identified as suspected human carcinogens.
- CFCs → were used upto 20th century as cleaning solvents, blowing agents for molded plastics and for refrigeration.
- CFCs have low toxicity (direct) to humans and wild life (non-inflammable & non-explosive)
- only single effect of CFCs is in causing depletion of O_3 layer, is a sufficient reason for not using them.
- A versatile solvent CO_2 is used as liquid CO_2 or supercritical CO_2 fluid). (the states of CO_2 most commonly used for solvent use)

  A gas ⟶ liquid state
  (↑ pressure exerted upon it)

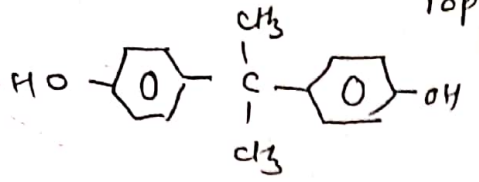
  at high T_c & P_c (72.8 atm for CO_2) a subst. convered into a supercritical fluid.
  ($31^{\circ}C$)

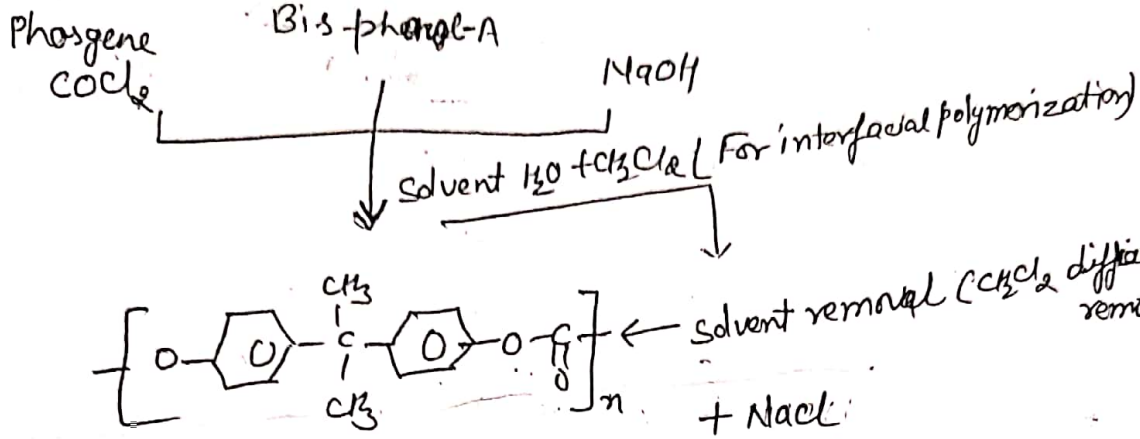
  T_c → a temp. above which a distinct liquid phase of the sub. can't exist, regardless of the pressure applied

  P_c → a pressure at which a sub. can no longer exist in gaseous state.

Green Synthesis of Polycarbonates

Popular Trade Name → 'LEXAN'
(Step-growth Polymerization)
(Condensation process)

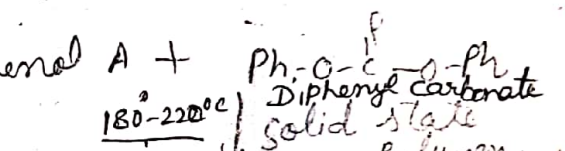




(Polycarbonates)

Polycarbonates so formed have been found to be contaminated with Cl- impurities.

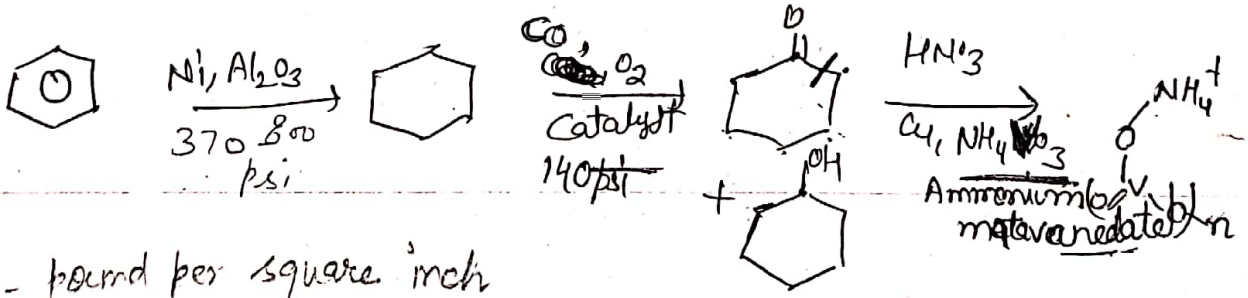
Alternative to using phosgene → Transesterfication of bisphenol-A



Green Synthesis of Adipic acid

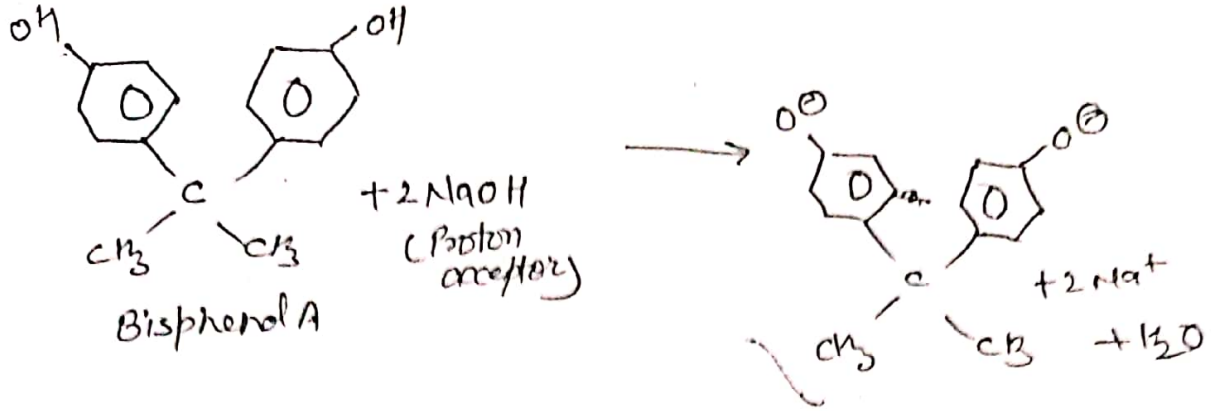
New synthetic pathway for the manufacture of Adipic acid is reaction of catechol and hydroquinone using glucose as the starting material in place of traditionally used benzene which is carcinogenic

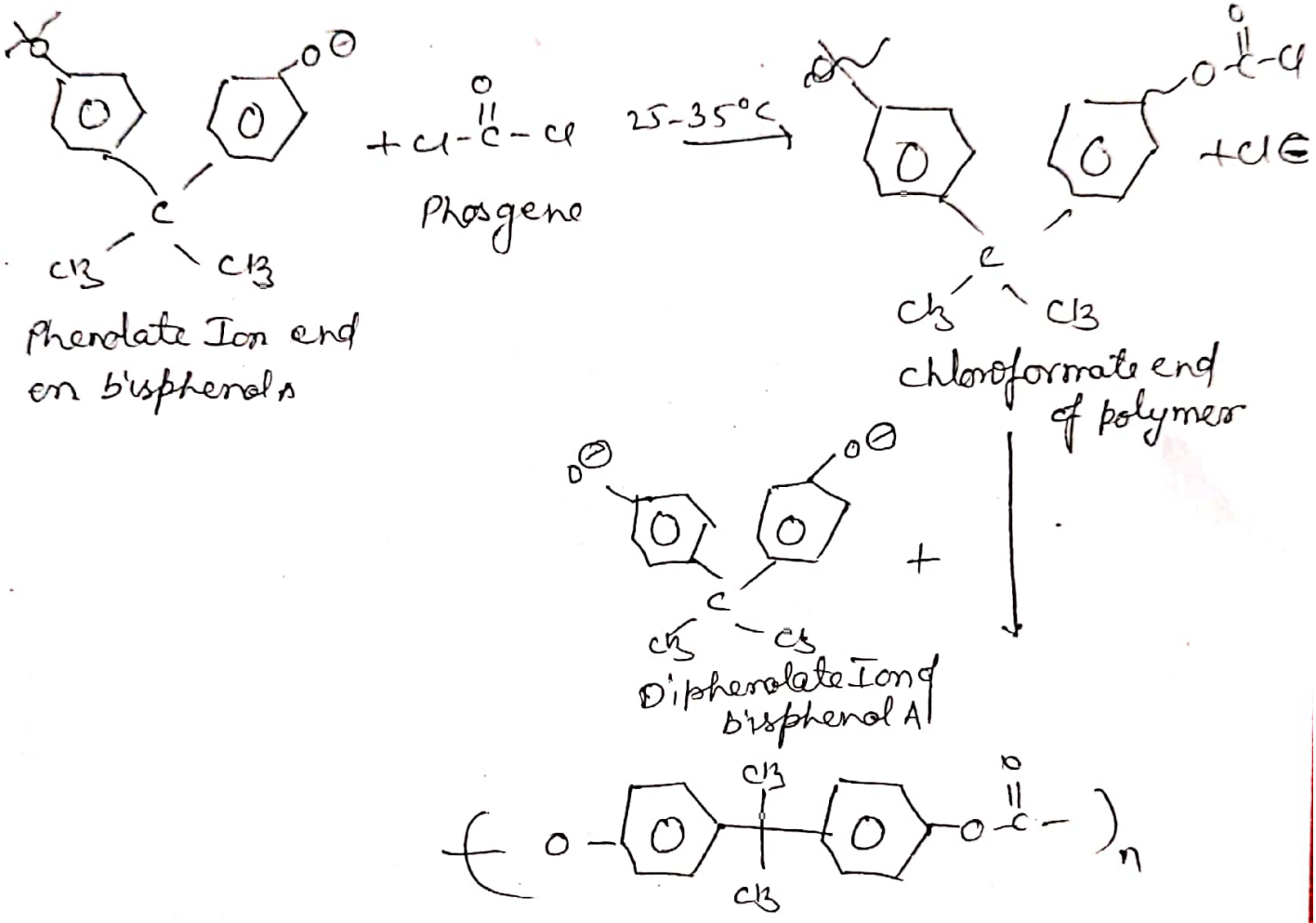
Traditional pathway :-



psi - pound per square inch

$HOOC-(CH_2)_4-COOH$
Adipic acid
$+ N_2O$

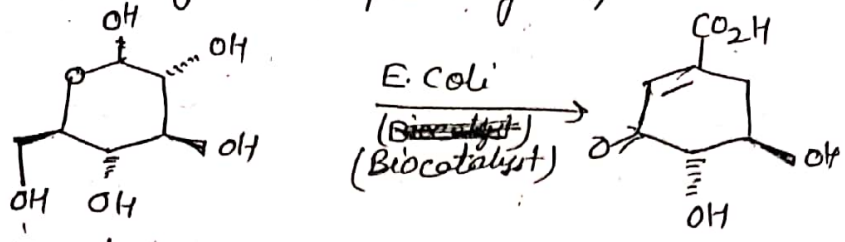




Green Synthetic Route (Asahi Solid state polymerization) → Asahi chemicals, Japan

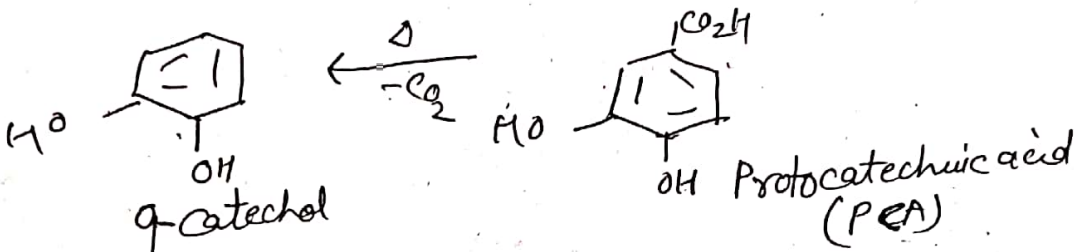
1. ~~To avoid~~ It eliminates the use of hazardous phosgene
2. The reaction is carried out in molten condition thereby avoiding the use of methylene chloride, which is a suspected carcinogen.

Alternative greener pathway :→



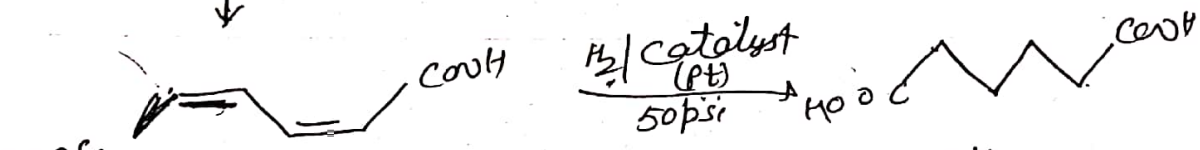
D-glucose

3 dehydroshikimic acid



Protocatechuic acid (PCA)

catechol

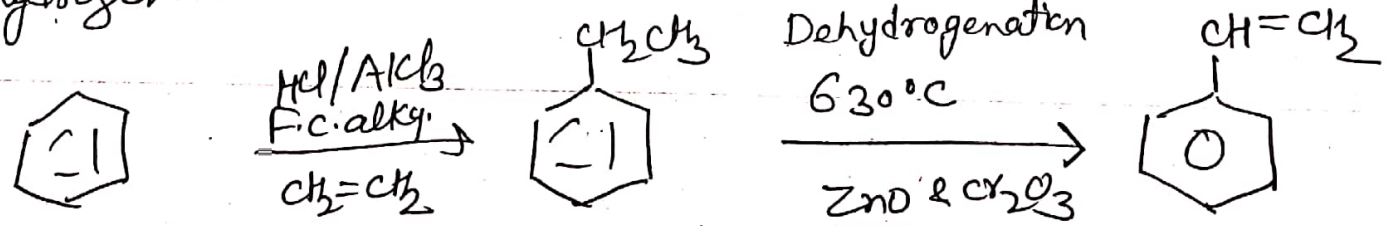


cis,cis-muconic acid

adipic acid

Green synthesis of Styrene

The chemical industry consumes, styrene, the monomer used for the manufacture of Polystyrene in large quantities per year. The commonly used industrial method for making it converts benzene into styrene by Friedal-crafts alkylation followed by dehydrogenation.

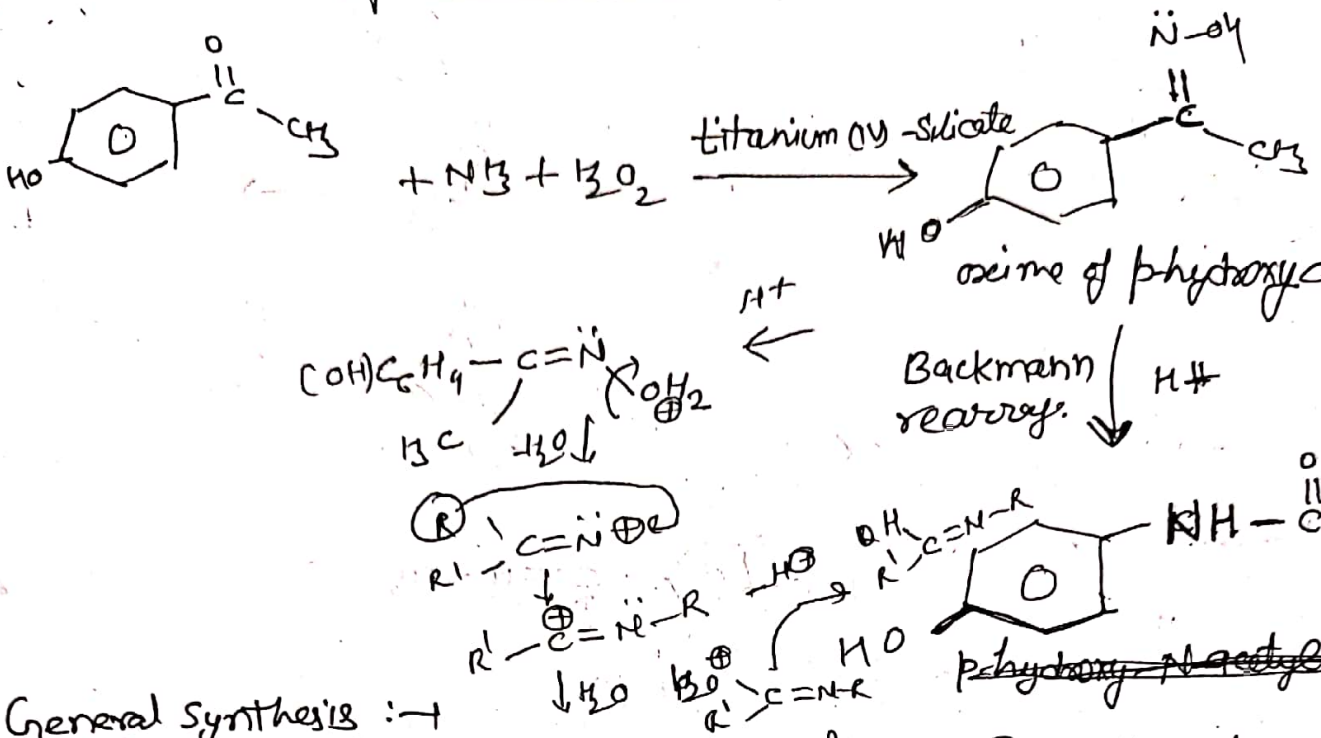


Ethylbenzene

Styrene (90-92

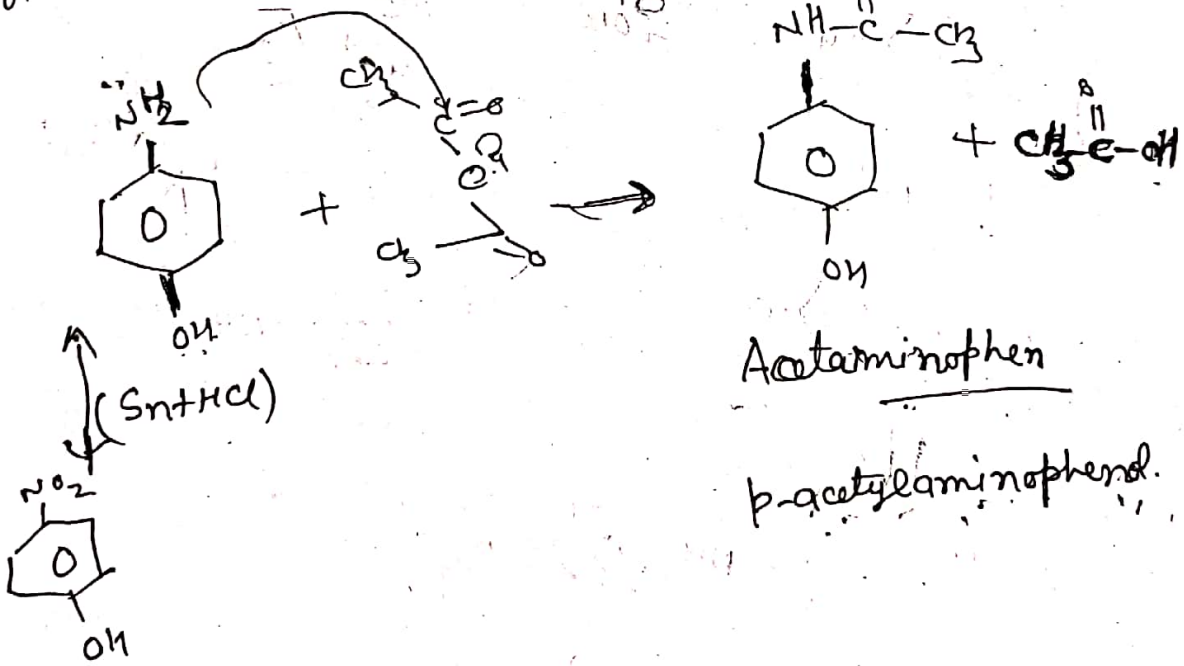
Chapman → New synthesis uses → only single step to convert mixed xylenes (compds that are noncarcinogenic) into styrene.

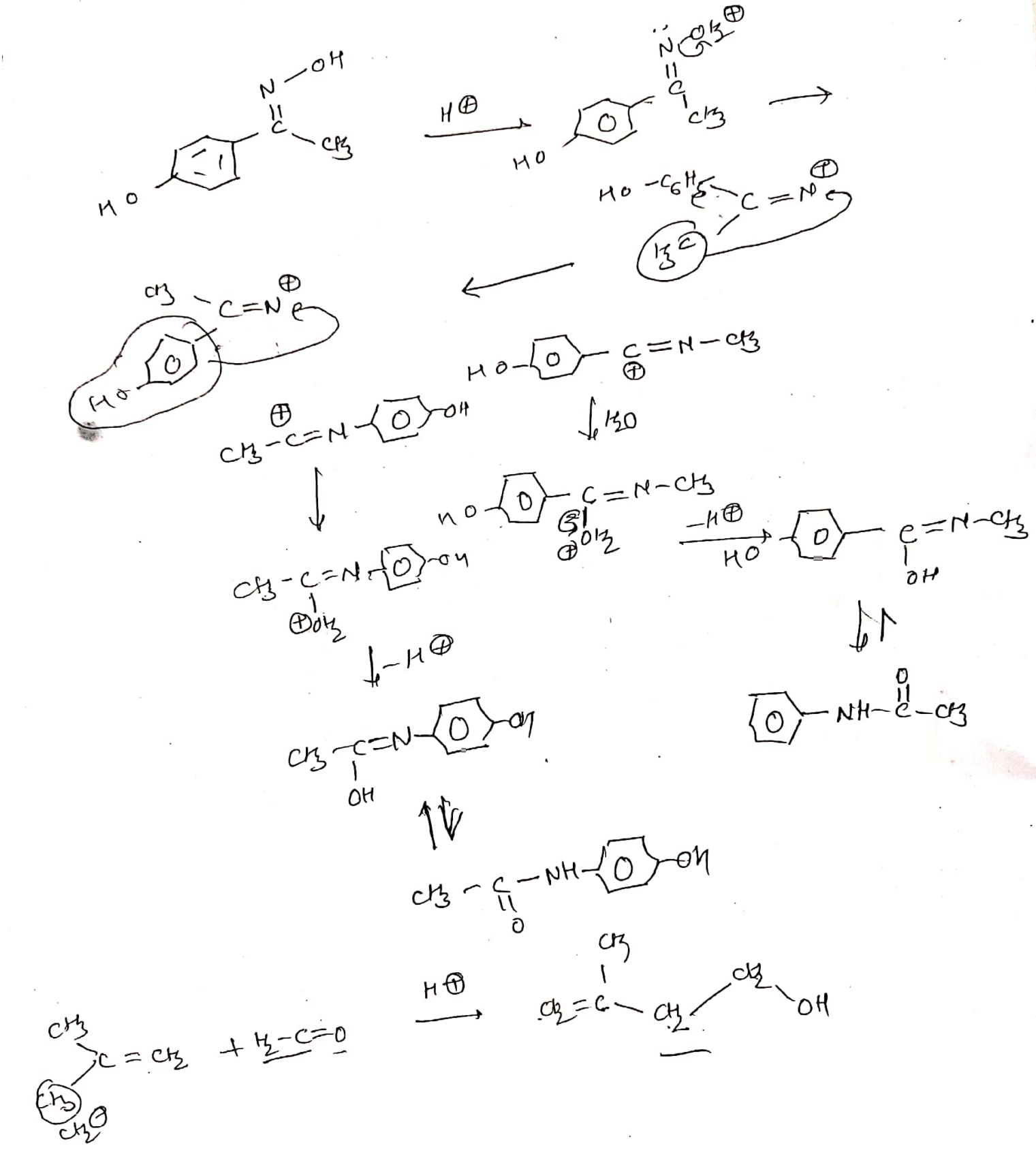
Green Synthesis of Paracetamol :→



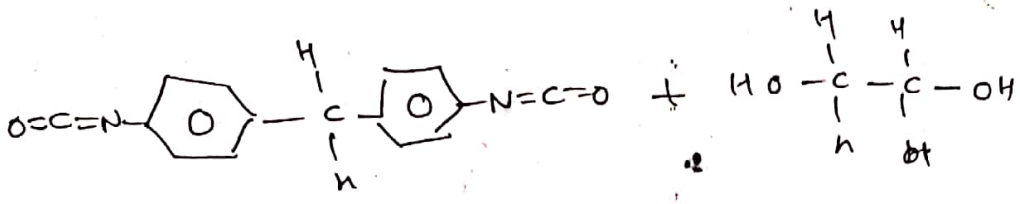
General Synthesis :→

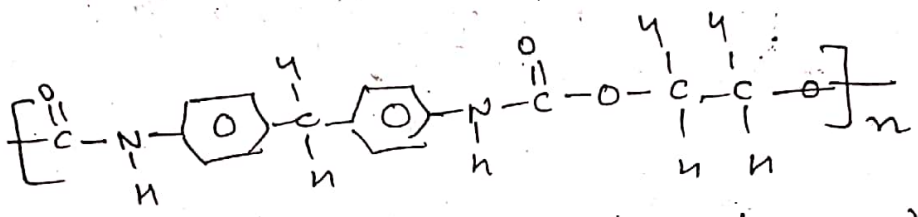
) By Acetylation of 4-aminophenol → Paracetamole





Green synthesis of Urethane :→ Used for manufacture of polyurethanes





Isocyanate functional grp → (-N=C=O)

$$ROH + R'NCO \longrightarrow ROC(O)N(H)R'$$

General method :→

$$RNH_2 + COCl_2 \longrightarrow R\text{-}NCO + 2HCl \xrightarrow{R'OH} R\text{-}NH\text{-}\underset{\underset{O}{\|}}{C}\text{-}OR'$$

Phosgene

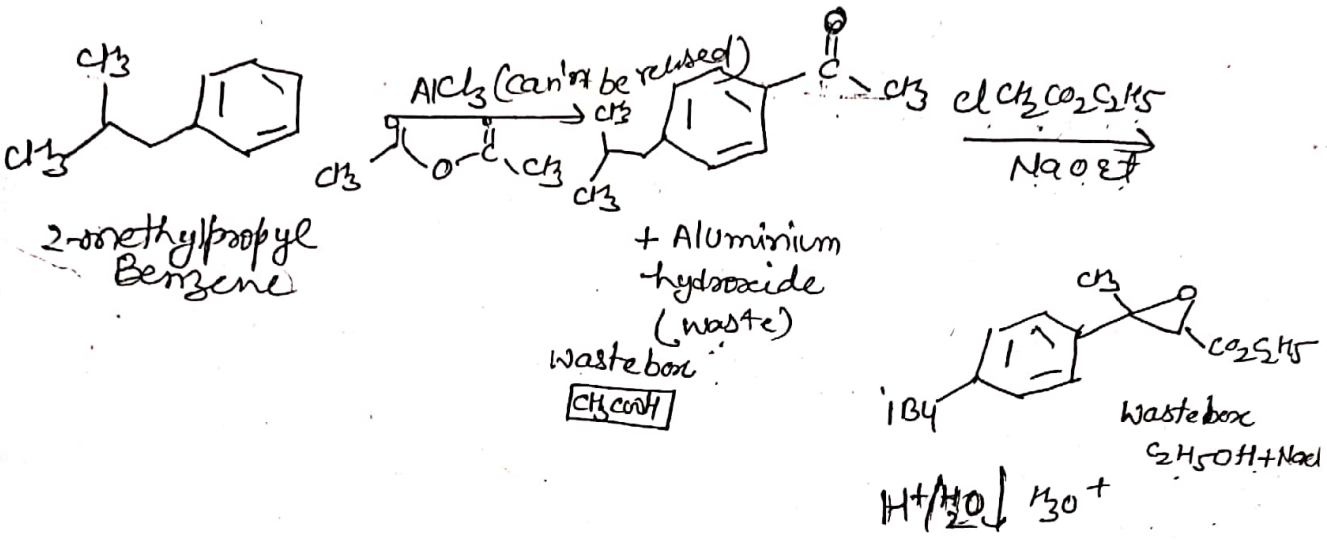
Monsanto company →

$$R\text{-}NH_2 + CO_2 \longrightarrow \underset{\text{Isocyanate}}{RNCO} + H_2O \xrightarrow{R'OH} R\text{-}NH\text{-}CO_2R'$$

Green Synthesis of Ibuprofen

It is a pharmaceutical drugs [Analgesics (pain killer)]

Traditional Synthesis :→ Synthesis of ibuprofen was developed by the Boots company of England in 1960s. Patent (USP 3,385,886)

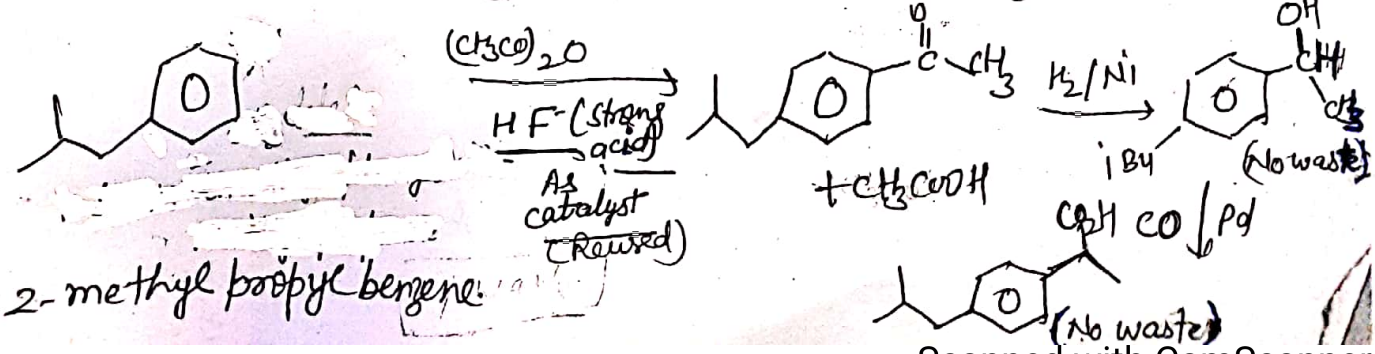


(Boot's synthesis)

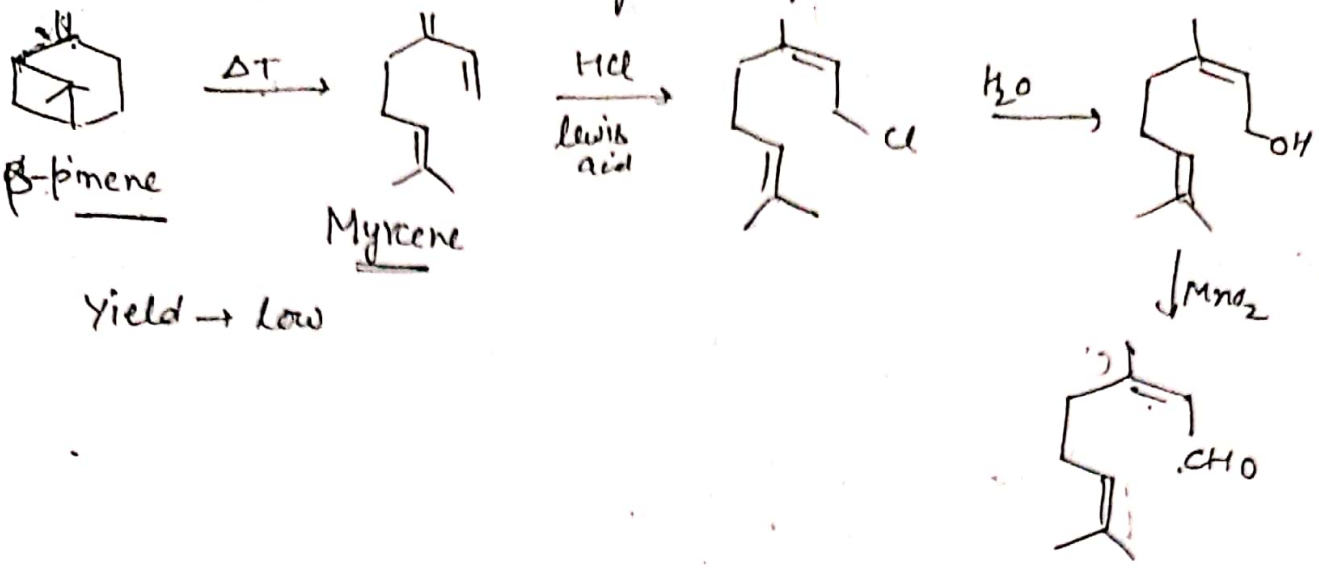
(6-step process)
↓
Results in large quantities of unwanted waste chemical byproducts.

(There is 40% atom economy in this synthesis)

Alternative Green Synthesis of Ibuprofen :→ Economy → 77% (77%)
(3-step) (Simpler process)

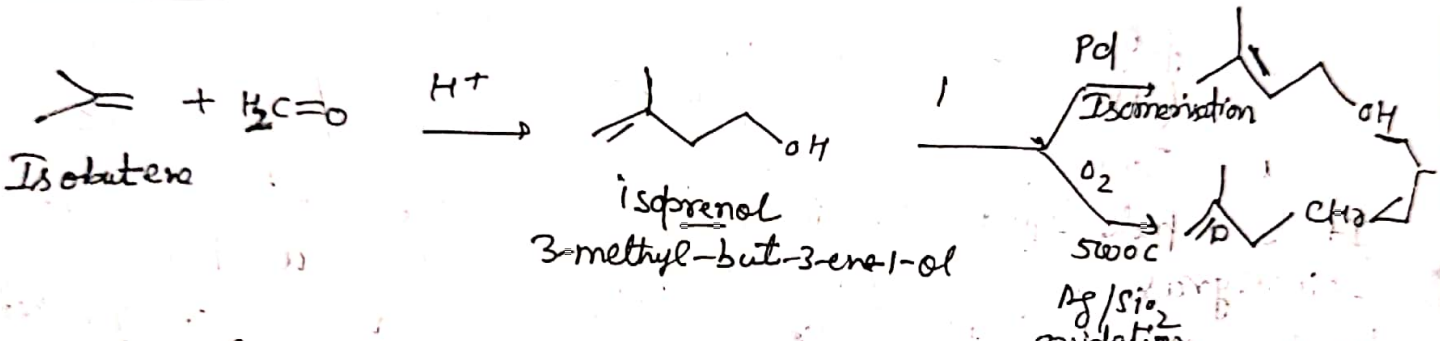


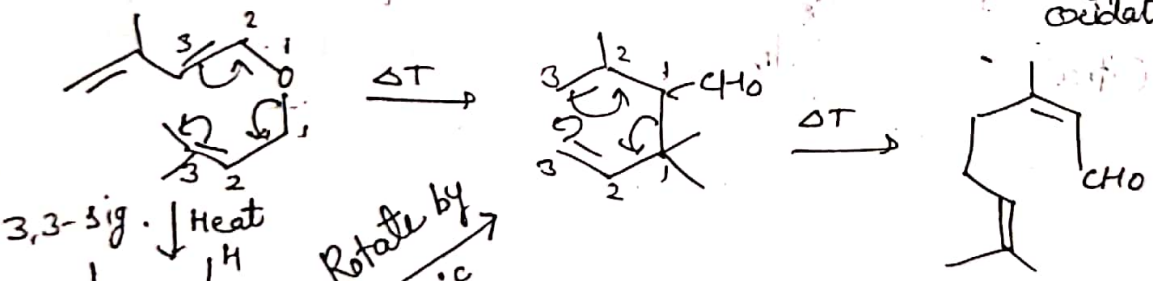
Green Synthesis of Citral :→ Building units for carotenoids & Vit-A.



Yield → Low

New Route :–

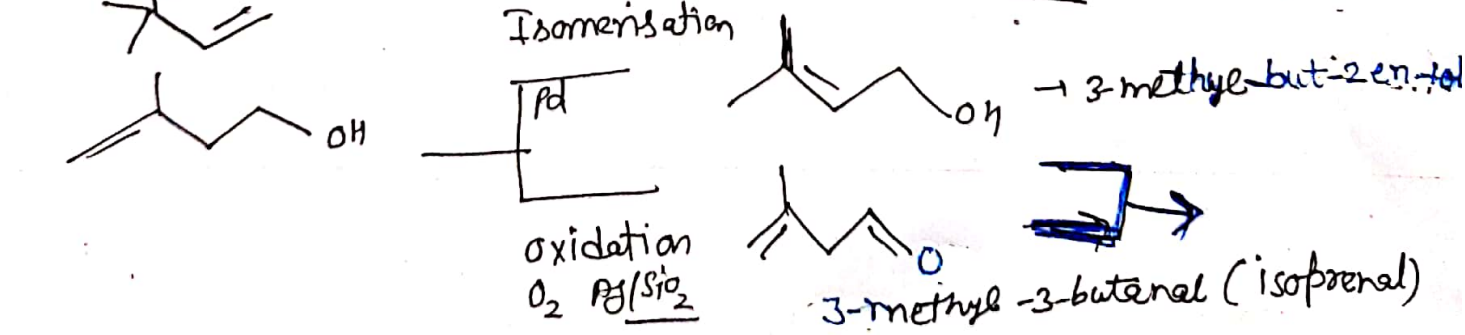


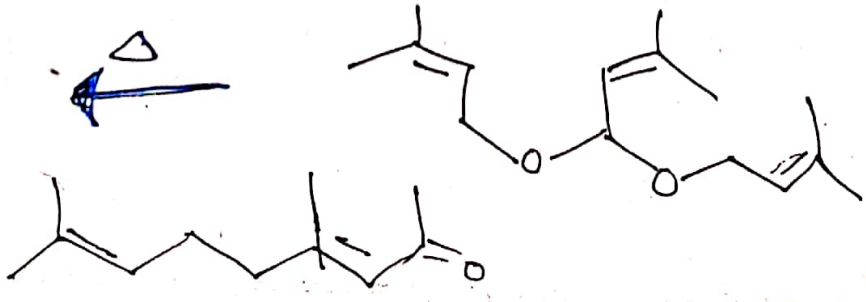


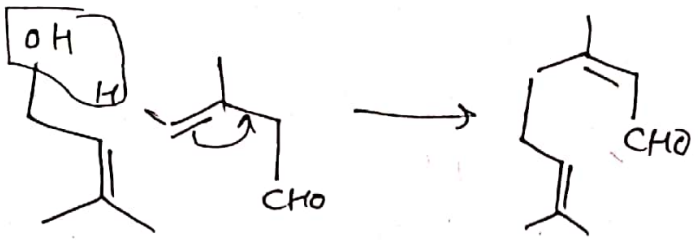
3,3-sig. ↓ Heat

Rotate by 180°c

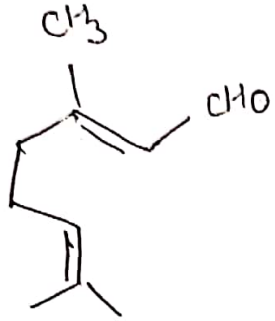
Citral



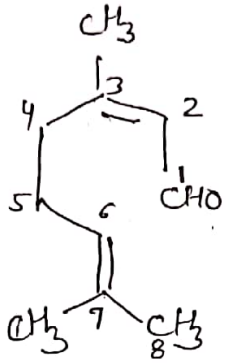




(95% yield)



geranial
(citral-a)
Trans



Neral
(citral b)
cis

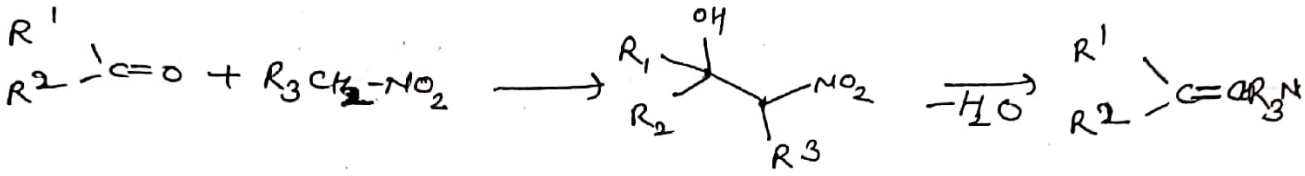
3,7-dimethyl-2,6-octadienal

It is a pale liquid with strong lemon odour (Lemon verbena). Lemongrass oil contains 70-80% citral. It is used in perfumes and flavourings and in the manufacture of other chemicals. Citral is a mixture of two aldehydes.

α, β-Unsaturated nitroalkenes

α, β-unsaturated nitroalkenes are molecules of great interest because of their biological and pharmacological properties, and the conversion of $-NO_2$ grp. to an NH_2 or carbonyl grp giving access to a large variety of building-block.

Synthesis :-



Two step procedure

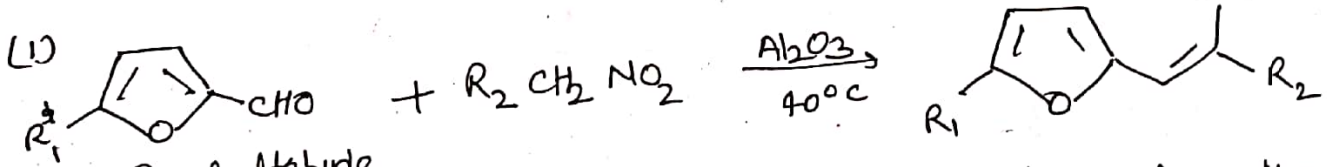
(i) An aldol type rxn of monosubstituted nitromethane with an aldehyde or a ketone (Henry's rxn)

(ii) A dehydration rxn of the β-nitroalcohol adduct.

Green Synthesis :-

(A) Solventless synthesis :-

(1)

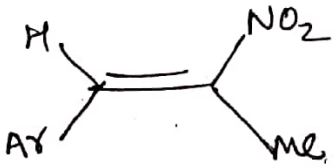


2-furylaldehyde or 5-methyl deriv.

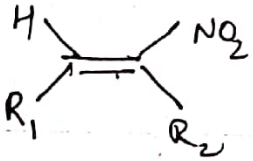
1-(2'-furyl)-2-nitroalkenes (yield is good)

(one-pot solventless synthesis)

(2) $Ar\text{-}CHO + Me\text{-}CH_2NO_2 \xrightarrow[140°C, 24h.]{\text{cat. (Zeolites)}}$



(3) $R_1CHO + R_2CH_2\text{-}NO_2 \xrightarrow[\text{Envirocat}]{EPZG}$



(5) Synthesis in Aqueous Medium:-