Module-4

Brief discussion on 12 principles of green chemistry.

The twelve principles of green chemistry that have been formulated are listed below:

1. Pollution Prevention

It is better to prevent waste than to treat or clean up waste after it is formed

2. Atom Economy

Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

3. Less Hazardous Chemical Synthesis

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

4. Designing Safer Chemicals

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

5. Safer Solvents and Auxiliaries

The use of auxiliary substances (solvents, separation agents, etc.) should be made unnecessary whenever possible and, when used, innocuous(harmless)

6. Design for Energy Efficiency

Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.

7. Use of Renewable Feedstocks

A raw material or feedstock should be renewable rather than depleting whenever technically and economically practical.

8. Reduce Derivatives

Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.

9. Catalysis

Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10. Design for Degradation

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

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11. Real-time Analysis for Pollution Prevention

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

12. Inherently Safer Chemistry for Accident Prevention

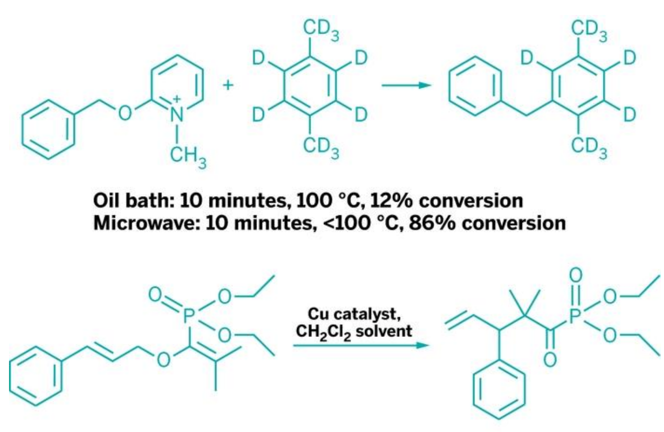
Substance and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

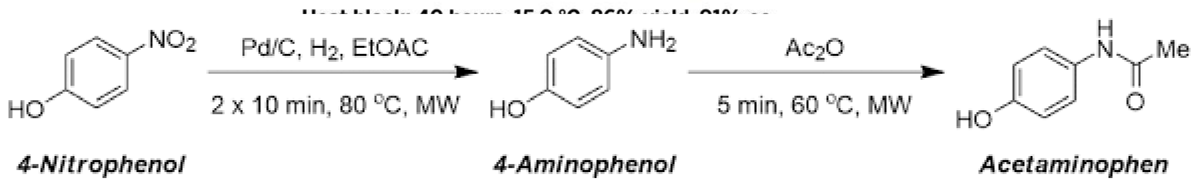
Microwave Synthesis

Components: 1. High Voltage Transformer: The 240V supply is jumped to a few thousand volts, which is then fed to the cavity magnetron. **2. Cavity Magnetron:** A cavity magnetron is a high-powered vacuum tube that transforms the electrical energy into long-range microwave radiations (frequencies between 300MHz and 300 GHz). **3. Waveguide:** A waveguide is a hollow metallic tube that guides the waves generated at the magnetron's output toward the target material.

Heating Mechanism: Reacting materials under microwave irradiation are heated by two mechanisms, such as **dipolar interaction, ionic conduction** and **interfacial polarization**. As the orientation of the electric field (of electromagnetic radiation) changes over time, the polar molecules (or ions) attempt to follow the field by changing their orientation inside the material to line up along the field lines in an energetically favorable configuration (namely, with the positive side pointing in the same direction as the field lines). As these molecules change direction rapidly (millions of times per second at least), they gain energy, which increases the temperature of the material. This process is called dielectric heating.
Nature of the material decides its interaction with microwave. For example, Sulfur – transparent, Copper – reflect, Water – absorb microwaves.

Example:





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Bio catalyzed reactions

Biocatalysis refers to the use of living (biological) systems or their parts to speed up (catalyze) chemical reactions.

Biocatalysts are derived from plants, microorganisms (yeast, bacteria, fungi) or animal tissue (Ex. Protease from pancreas).

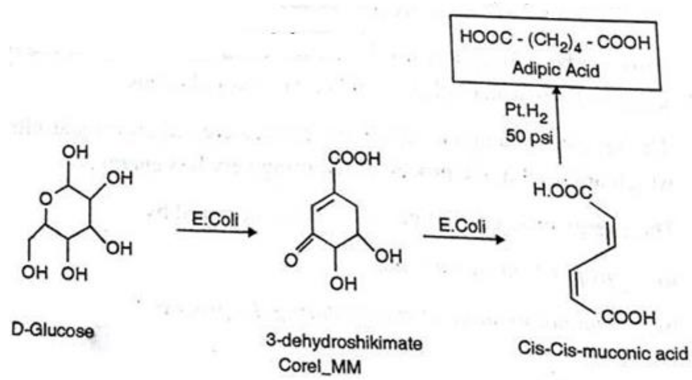
Enzymes are one of the well-known and largely used biocatalysts. Enzymes are bulky molecules (mostly proteins) which has got three-dimensional structure. Active site of the enzyme reacts with the substrate (reactant) through a mechanism similar to lock and key model.

Microbial strains are used to produce the desired enzyme in large quantities for commercial (industrial) applications following the FDA regulations.

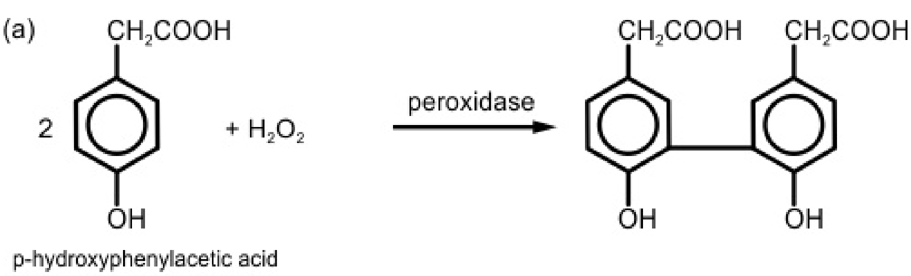
Catalytic activity of the enzymes is affected by enzyme concentration, temperature, pH, inhibitors, substrate concentration etc.

Enzymes provide more powerful way of producing enantiomerical pure compounds through chemoselectivity, regioselectivity and stereoselectivity.

Examples



(a)



(b) $$2\,H_2O_2 \xrightarrow{\text{catalase}} 2\,H_2O + O_2$$

Module-4

Solvent Free Reactions

Solvent less reaction is chemical reaction system in the absence of a solvent.

Advantages

Economic: Expensive solvent usage can be avoided. That in turn save money on solvent.

Simple: Laborious extraction steps, separation of product from the mother liquor, evaporation of solvent can be avoided.

Environmental benign and safe: Eliminates the usage of carcinogenic, toxic, neurotoxin, flammable solvents.

Efficient: Rate of the solvent free reactions is usually high due more availability of reactants. Also, selectivity is better compared to conventional approach.

Conditions

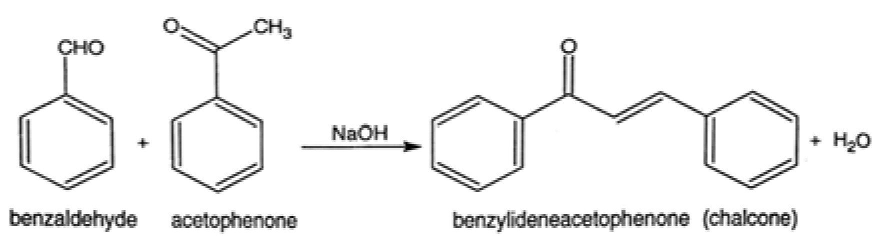
1. No reaction media to separate, purify, dispose, recycle

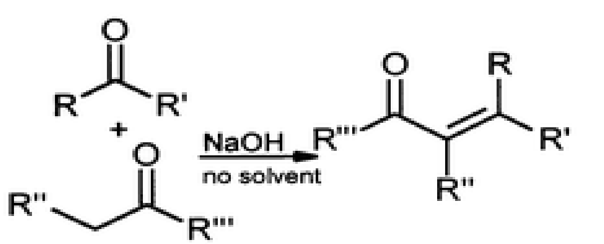
2. No need of specialized equipment for a laboratory scale preparation.

3. Chromatography can be avoided due to formation of sufficiently pure compounds.

4. Reactions can be performed by milling, grinding, microwave irradiation, UV light irradiation, heating etc.

Examples





Single product in high yield.

$NH_4CNO \xrightarrow{Heat} NH_2\ CO\ NH_2$

Module-4

Photo electrocatalytic hydrogen production

Semiconductor (photoactive) material is used to construct the electrode (photo electrode). This photo electrode is combined with the Pt electrode to construct the photo electrocatalytic cell.

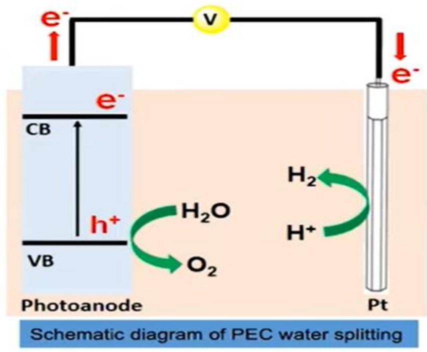
Charge carrier (electron and hole) – generation, separation, transportation are the three important steps decides the efficiency of the cell to produce hydrogen.

Light is illuminated on the photo electrode. Electrons present in the valence band (VB) of the semiconductor absorb the light energy and excite to the conduction band (CB). Immediately those electrons are separated to move on to the collector.

Electrons are collected and travel through the external circuit to the counter electrode to drive the hydrogen evolution half reaction (HER): $\mathbf{2\ H^+ + 2\ e^- \rightarrow H_2}$

Holes diffuse to the semiconductor surface and drive the oxygen evolution half reaction (OER):

$\mathbf{H_2O + 4h^+ \rightarrow O_2 + H^+}$



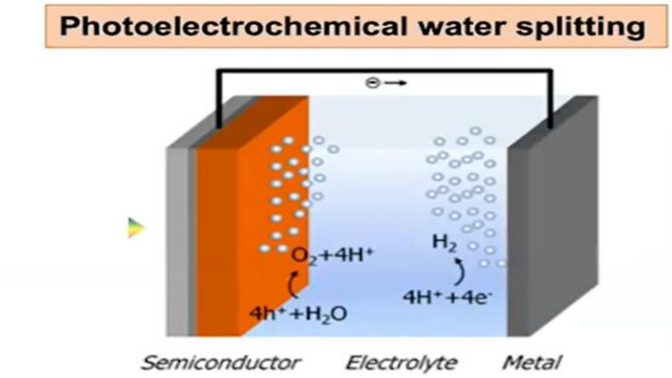


Photo catalytic hydrogen production

Semiconductor (photoactive) material is used in the form of powder or film (coating). And it is dispersed or submerged in the reaction medium.

Charge carrier (electron and hole) – generation, separation are the two important steps decides the efficiency of material to produce hydrogen.

Light is illuminated on the photo active semiconducting material. Electrons present in the valence band (VB) of the semiconductor absorb the light energy and excite to the conduction band (CB). Immediately those electrons are separated to move on to the surface of the material.

Electrons reach out the surface to react with protons adsorbed onto the surface to drive the hydrogen evolution reaction (HER): $\mathbf{2\ H^+ + 2\ e^- \rightarrow H_2}$

Holes diffuse to the semiconductor surface and drive the oxygen evolution reaction (OER):

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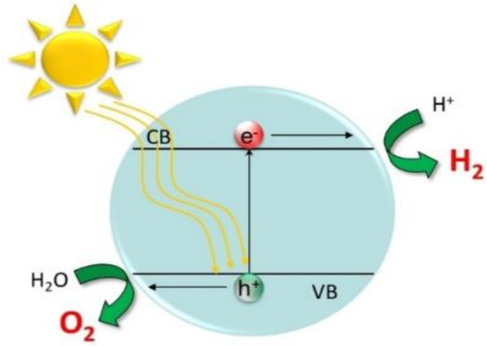
$H_2O + 4h^+ \rightarrow O_2 + H^+$



Schematic of the photocatalytic hydrogen evolution

Fuel Cells
Fuel cells are the galvanic cells in which chemical energy of fuel is directly converted into electrical energy.

Cell Representation
Fuel/Anode //Electrolyte// Cathode /Oxidant

Methanol – oxygen fuel cell

It consists of two electrodes made up of platinum. In between the electrodes H_2SO_4 is placed as an electrolyte. Methanol is supplied at the anode and pure oxygen gas is supplied at the cathode. The Methanol is oxidized to CO_2 & H_2O with the Liberation of electrical energy. And the oxygen is reduced at the cathode to produce water.

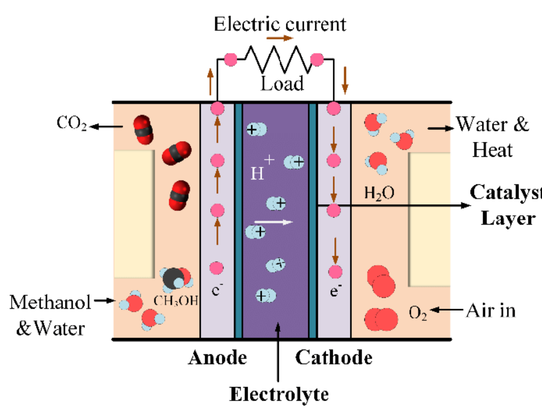
The cell reactions are as follows,

At Anode: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$

At Cathode : $O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$

Net reaction : $CH_3OH + 3/2\ O_2 \rightarrow CO_2 + 2H_2O$

The cell delivers an emf of 1.20 V.



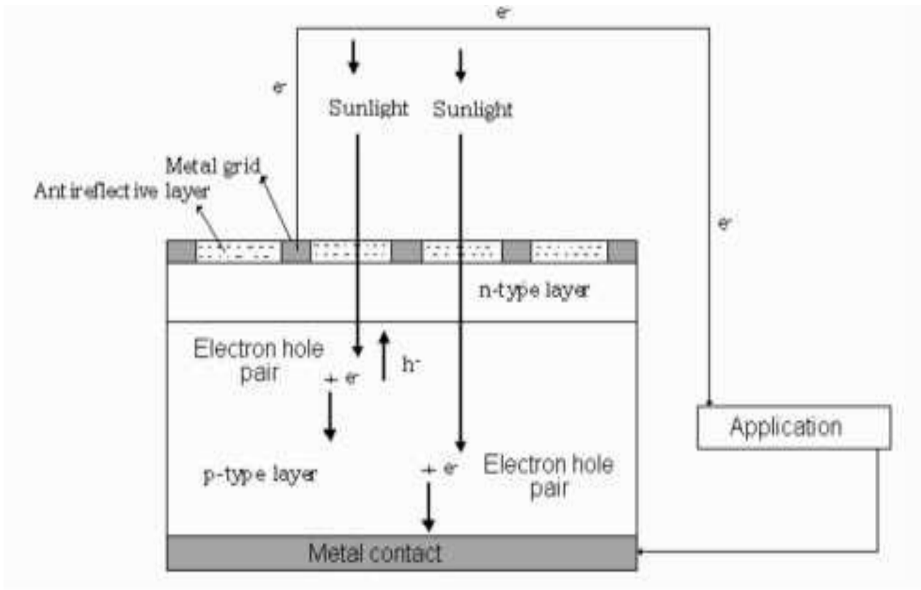
Uses
• Used in Military Applications
• for large scale power production stations

Introduction, construction, working and applications of photovoltaic cell

Photovoltaic cell

Module-4

Photovoltaic cell is semiconductor device that convert sunlight into direct current electricity. Photovoltaic cell is based on photoelectric effect.



Construction and working of a solar cell/photovoltaic cell Construction

- Polycrystalline silicon wafers are made by block-cast silicon ingots into very thin wafers/slices (250-350□m).

- The wafers etched slightly to remove saw damage. Wafer is lightly p- doped to make a solar cell form wafer, surface diffusion of n-type dopant is done on the front side, this forms a p-n-junction few hundred nanometers below the surface (10-9m).

- Antireflecting coating of silicon nitride/TiO_2 is then applied in a layer using plasma enhanced chemical vapor deposition (PECVD) technique contact made by using silver paste.

- The wafer is then metallized.

- The rare contact is made by screen printing using aluminium paste. Metal rods are then given to make ohmic contact with the silicon

Working

Photovoltaic cells or Solar cells are the semiconductor devices which converts sunlight into electricity. Sunlight consists of Electromagnetic radiation of particles called Photons ($h\nu$). The photons carry a certain amount of energy given by the Planck quantum equation,

$E=hc / \lambda$

Where h is Planck's constant, c is the velocity of light and λ is the wavelength of the radiation. When light radiation falls on the p-n-junction diode, electron-hole pairs are generated by the absorption of radiation. The electron is drifted and collected at n-type end and holes are drifted and collected at the p-type end. When these two ends are electrically connected through a conductor, there is a flow of current between the two ends the external circuit. Thus, photoelectric current is produced and available for the use.

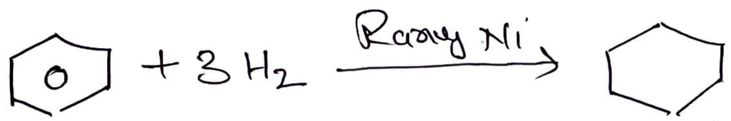
Adipic Acid

M.F ; $(CH_2)_4(COOH)_2$

IUPAC name ; Hexanedioic Acid

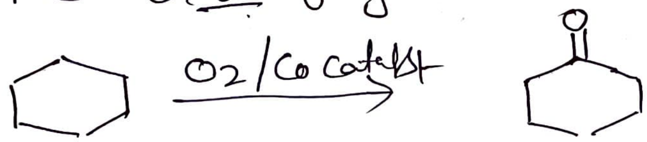
M.S ; $H-O-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-O-H$

Step ① Reduction of benzene to cyclohexane



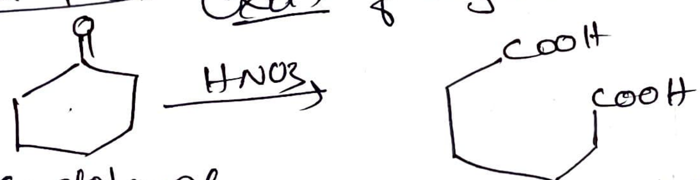
Benzene Cyclohexane

Step ② Oxdn of Cyclohexane to Cyclohexone



Cyclohexane Cyclohexone

Step ③ Oxdn of Cyclohexone to adipic Acid

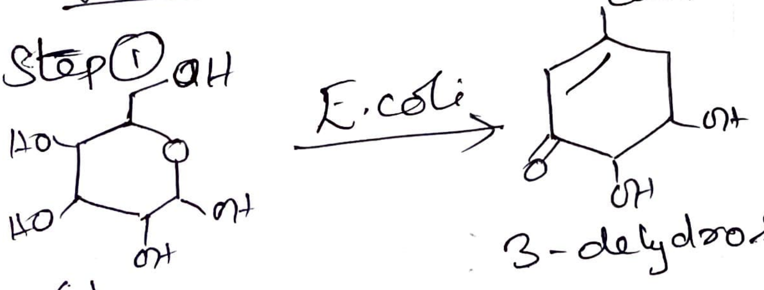


Cyclohexone Adipic Acid.

Atom Economy is less.

Green chemistry [from Glucose] of Adipic Acid

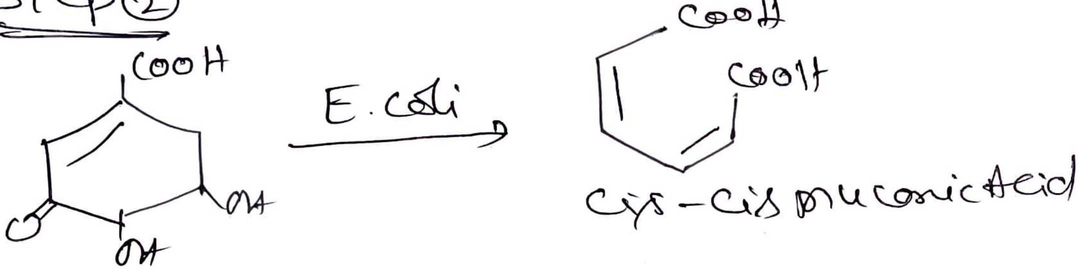
Step ①



3-dehydroshikimate

Glucose

Step ②



Cis-cis muconic Acid

Step ③

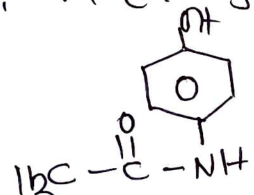
Cis-cis muconic Acid

adipic acid.

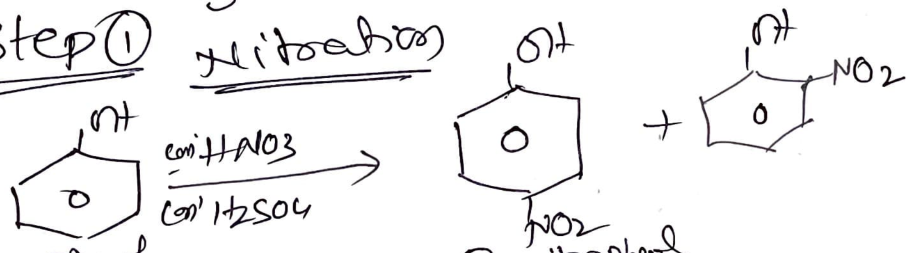
Paracetamol: also called acetaminophen

IUPAC: N-(4-hydroxyphenyl) ethanamide.

Str:



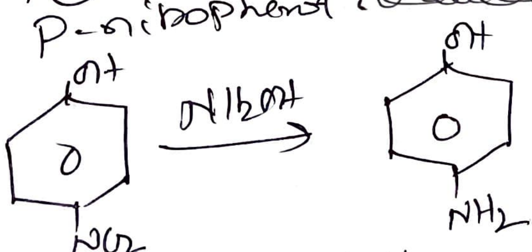
Step ① Nitration



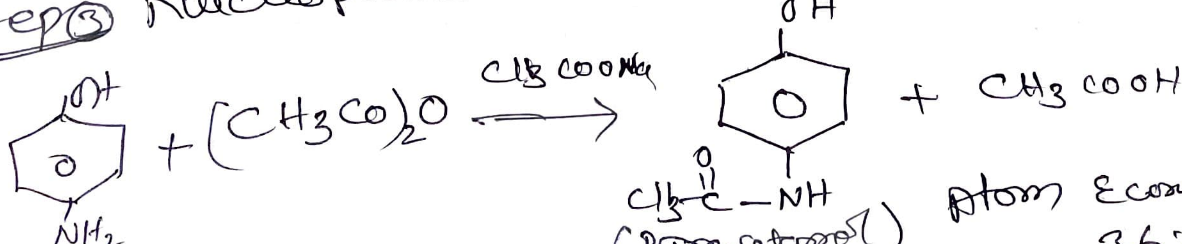
phenol

P-nitrophenol.

Step ② P-nitrophenol reduced to P-aminophenol.



Step ③ Nucleophilic addition

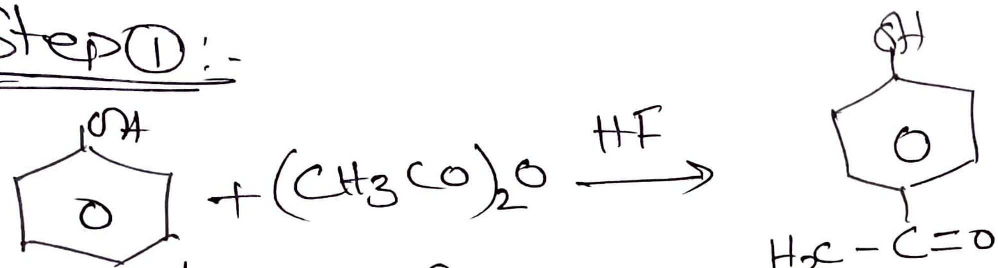


(paracetamol)

Atom Econmy 36%

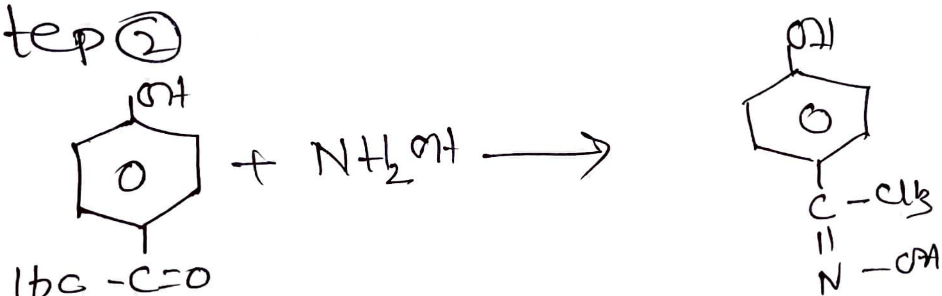
Green Synthesis of paracetamol

Step ①:-



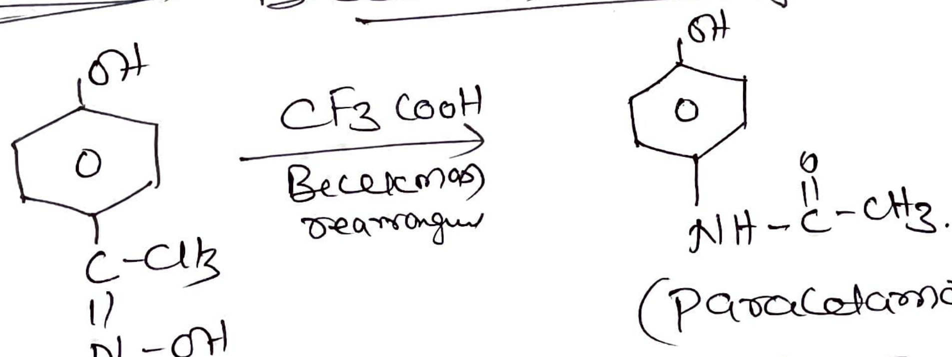
Phenol   a-a   4-Hydroxy acetophenone

Step ②



Ketoxime

Step ③   Beckman rearrangement.



(Paracetamol).

Atom Economy ≃ 58%.