C_Tech (CY8292) YEAR/SEM : II/IV

UNIT I : UNIT PROCESSES

B.TECH PETROLEUM ENGINEERING
CY8292 CHEMISTRY FOR TECHNOLOGISTS

(1) What is nitration? Explain the mechanism of nitration?

⇒ It involves introduction of nitro group into a compound.

⇒ Aromatic compounds are nitrated via electrophilic aromatic substitution mechanism.

⇒ Overall transformation is from R-H to $R-NO_2$

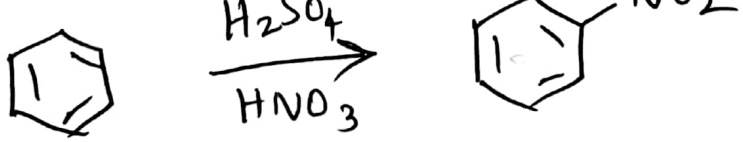
⇒ Fuming Conc. HNO_3 and mixture of HNO_3 & H_2SO_4 are generally used as a reagents.

⇒ Nitration reactions are notably used for the production of explosives.

Example: Conversion of guanidine to nitro guanidine.

Conversion of toluene to trinitrotoluene.

⇒ The nitrated derivatives have application in industry as solvents, explosives, TNT and nitrobenzene.

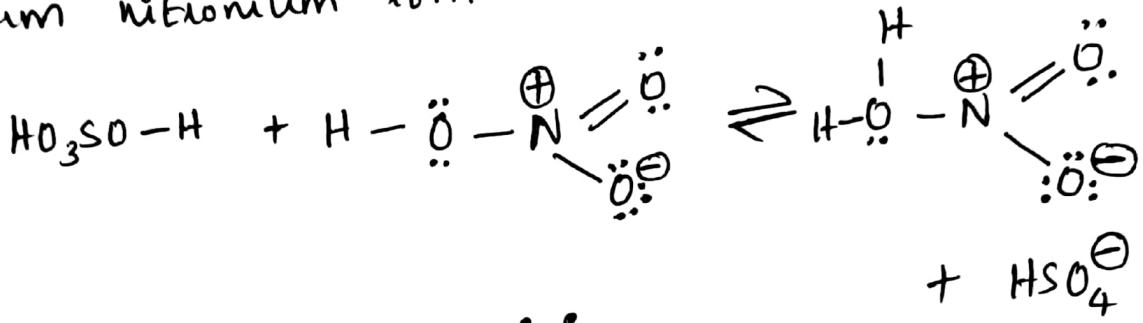


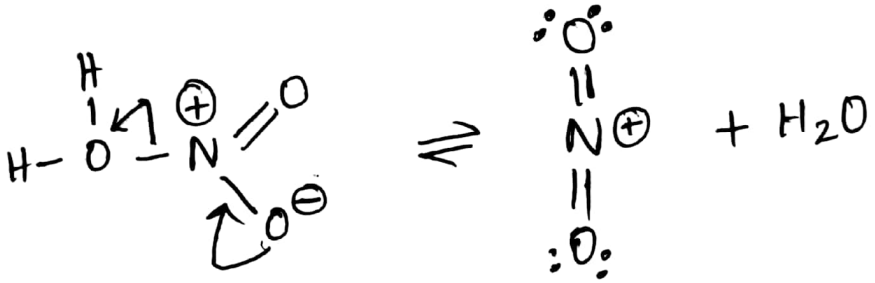
Benzene Nitrobenzene.

Reaction mechanism:

Step 1

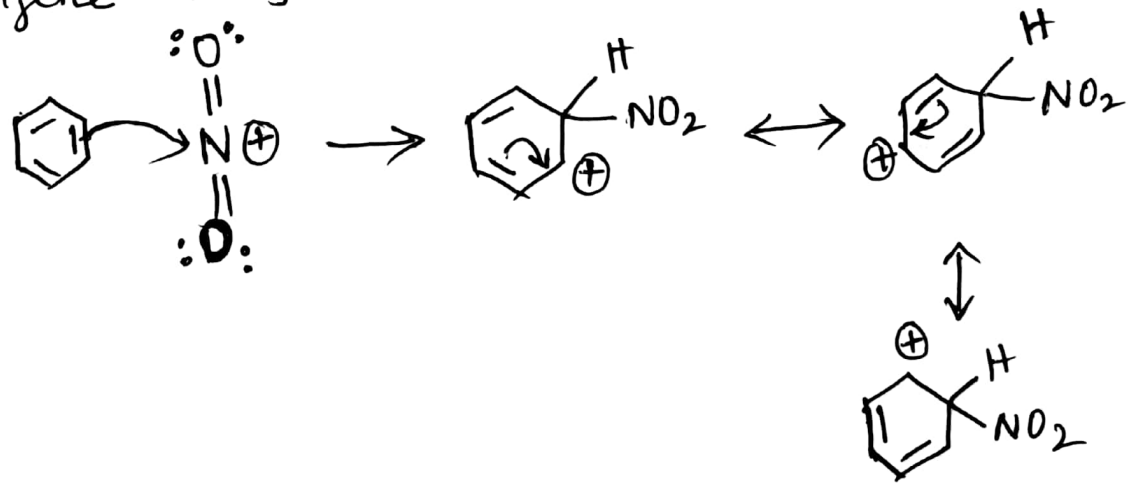
Nitric acid (HNO_3) accepts a proton from sulphuric acid (H_2SO_4) and then dissociates to form nitronium ion.





Step 2

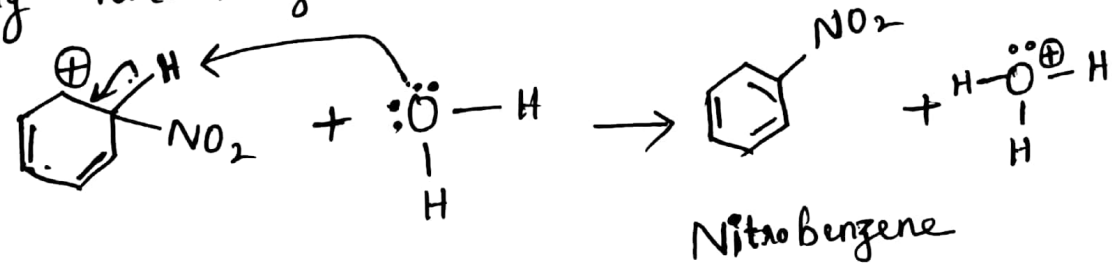
The nitronium ion acts as an electrophile in the process which further reacts with benzene to form arenium ions.



Arenium ions.

Step 3

The arenium ion then loses its proton forming nitrobenzene



Nitrobenzene

2.) Write down the role of sulphonation in pharmaceutical industries.

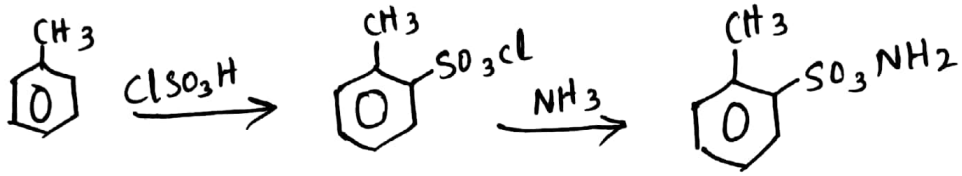
⇒ Sulfonation has a major function in modulating the biological activities of a wide number of endogenous and foreign chemicals, including: drugs, toxic chemicals, hormones, and neuro transmitters. The activation as well as inactivation of many xenobiotics and endogenous compounds occurs via Sulfonation. The process is catalysed by members of the cytosolic sulfotransferase (SULT) superfamily consisting of atleast ten functional genes in humans.

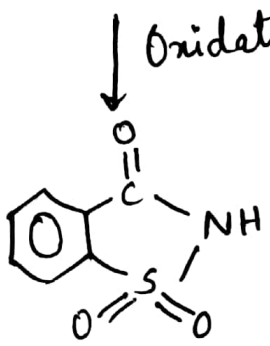
⇒ Under physiological conditions, Sulfonation is regulated, in part, by the supply of the co-substrate / donor molecule 3'-phosphadensoine-5-phosphosulfate (PAPS), and transport mechanisms

by which sulfonated conjugates enter and leave cells.

The major application of sulphonation is in the production of linear alkyl benzene sulphonates, toluene sulphonates, and saccharin etc.

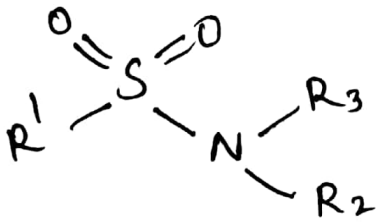
① It is used in the preparation of sweetening agents.





Saccharin

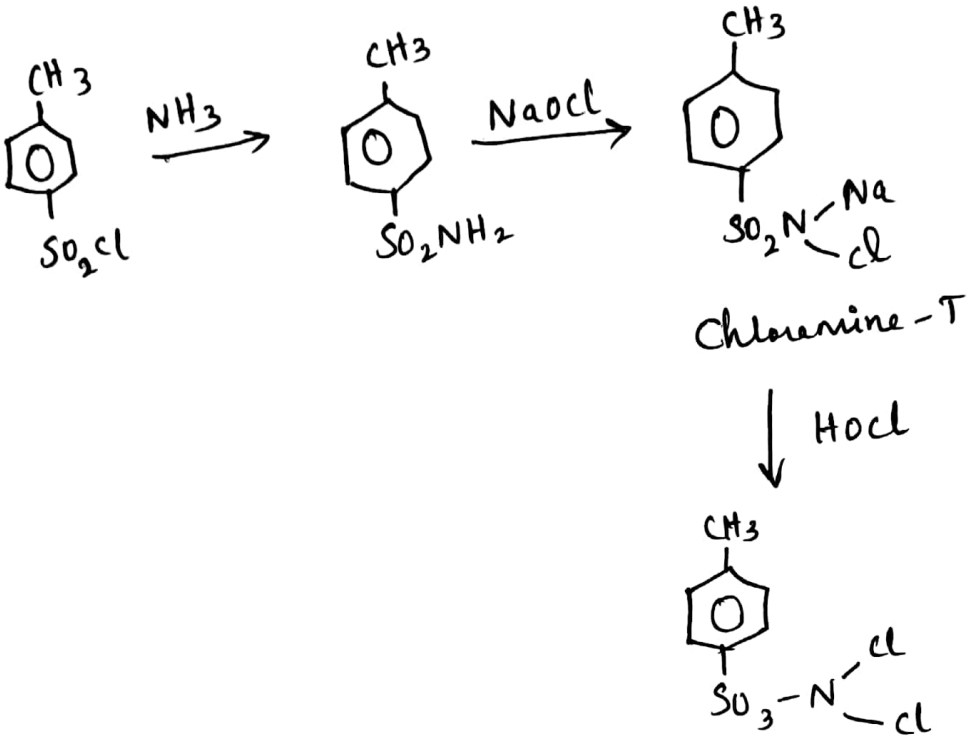
② Sulfa drugs



Sulfonamide functional groups.

Sulfonamide is a functional group that is the basis of several groups of drugs which are called as sulfa drugs. Antimicrobial agents that contain the sulfonamide group.

③ Chloramine-T and dichloramine-T are used for preparing disinfectant lotion and antiseptic cream.



Chloramine-T

Dichloramine-T.

④ Halozone is used for sterilizing drinking water.

⑤ Sulphonated polystyrene is used as ion exchange resin in water treatment.

⇒ Electrophilic species SO_3 which can be formed by the loss of water from H_2SO_4.

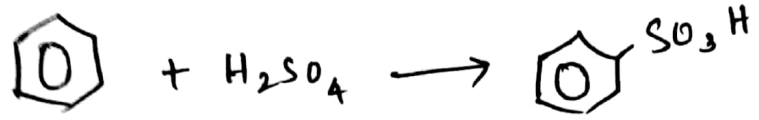
⇒ The chemical transformation is from R–H to $R-SO_3H$.

⇒ Conc. H_2SO_4, chlorosulfonic acid, metallic sulfates, etc are used as reagents.

⇒ It is exothermic, but not highly corrosive.

⇒ Unlike other electrophilic aromatic reactions, sulphonation is reversible.

⇒ Example, sulfonation of benzene.

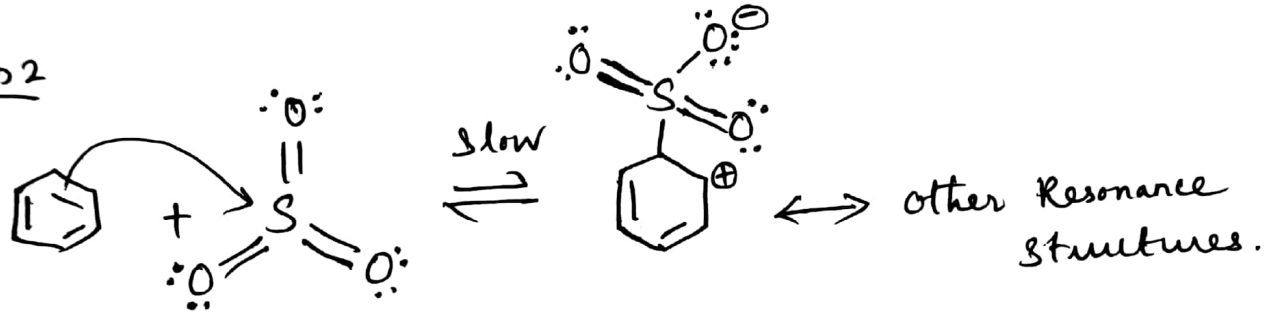


Mechanism:

Step 1

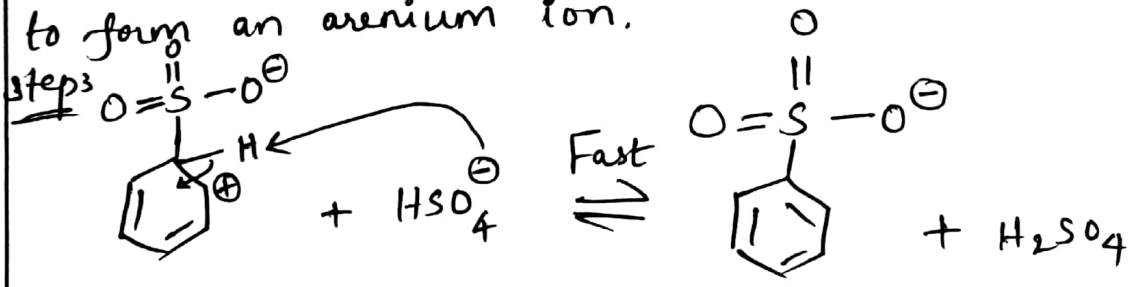
$$2\,H_2SO_4 \rightleftharpoons SO_3 + H_3O^+ + HSO_4^-$$

Step 2



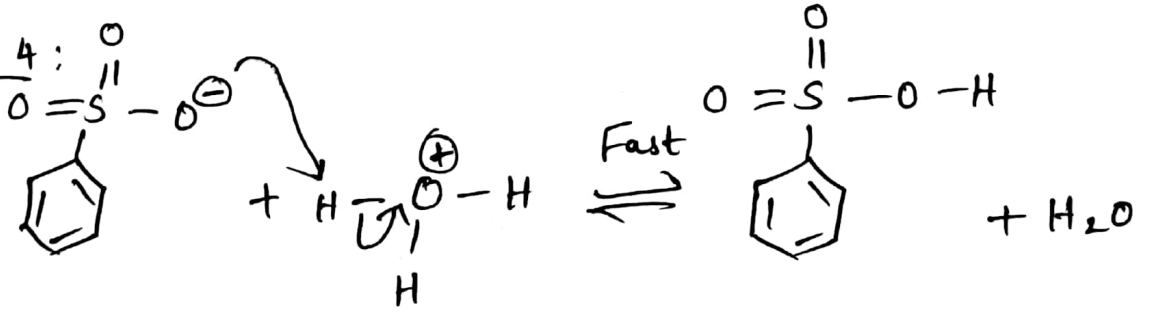
SO_3 is the electrophile that reacts with benzene to form an arenium ion.

Step 3



A proton is removed from the arenium ion to form benzenesulfonate ion.

Step 4:



The benzenesulfonate ion accepts a proton to become benzenesulfonic acid.

(3) Define halogenation? Explain the mechanism of halogenation.

⇒ The overall transformation is R-H → R-X. The halogenation is a chemical reaction that involves the addition of one or more halogens to a compound or material.

⇒ The inorganic elements such as F, Cl, Br and I are called as halogens.

⇒ The main function of halogen carrier is to polarise the halogen - halogen bond and generate the electrophile.

⇒ The product resulting from halogenation will have quite distinct properties from the reactants.

Example:

Methane, CH_4 is a gas that burns easily if you chlorinate (Halogenation of chlorine) forms different substances like CH_3Cl or CH_2Cl_2 or $CHCl_3$ or CCl_4 named mono-, di-, tri- and tetra- chloromethane. The completely chlorinated compound CCl_4 is a strong de-greasing cleaning fluid but highly harm for liver and kidneys.

There are three types of halogenation.

1. Free radical halogenation
2. Addition halogenation
3. Substitution halogenation.

1) Free radical halogenation

$$RCH_3 + X_2 \longrightarrow RCH_2X + HX$$

Alkane — Halogen — Alkyl halide — Hydrogen halide.

Initiation

$$X_2 \xrightarrow{h\nu} 2X^{\cdot}$$

Halogen — Halide Radical

propagation

$$X^{\cdot} + RCH_3 \longrightarrow RCH_2^{\cdot} + HX$$

Halide Radical — Alkane — Alkyl radical

$$X_2 + RCH_2^{\cdot} \longrightarrow RCH_2X + X^{\cdot}$$

Termination

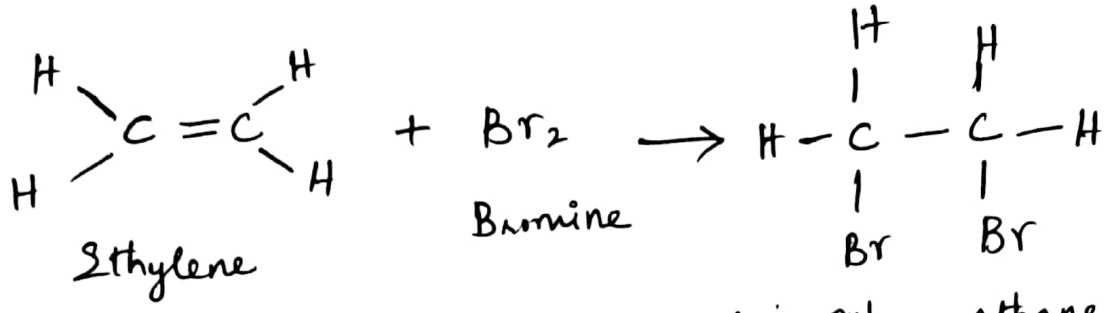
$$X^{\cdot} + RCH_2^{\cdot} \longrightarrow RCH_2X$$

$$X^{\cdot} + X^{\cdot} \longrightarrow X_2$$

$$RCH_2^{\cdot} + RCH_2^{\cdot} \longrightarrow RCH_2CH_2R$$

2) Addition halogenation

Addition of bromine to ethane.



Ethylene

1,2-Dibromoethane.

3) Substitution halogenation:

⇒ Halogen react with alkanes under the influence of heat or light to form alkyl halides.

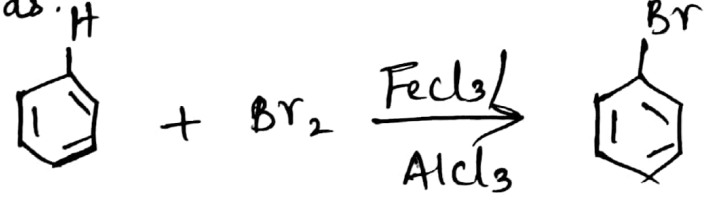
$$CH_4 + Cl_2 \xrightarrow[h\nu]{\Delta} CH_3Cl + HCl$$

Methyl Chloride.

$$CH_3CH_3 + Br_2 \xrightarrow[h\nu]{\Delta} CH_3CH_2Br + HBr.$$

⇒ The halogen atom replaces a hydrogen atom in the alkane is called substitution halogenation reaction.

⇒ Aromatic compounds undergo halogen substitution reactions in the presence of Lewis acids.



(4) Explain with reactions about the industrial applications of esterification process.

⇒ When alcohols or phenols reacts with carbonylic acid in presence of acid medium forms ester and the process known as esterification.

⇒ Esterification is a reversible process and is also called as Fischer esterification.

⇒ Esterification is one of the condensation reactions of carbonylic acid.

⇒ The acid catalyst promotes the esterification reaction in two way,

1) It causes the carbonyl function (makes the carbonyl carbon more electrophilic) to undergo nucleophilic attack by alcohol.

2) protonation of the hydroxyl group gives water, which is a superior leaving group in the elimination step.

⇒ Commonly used catalysts for Fischer esterification are H_2SO_4, p-toluenesulfonic acid and Lewis acids.

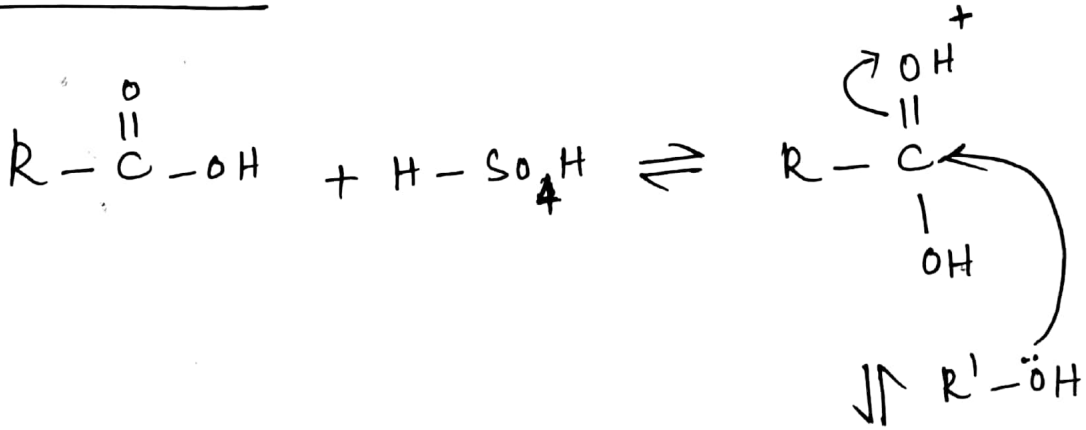
⇒ Esterification reaction is playing major role in polymer industry (To synthesis terylene, PMMA

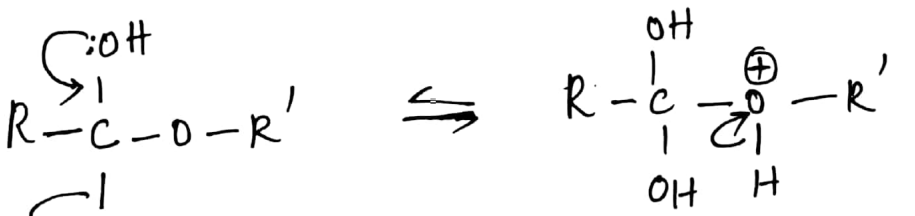
and cellulose ester), food industry (synthetic oils, soup and artificial sweetening agent) and pharmaceutical industry (Aspirin in the treatment of fever, as pain killer, to prevent heart attacks).

$$R-COOH + R'-OH \xrightarrow{H_2SO_4} R-COO-R'$$

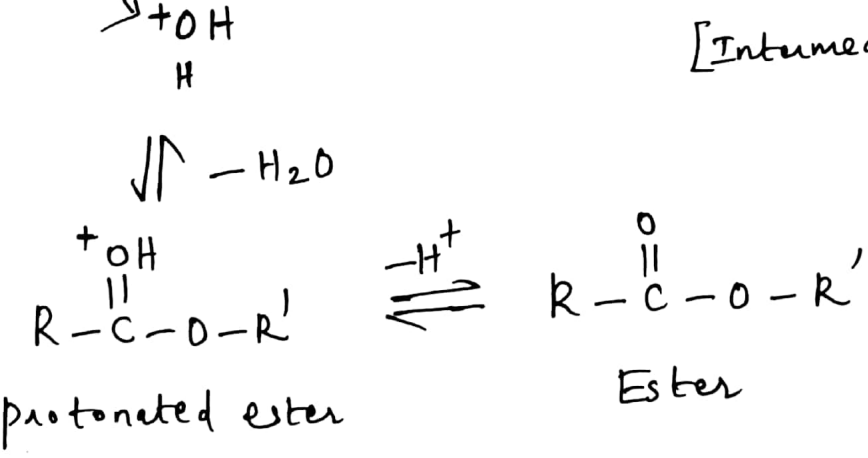
Acid Alcohol Ester

Reaction mechanism





[Intermediate]



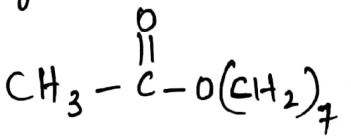
protonated ester Ester

⇒ Esters are used as food and drugs preservative.

⇒ Esters are used as food additives to improve the flavour and smell.

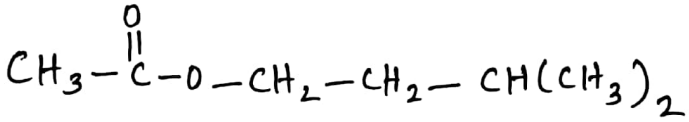
Examples:

* Octylacetate



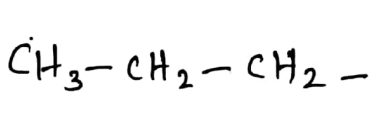
(Orange flavour)

* Isoamide acetate



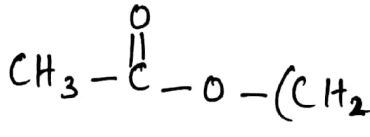
(Banana flavour)

* Ethyl butyrate



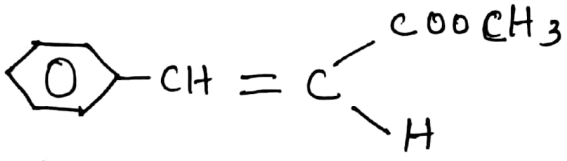
(Pine apple flavour)

* Butyl acetate



(Apple flavour)

* Methyl trans cinnamate



(Strawberry flavour)

⇒ It is an important unit process in the manufacture of polyethylene terephthalate (PET), methylmethacrylate, cellulose ester in viscous Rayon manufacture.

5.) **Define amination ? Explain the mechanism of amination.**

⇒ Amination is the process by which an amine group is introduced into an organic molecule through the formation of new C–N bond.

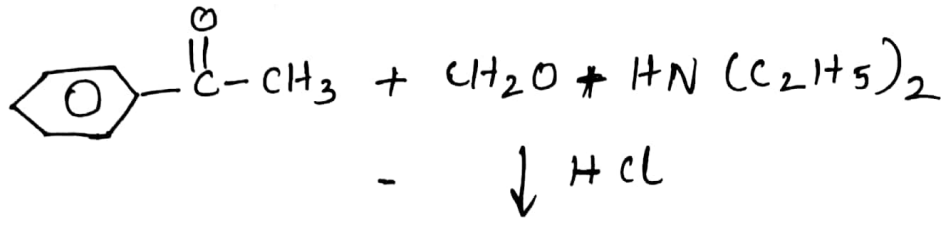
⇒ Nitrogen is a constituent elements in amino acids, proteins and nucleic acids.

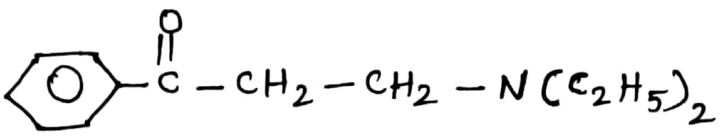
⇒ C–N bonds are found in the majority of organic molecules, especially biologically active molecules.

⇒ Nitrogen containing compounds are valuable and commercially important bulk chemicals and pharmaceuticals.

Examples

Acetophenone reacts with formaldehyde and ammonia (or) a primary amine (or) a secondary amine to form β – aminoketones.





β – Aminoketone

All aromatic ketones containing an α-hydrogen give this reaction. The products of the mannich reaction are known as mannich bases.

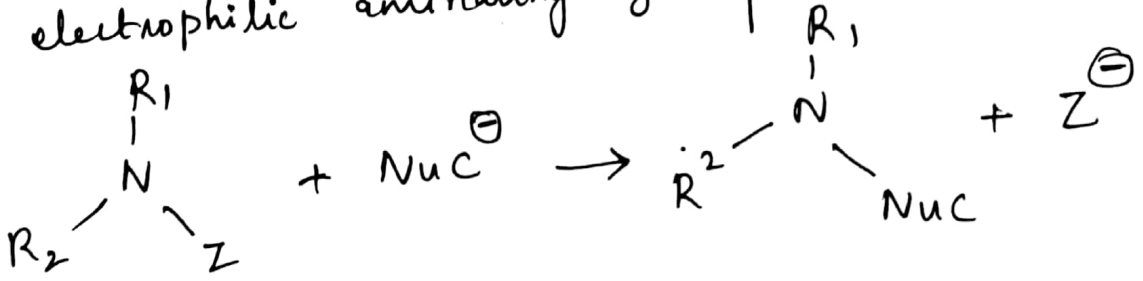
Many alkyl amines are produced industrially by the amination of alcohols using ammonia in the presence of acid catalysts.

$$CH_3OH + HNH_2 \xrightarrow[\Delta]{Al_2O_3} CH_3NH_2 + H_2O$$

Types of amination:

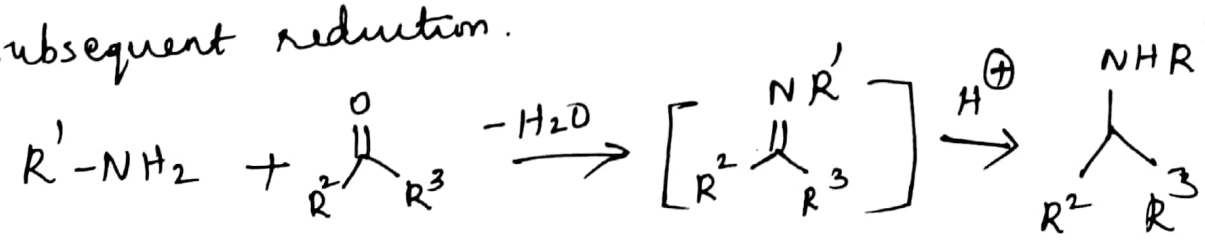
1) Electrophilic amination

Combination of nucleophilic carbon and an electrophilic aminating groups.



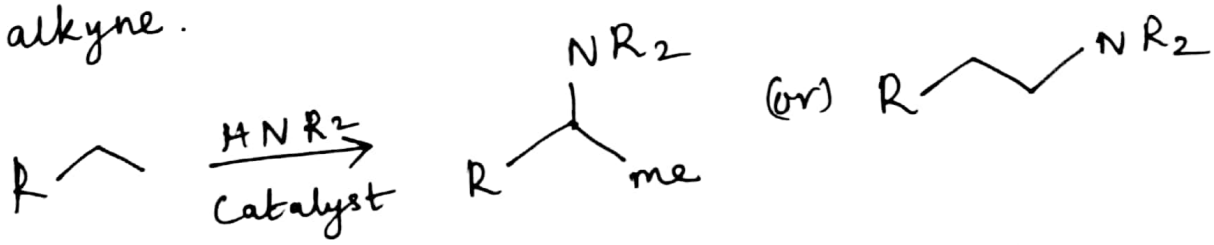
2) Reductive amination

Conversion of a carbonyl group of an amine via an intermediate imine and subsequent reduction.



3) Hydroamination

Addition of N–H bond over an alkene or alkyne.



4) Nucleophilic Amination

Introduction of an amino group via nucleophilic aminating group.

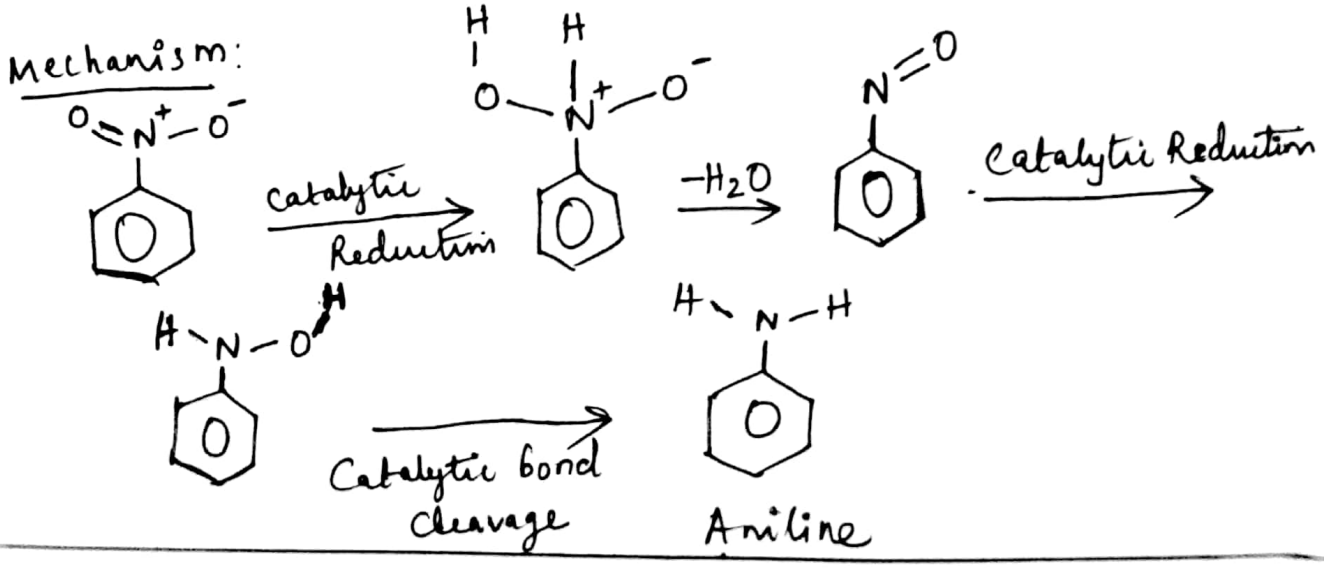
Example : Gabriel amine synthesis.

⇒ Amination by Reduction involve the synthesis of amines by reductive methods.

$$C_6H_5NO_2 + 2Fe + 6HCl \longrightarrow \underset{\text{Aniline}}{C_6H_5NH_2} + 2H_2O + 2FeCl_3$$

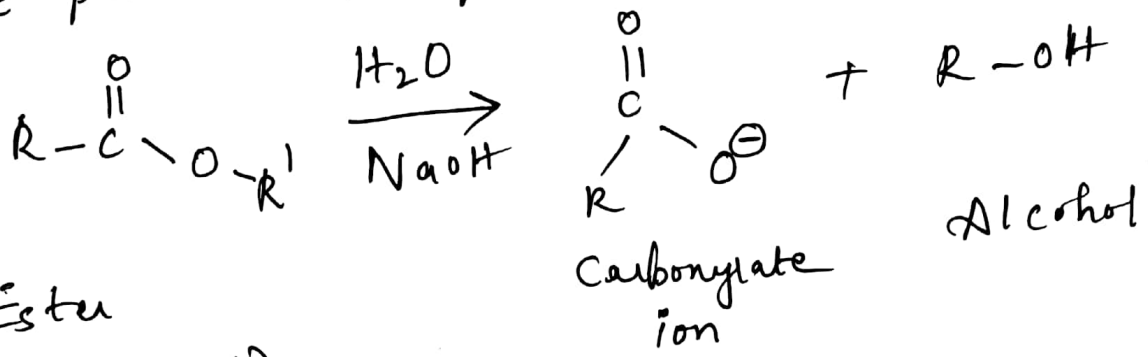
Nitrobenzene

Mechanism:



(6) **What is saponification process? Explain how soap is manufactured?**

⇒ Saponification is a chemical process that involves conversion of fat or oil into soap and alcohol by the action of heat in the presence of aqueous alkali (ex. NaOH).

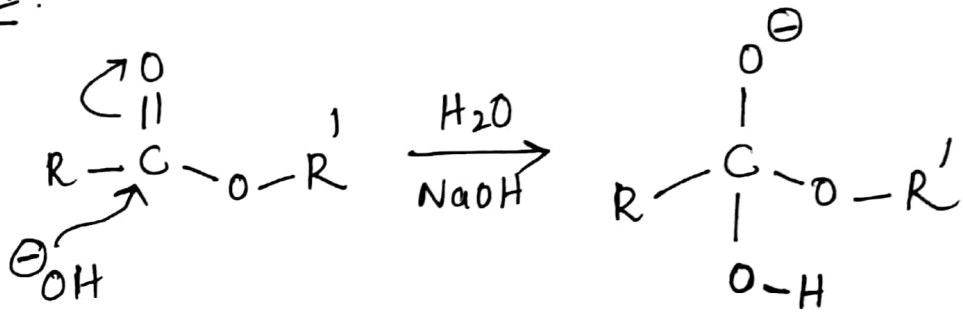


⇒ Alkali (base) that dissolves in solution producing hydroxide ions.

⇒ It is the important reaction used in soap industries. This method is ideal for producing ~~⇒ Alkali (base) that dissolves in solution producing hydroxide ions~~ soaps that are derived from a single fatty acids which leads to soaps with predictable physical properties, as required by many engineering applications.

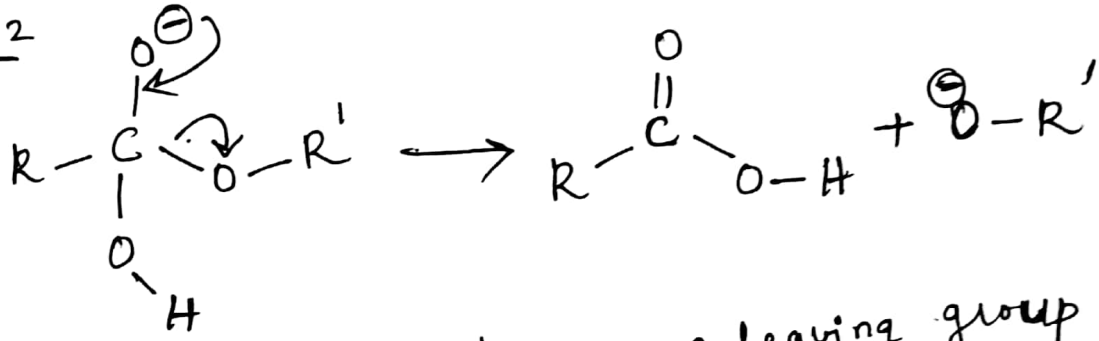
Reaction mechanism

Step 1:



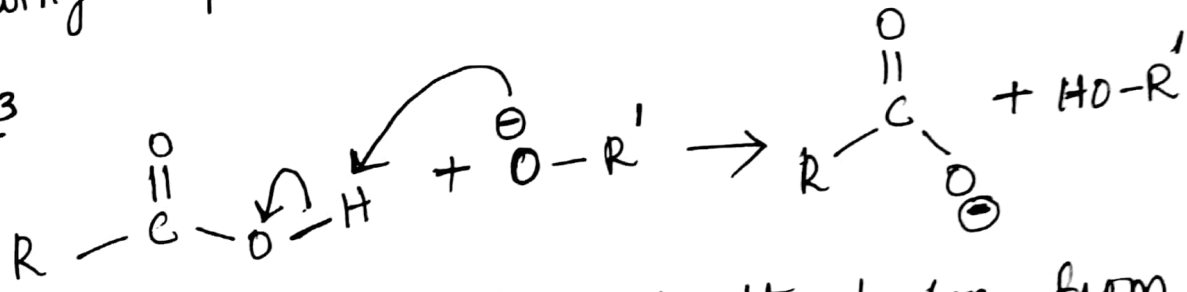
The hydroxide ion from the alkali molecule undergo nucleophilic attack on the ester or fatty molecule.

Step 2



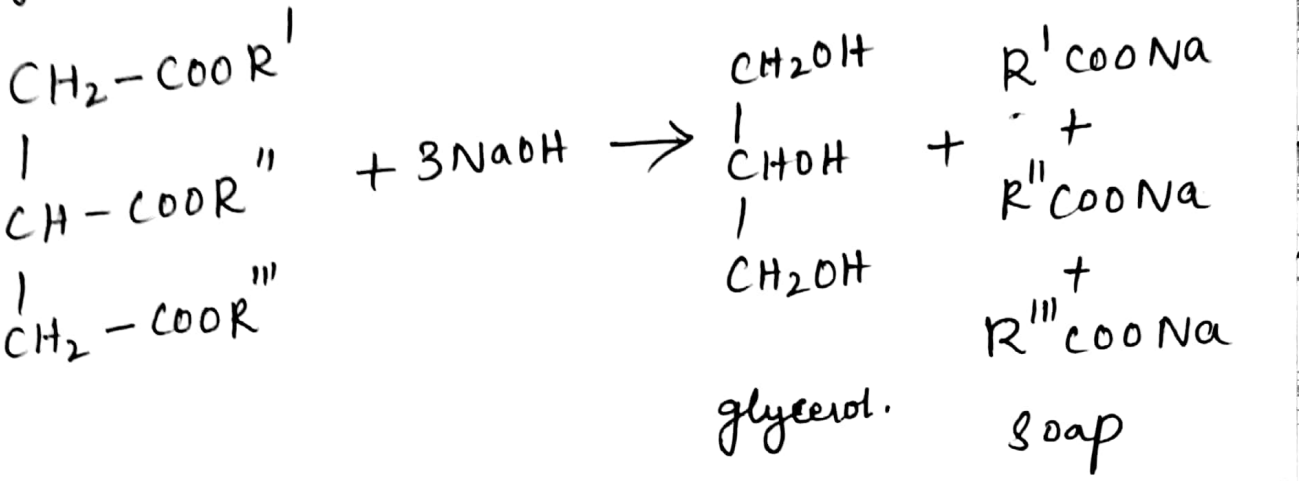
The -OR group becomes a leaving group following step 1 creates a carbonyl group.

Step 3



The -OR group abstracts the proton from carboxylic acid. This process of removing a proton from a molecule is called deprotonation. Once deprotonated the final products such as carboxylate and alcohol are formed.

⇒ Triglycerides of oil or fat react with aqueous NaOH or KOH to give soap and glycerol.



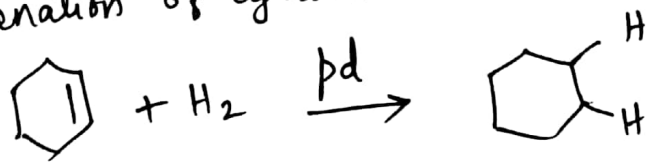
---

(7) Explain with reactions about the industrial applications of hydrogenation process.

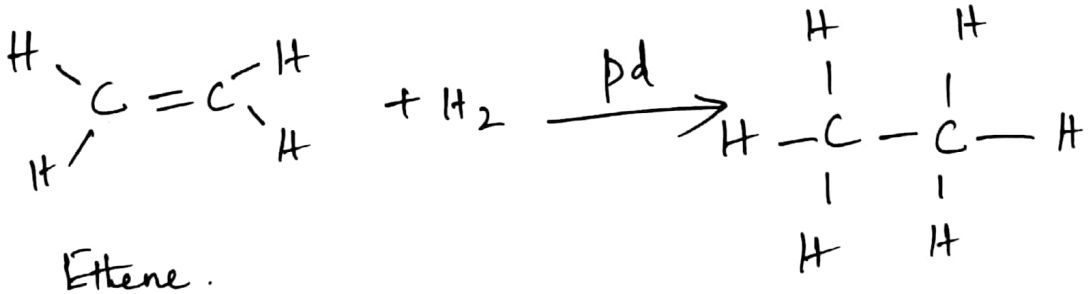
This process is commonly employed to reduce or saturate organic compounds. Hydrogenation typically constitutes the addition of pairs of hydrogen atoms to an alkene molecule. Hydrogenation reduces double and triple bonds present in the hydrocarbons. in presence of a catalyst such as Ni, pd or pt.

The major application areas of hydrogenation reaction are food industry, processing of vegetable oils, petrochemical industry, to convert alkenes and aromatics into saturated alkanes and cycloalkanes.

Hydrogenation of cyclohexane.



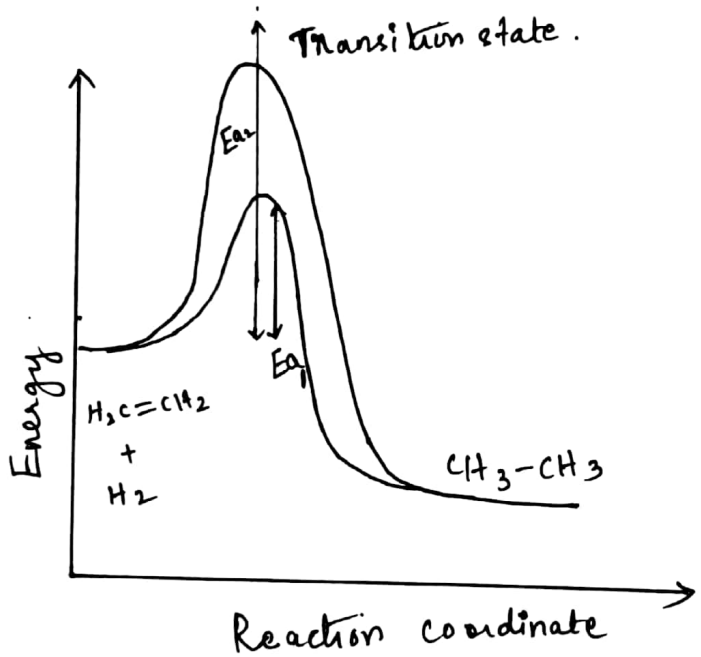
Hydrogenation of ethene



Ethene.

Ethane

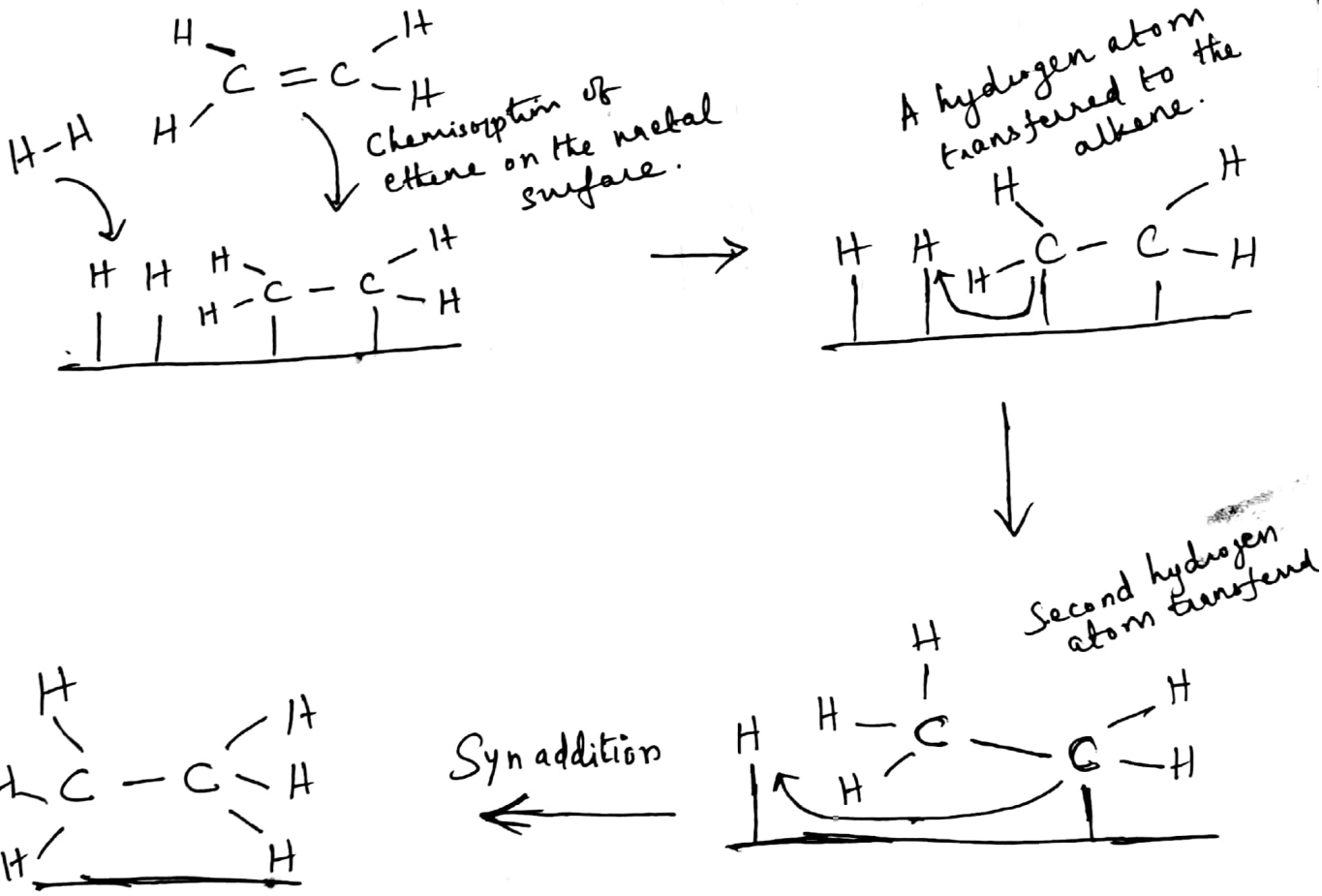
Hydrogenation energy diagram :



Reaction Mechanism

Common catalysts used are insoluble metals such as palladium in the form of pd-c, platinum in the form of PtO_2 and nicked in form of Ra-Ni. In the presence of metal catalyst,

The H–H bond (H_2) attaches to the metal catalyst surface. At the same time, substrate (Ethene) also chemisorbed on the surface of the catalyst. Then, the two hydrogens have added to the each carbon of ethene and is also called as syn addition



⇒ Some of other reaction involving hydrogenations are hydroformylation, hydrocracking hydroaminolysis and synthesis of ammonia, etc.

⇒ ⇒ preparation of aldehyde (Hydroformylation)

$$H_2 + CO + \underset{\text{propene}}{CH_3-CH=CH_2} \longrightarrow \underset{\text{Butynaldehyde}}{CH_3-CH_2-CH_2-CHO}$$

⇒ Hydrogenation of coal to synthetic gasoline or petrol.

⇒ Hydrogenation of oil or fat to give vanaspathi.

⇒ Selective hydrogenation catalyst like Wilkinson's Catalyst, Crabtree's catalyst are the most popular catalyst which utilised by the pharmaceutical and pesticide industries.