LECTURE

CHEM-461

UNIT PROCESSES IN ORGANIC INDUSTRIES

INTRODUCTION

- Chemical process is combination of unit processes and Unit operation.
- A process may require many unit operations to obtain the desired product from the starting materials, or feedstocks.
- Unit process involves Principle chemical conversions leading to synthesis of various useful product and provide basic information regarding the reaction temperature and pressure, extent of chemical conversions and yield of product of reaction nature of reaction whether endothermic or exothermic, type of catalyst used.
- Unit operations involve the physical separation of the products obtained during various unit processes. Various unit processes in chemical industries are given in following Table

Table M-I 3.1: Unit Processes in Chemical Process Industries

Alkylation and Hydro delkylation	Decomposition
Acylation	Fermentation
Ammonoxidation	Halogenation
Amination by reduction	Hydsogenation
Amination	Hydrohenatlysis
Aromatisation	Hydroformylation
Amination by ammonalysis	Hydro lysis
Calcination	Hydration
Carbonation	Hydroammonalysis
Causticisation	Isomerisation
Chlorination and Oxy chlorination	Neutralistion
Condensation	Nitration
Biomethhanation	Methanation
Carbinisation	
Disproportination	Oxidation and partial oxidation
Cracking: Thermal, steam cracking, catalytic cracking	Pyrolysis
Dehydration	Polymeristion: Addition and condensation Chain growth and step growth,Bulk, Emulsion, suspension, solution, Radical and coordination polymeristion
Dehydrogenation	Reduction
Ditozitation and coupling	Reforming: Steam reforming Catalytic reforming
Gasification of coal and biomass	Sulphidation
Desulphurisation and hydro desulphurisation	Sulphonatiomn
Electrolysis	Sulphation
Etherification	Xanthation
Estertification and Trans Estrerificartion	

SULPHONATION

- Overall transformation: Ar/R-H to Ar/R-SO3H
- Reagents: Conc. H2SO4, chlorosulfonic acid, metallic sulfates,etc.
- Electrophilic species: SO3 which can be formed by the loss of water from the sulphuric acid.
- It is exothermic, but not highly corrosive.
- Unlike the other electrophilic aromatic substitution reactions, sulphonation is reversible.

❖ Reaction mechanism

- Typical conditions involve heating the aromatic compound with sulfuric acid.
- Sulfur trioxide or its protonated derivative is the actual electrophile in this electrophilic aromatic substitution.
- To drive the equilibrium, dehydrating agents such as thionylchloride can be added.

❖ Applications:

- In production of linear alkyl benzene sulphonates, toluene sulphonates, saccharin,etc.

REACTION MECHANISM

Step 1

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

This equilibrium produces SO_3 in concentrated H_2SO_4.

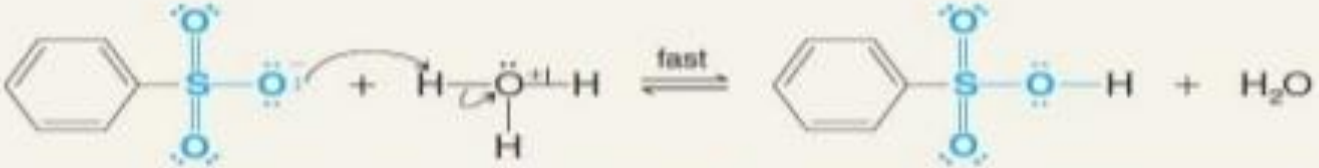
Step 2

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

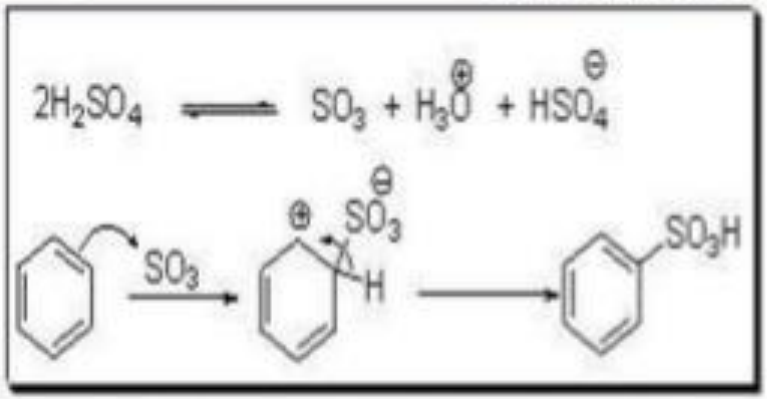
Step 3

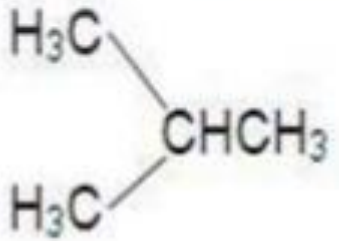
A proton is removed from the arenium ion to form the benzenesulfonate ion.

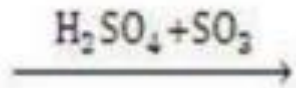
Step 4

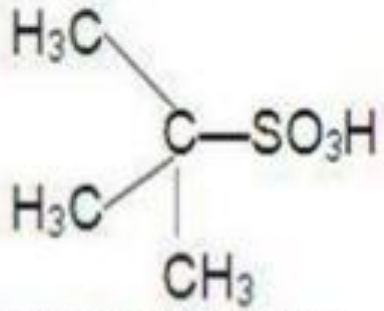


The benzenesulfonate ion accepts a proton to become benzenesulfonic acid.









t-butylsulphonic acid

HALOGENATION

- Overall transformation: Ar/R-H to Ar/R-X
- Reagents: Chlorine, hypochloite ,hydrobromic acid,etc.

- It is carried out in the presence of a catalyst which acts as a halogen carrier.

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

- Halogenation of aromatic compounds differs from the halogenation of alkenes ,which do not require a lewis acid catalyst.

- Halogenation by reaction type:-

1)Free radical halogenation
2)Addition of halogens to alkenes and alkynes
3) Halogenation of aromatic compounds

❖ Applications:

- In formation of halogen derivatives such as CCl4, CFCs, Alkyl halides,etc.

REACTION MECHANISM

$$\underset{\text{Alkane}}{RCH_3} + \underset{\text{Halogen}}{X_2} \longrightarrow \underset{\text{Alkyl halide}}{RCH_2X} + \underset{\text{Hydrogen halide}}{HX}$$

Initiation

$$\underset{\text{Halogen}}{X_2} \xrightarrow{h\nu} \underset{\text{Halide radical}}{2\,X\cdot}$$

Propagation

$$\underset{\text{Halide radical}}{X\cdot} + \underset{\text{Alkane}}{RCH_3} \longrightarrow \underset{\text{Alkyl radical}}{RCH_2\cdot} + HX$$

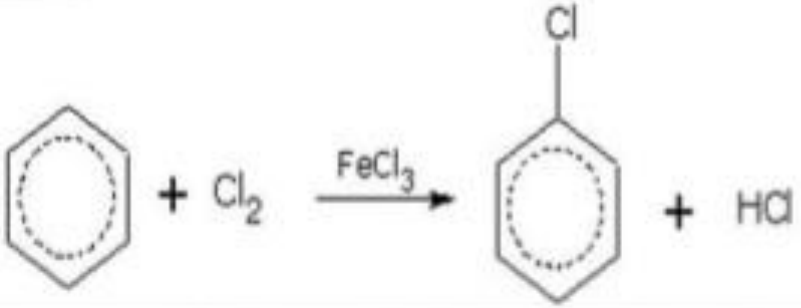
$$\underset{\text{Halogen}}{X_2} + \underset{\text{Alkyl radical}}{RCH_2\cdot} \longrightarrow \underset{\text{Alkyl halide}}{RCH_2X} + \underset{\text{Halide radical}}{X\cdot}$$

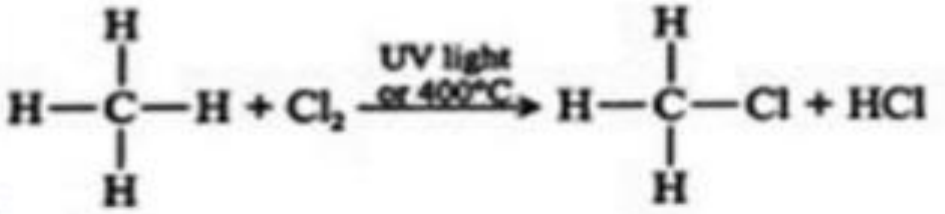
Termination

$$X\cdot + RCH_2\cdot \longrightarrow RCH_2X$$

$$X\cdot + X\cdot \longrightarrow X_2$$

$$RCH_2\cdot + RCH_2\cdot \longrightarrow RCH_2CH_2R$$





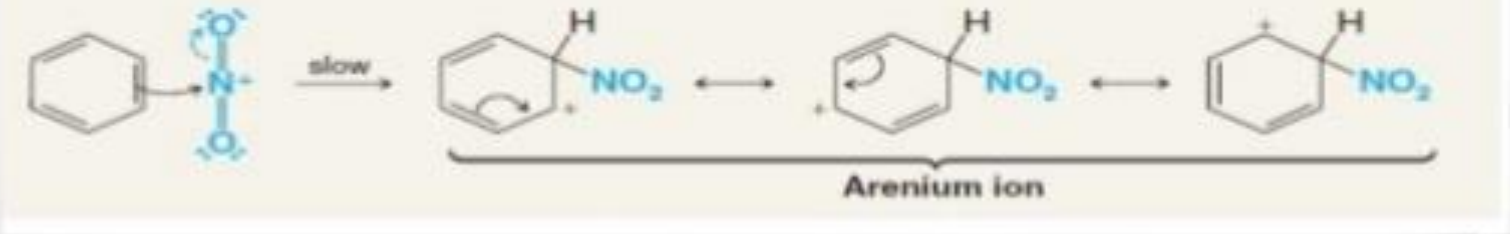
NITRATION

- Overall transformation: Ar/R-H to Ar/R-NO_2.
- Reagents: Fuming Conc. HNO_3, mixture of HNO_3 & H_2SO_4.
- It involves introduction of nitro group into a compound.
- Aromatic compounds are nitrated via EAS mechanism.
- The formation of a nitronium ion from HNO_3 & H_2SO_4 and subsequent reaction of the ion with the sample takes place.
- Nitration reactions are notably used for the production of explosives, for example the conversion of guanidine to nitroguanidine and the conversion of toluene to trinitrotoluene.
- Applications: The nitrated derivatives have applications in industry as solvents, explosives, TNT, Nitro benzene, etc.

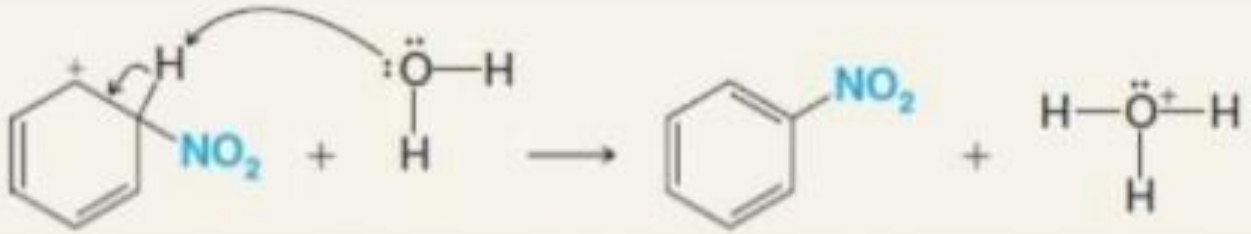
REACTION MECHANISM

Step 1: Nitric acid accepts a proton from sulphuric acid and then dissociates to form nitronium ion.

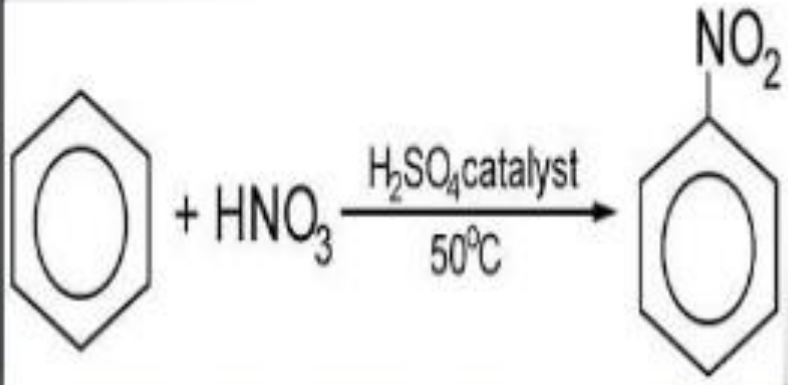
Step 2: The nitronium ion acts as an electrophile in the process which further reacts with benzene to form arenium ion.



Step 3: The arenium ion then loses its proton to Lewis base forming nitrobenzene.



Examples:-



$CH_3CH_2CH_3 + HNO_3 \longrightarrow$

- $CH_3CH_2CH_2NO_2$ 1-nitropropane (25%)
- CH_3CHCH_3 with NO_2 — 2-nitropropane (40%)
- $CH_3CH_2NO_2$ nitroethane (10%)
- CH_3NO_2 nitromethane (25%)

ESTERIFICATION

- When alcohols or phenols reacts with carboxylic acid in presence of acidic media formation of ester take place this process is know as Esterification reaction.
- Reversible reaction.
- Known as (ficher-speier Esterification).

❖ Uses of Esterification reaction

1.Polymer industry

- Terylene,PMMA and cellulose ester.

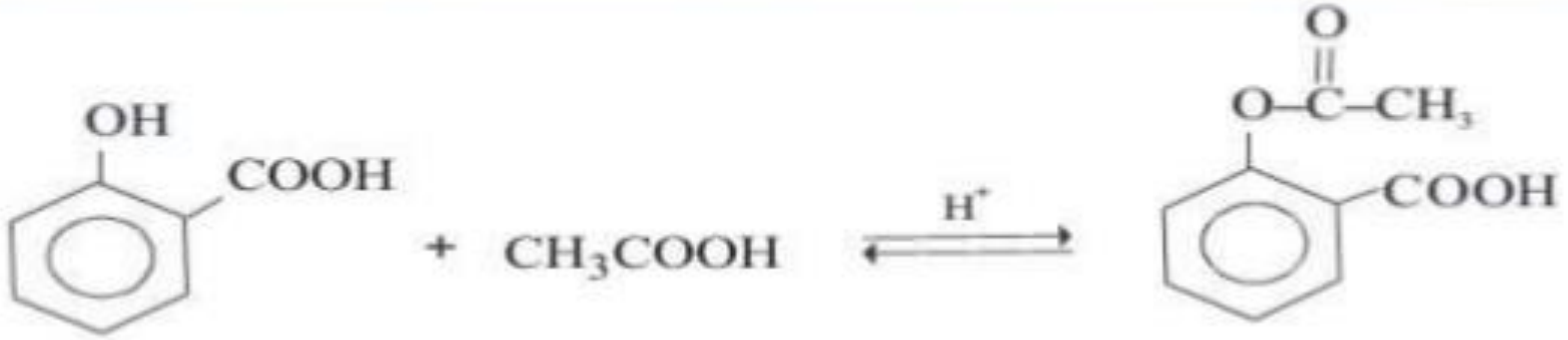
2.Food industry

- Synthetic oils,soap and artificial sweetening agent.

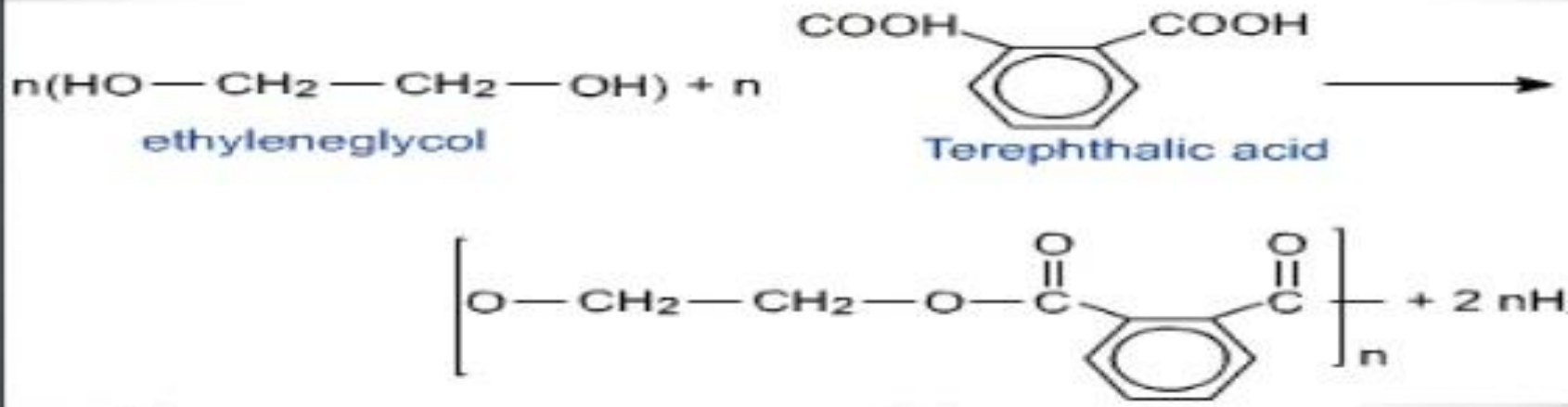
3.Pharmaceutical industry

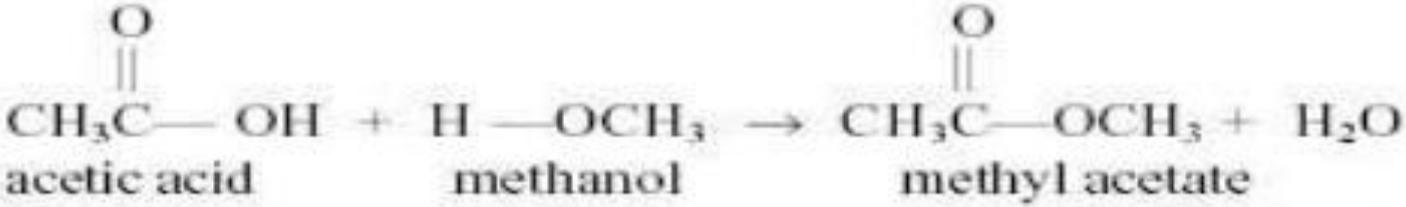
- Aspirin- in treatment of fever,as pain killer,to prevent heart attacks.

EXAMPLES OF ESTERIFICATION REACTION

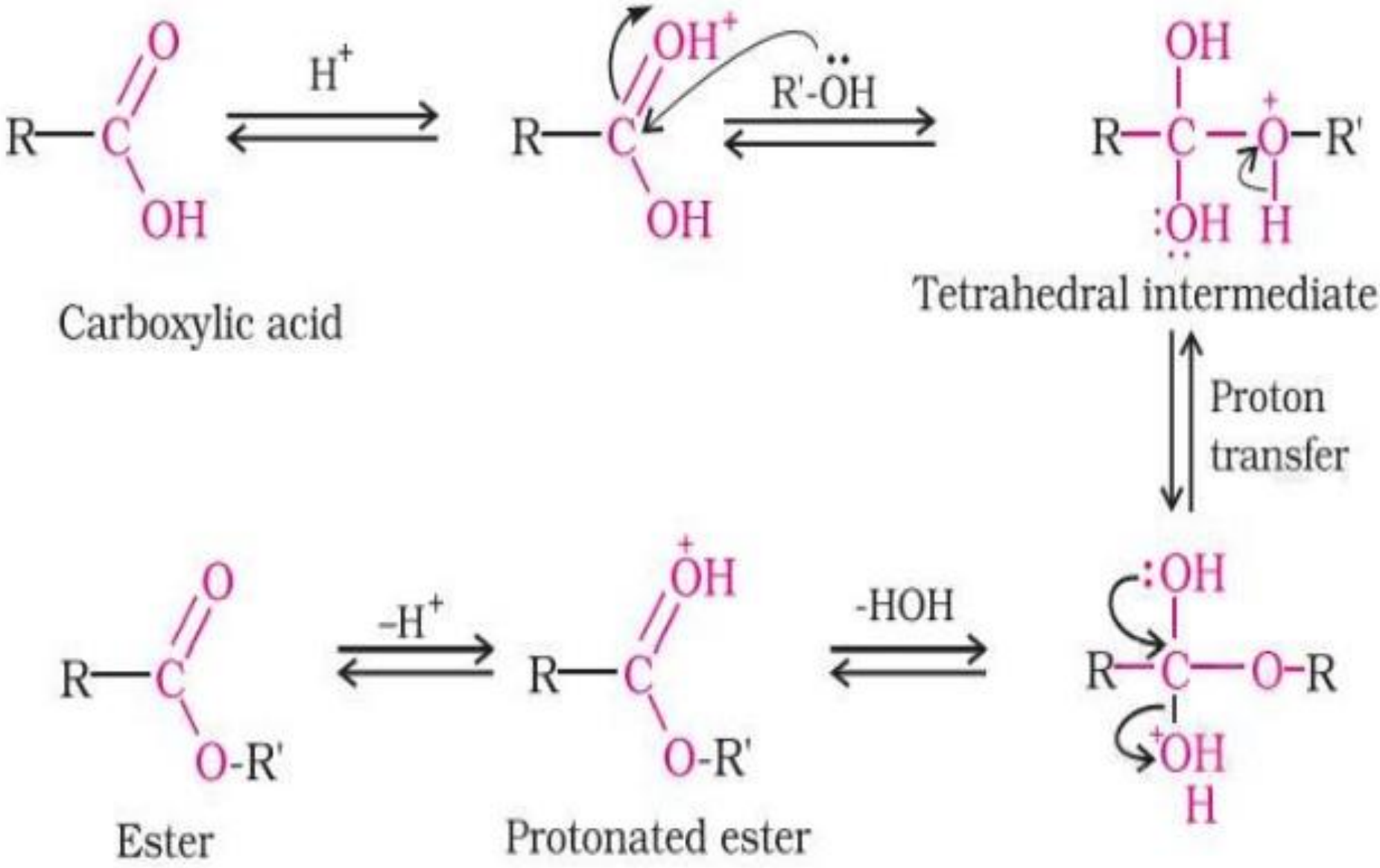


2-Hydroxybenzoic acid **Ethanoic acid** **Acetyl salicylic acid**





MECHANISM OF REACTION



HYDROGENATION

- When unsaturated organic compound reacts with Hydrogen gas in presence of a catalyst such as Ni,Pd,or Pt.formation of less unsaturated organic compound take place .these types of reaction is called Hydrogenation.
- Industrial application of Hydrogenation reaction

➢ Food industry

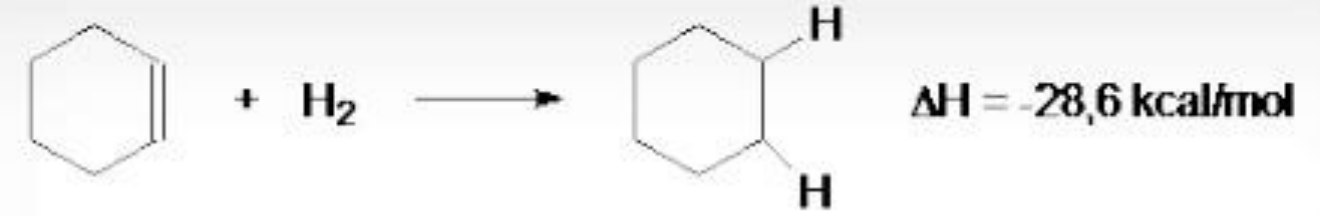
➢ Processing of vegetable oils.

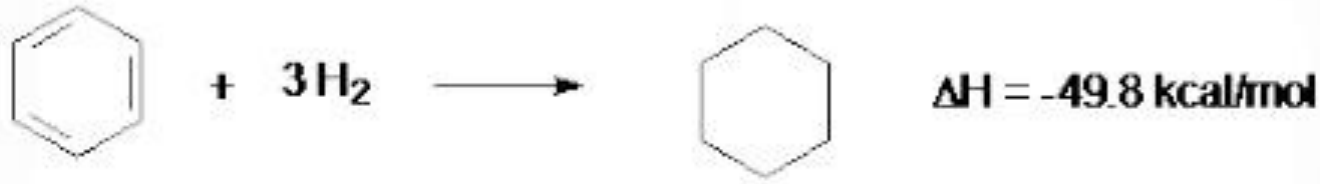
➢ Petro chemical industry

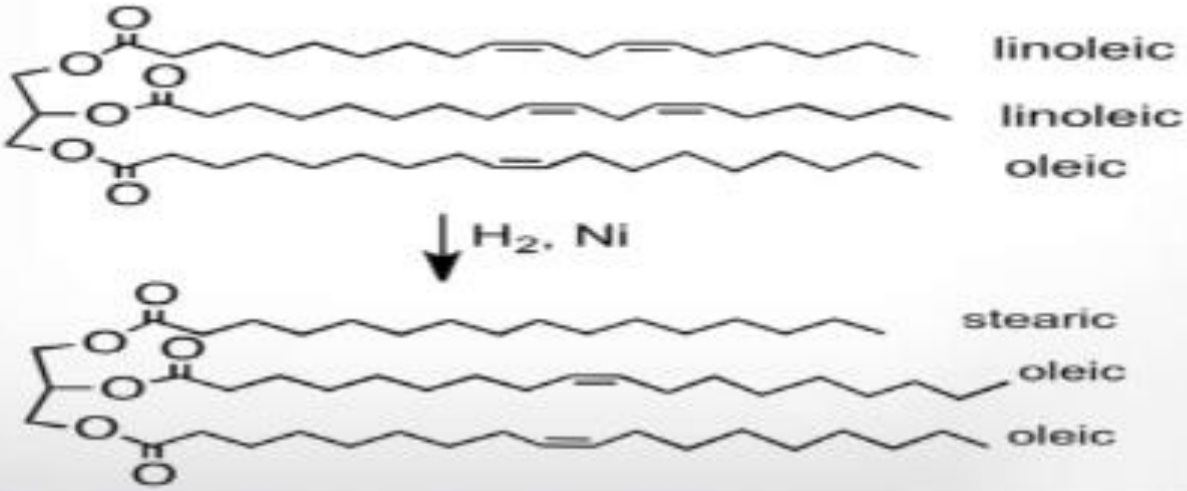
➢ To convert alkenes and aromatics into saturated alkanes and cycloalkanes.

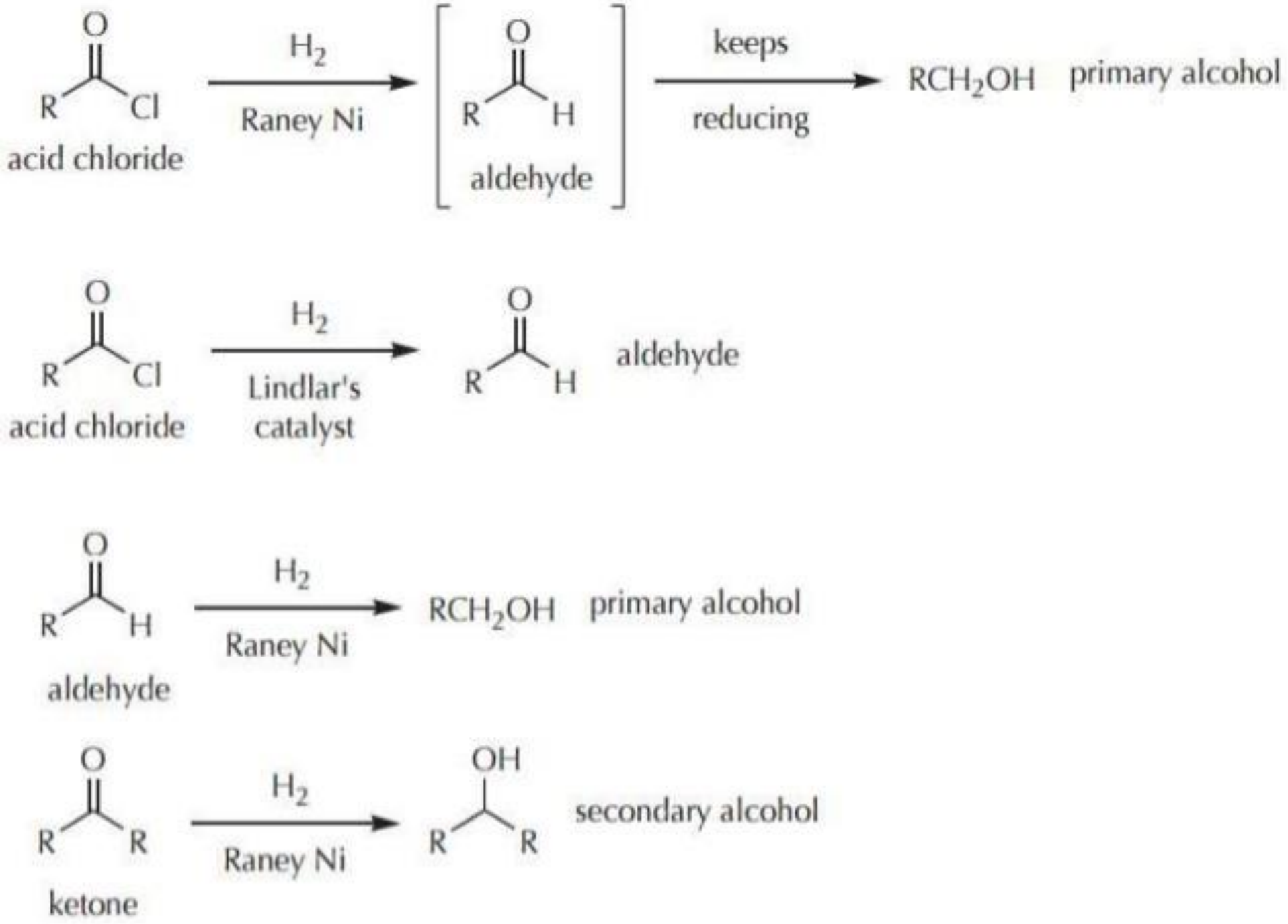
➢ Organic chemistry

EXAMPLES OF HYDROGENATION REACTION

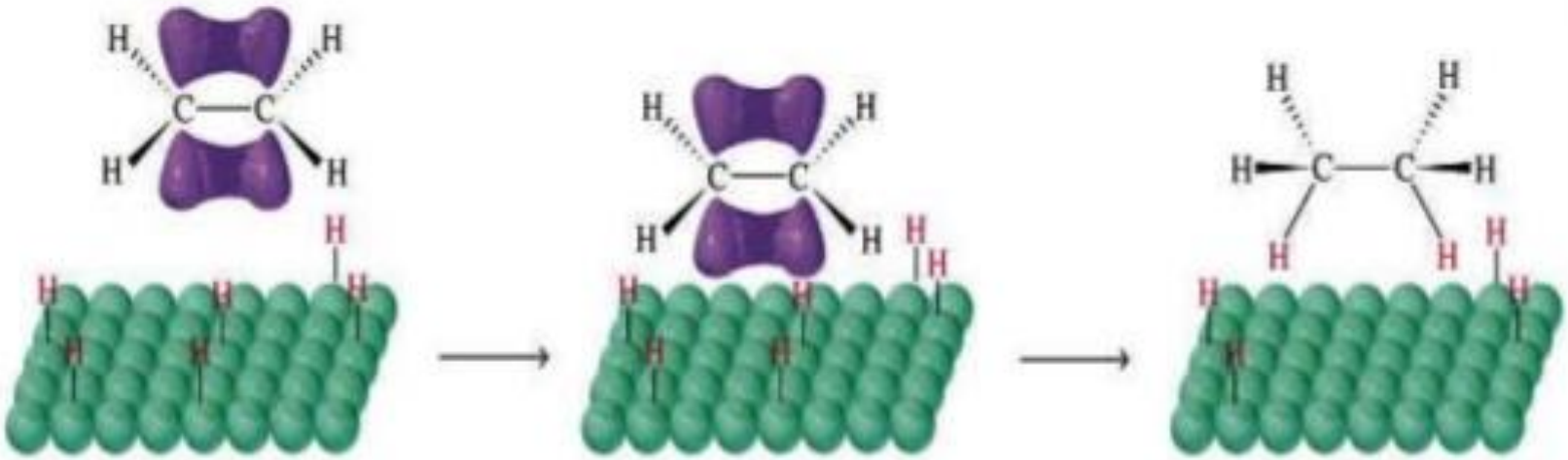


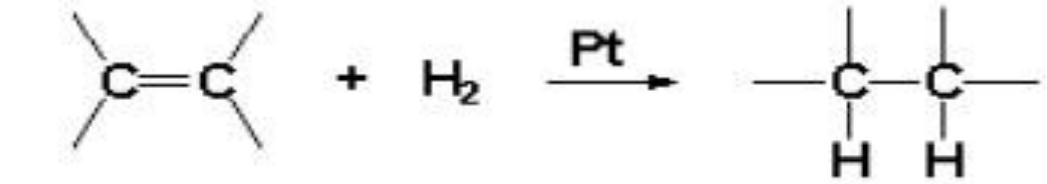


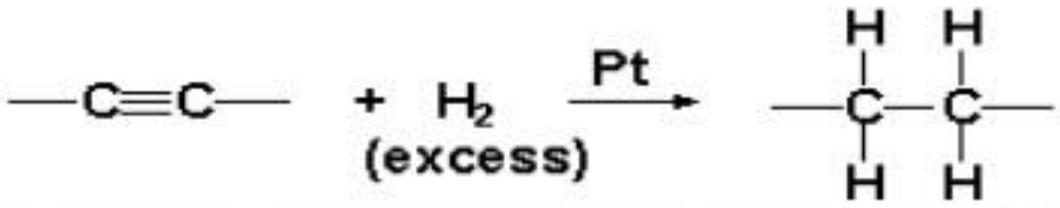



O
R
Cl
acid chloride
H_2
Raney Ni
O
R
H
aldehyde
keeps
reducing
RCH_2OH
primary alcohol
O
R
Cl
acid chloride
H_2
Lindlar's
catalyst
O
R
H
aldehyde
O
R
H
aldehyde
H_2
Raney Ni
RCH_2OH
primary alcohol
O
R
R
ketone
H_2
Raney Ni
OH
R
R
secondary alcohol

MECHANISM OF REACTION AND EXAMPLE







OXIDATION

- In reference to organic molecules, carbon atom gain bond to more electro negative elements, most commonly oxygen.
- some important oxidising agents.

KMnO4,K2Cr2O7, conc.H2So4,O2,O3, H2O2,Mno2, Oso4,pcc,m-cpba etc.

- Important products of oxidation reaction and their application

1. ketone

- Acetone-nail paint remover and for acne treatment.
- Organic solvent.

2. Aldehyde

- Formaldehyde + 37% H2O=formalin.
- Germicide, fungicide and insecticide for plant and vegetables.
- For bakelite,u.f resin and melamine.
- Solvent
- Perfumes and flavouring agent.

3.Vanillin

- Flavouring agent of vanilla beans.

4.Benzoic acid

- It's salts are used as food preservatives.

5.Acetic acid

- Solvent
- Food preservative.
- 3-9% acetic acid by volume is vinegar.

TABLE OF IMPORTANT OXIDATION REACTIONS

Alcohol → Aldehyde
- PCC
- CrO_3/pyridine

Alcohol → Ketone
- PCC
- CrO_3/pyridine

Aldehyde → Carboxylic acid
- H_2CrO_4
- $KMnO_4$
- H_2O_2

Alcohol → Carboxylic acid
- $KMnO_4$
- H_2CrO_4

Alkane → Carboxylic acid
- $KMnO_4$

Alkene → Aldehyde/Ketone
- O_3, then Zn
- O_3, then CH_3SCH_3

Alkene → Carboxylic acid/Ketone
- O_3, then H_2O_2
- $KMnO_4$, heat, $H_3O^{\oplus}$

Alkyne → Carboxylic acid
- O_3, then H_2O_2
- $KMnO_4$, heat $H_3O^{\oplus}$

Alkene → Diol (vicinal diol)
- OsO_4
- $KMnO_4$, $HO^{\ominus}$

Alkene → Epoxide
- mCPBA

Diol → Aldehyde
- $NaIO_4$
- $Pb(OAc)_4$
- HIO_4

Ketone → Ester
- mCPBA