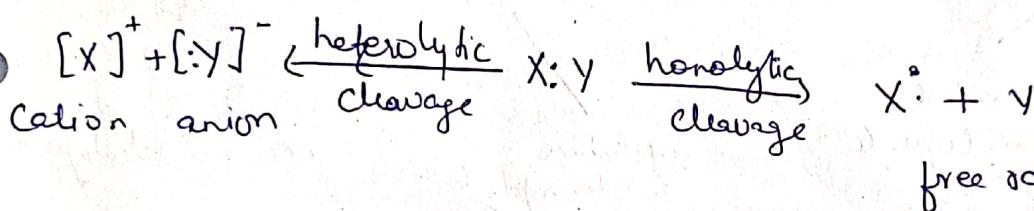


Organic compds  $\rightarrow$  hydrocarbons  
&  
their derivatives

$\rightarrow$  contains  
covalent  
bond,  
depending on elec.  
negativity

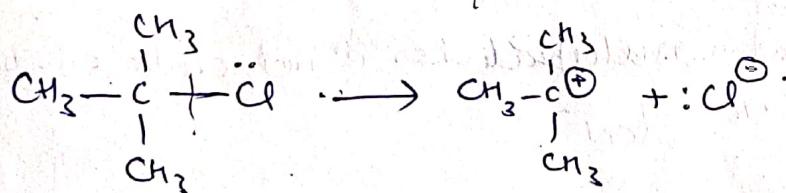
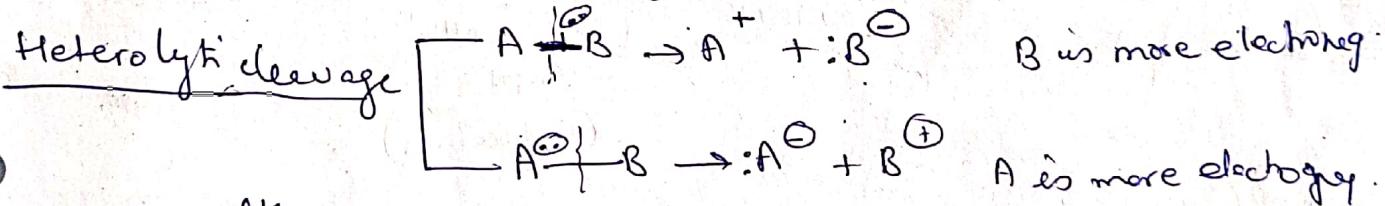
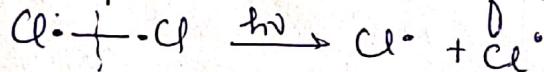
Homolytic  
cleavage

Heterolytic  
cleavage



eq.

Homolytic cleavage - Cleavage where in two bonded atoms separate  $\pm$  one  $e^-$  of the shared pair



Reagents: When rxn take place b/w 2 substances -

Substrate + Attacking reagent  $\rightarrow$  Product

↓  
Substance which get attacked.

Attack Reagents are of 2 types

### Nucleophile

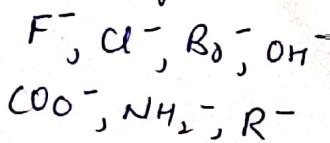
- have at least one lone pair of  $e^-$
- nucleus loving
- electron rich
- capable to donate  $e^-$  pairs
- Lewis bases

### Electrophile

- positively charged / neutral species which
- electron deficient
- can accept a pair of  $e^-$
- electron loving
- Lewis acids

#### Negative nucleophile

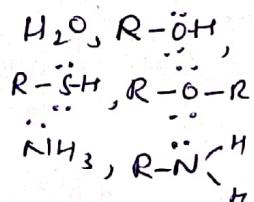
→ carry excess of electron pair lone -ve charged



(carbanion)

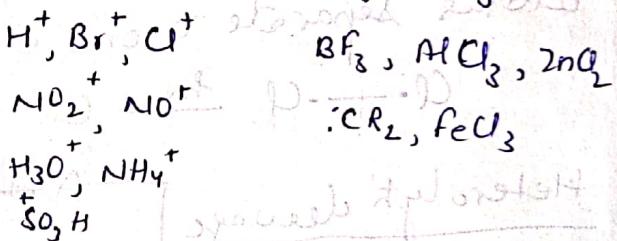
#### Neutral nucleophile

→ carry excess  $e^-$  pair but are neutral



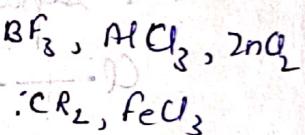
#### positive electrophile

→ carry +ve charge



#### neutral electrophile

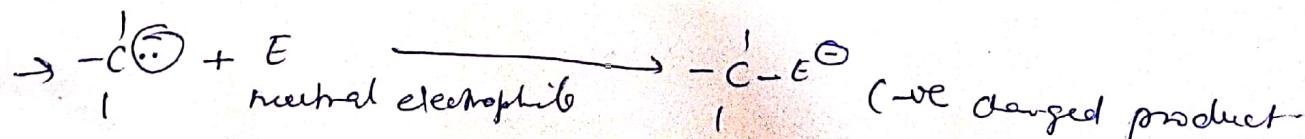
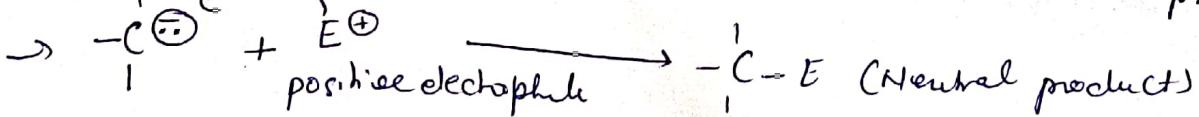
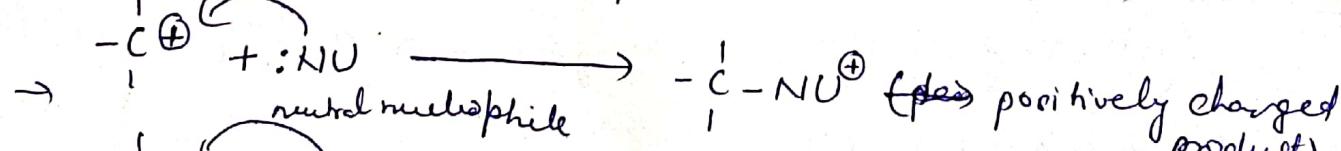
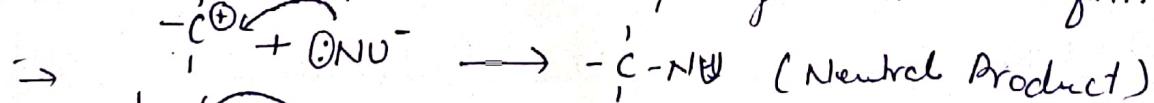
→ electron deficient species don't carry charge.



(carboocation)

Bidentate nucleophile: when nucleophile has  $e^-$ -rich centre on both sides such as  $CN^-$ ,  $NO_2^-$ ,  $SCN^-$

→ Negative nucleophile attack +vely charged substrate to form neutral product



## Organic Reactions

### Addition Rxn

- Nucleophilic add<sup>n</sup> rxn
- Electrophilic add<sup>n</sup> rxn
- free Radical add<sup>n</sup> rxn

### Substitution Rxn

- Nucleophilic sub<sup>n</sup> rxn
- S<sub>N</sub>1 & S<sub>N</sub>2
- Electrophilic Sub<sup>n</sup> rxn

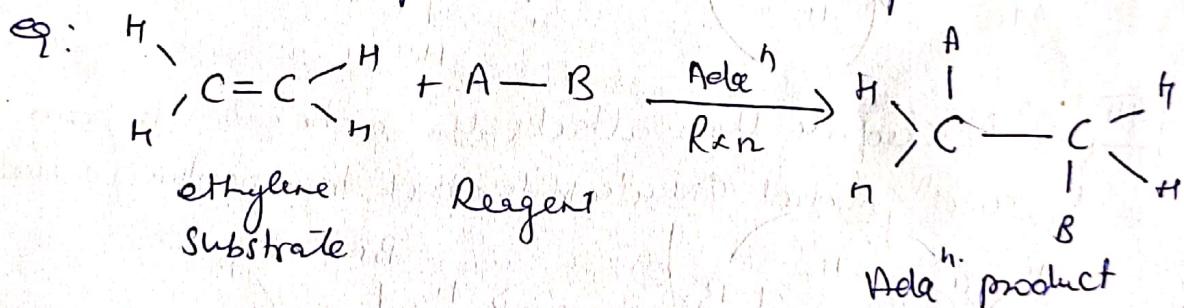
### Elimination Rxn

- E<sub>1</sub>

- E<sub>2</sub>

- E<sub>1,2</sub>

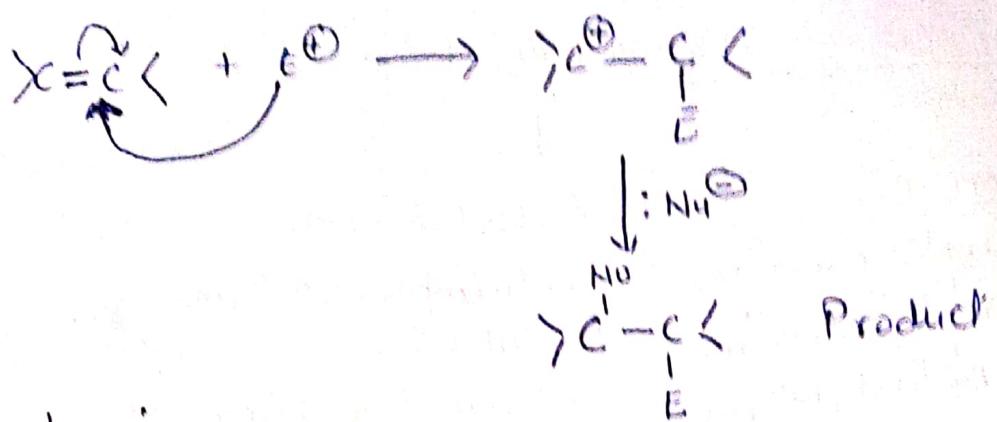
Addition Rxn : Rxn in which atoms/gps of atoms are added to a molecule  $\overset{\text{out}}{\text{C}}$  elimination of any atom/gp of atom  
 → no part of original molecule is lost & the product contains all the atoms of the reactant as well as that of the reagent.  
 → unsaturated compds, add<sup>n</sup> rxn takes place.



π bond is weaker than σ, hence more reactive.

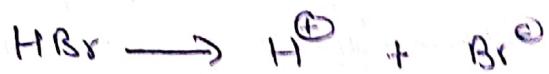
Electrophilic Add<sup>n</sup> Rxn : When add<sup>n</sup> rxn is effected by the add<sup>n</sup> of an electrophile followed by the add<sup>n</sup> of nucleophile, it is b/d Electrophilic add<sup>n</sup> rxn.

- characteristics of double bonds ( $>\text{C}=\text{C}<$ )
- typical rxns of alkenes & alkynes.

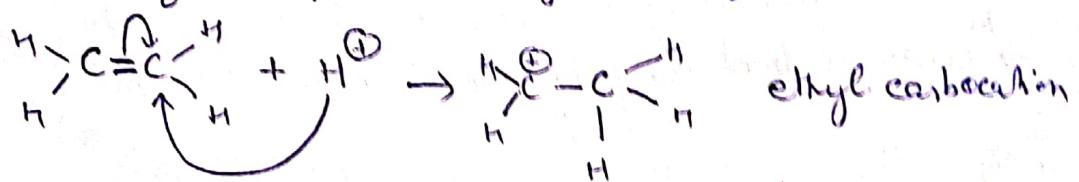


Mechanism: Ethylene + HBr  $\rightarrow$  ethyl bromide

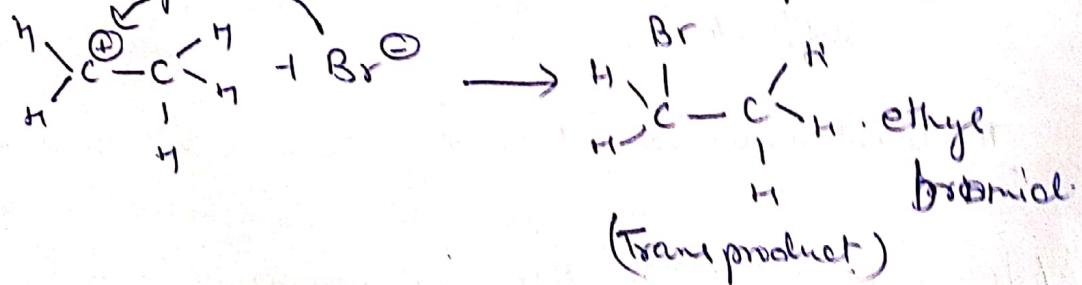
Step I: Ionizat<sup>n</sup> of HBr leads to generation of electrophile & nucleophile.



Step II: Attack of electrophilic ethylene to form carbocation



Step III: Nucleophile then attacks the carbocation to form add<sup>n</sup> product (Nucleophile attack trans position of ethene)



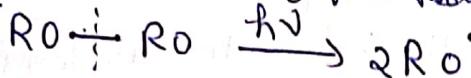
## FREE RADICAL ADD<sup>n</sup> RXN :

→ Also known as Kharasch Peroxide effect

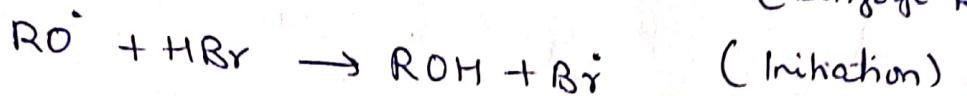
→ brought about by free radicals.

→ free radicals are highly reactive bcs of unpaired e-

Step I : Generation of free radical

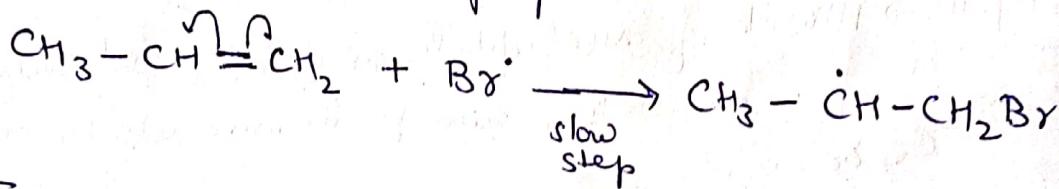


{ Hydrogen peroxide }  
 { benzoyl peroxide }



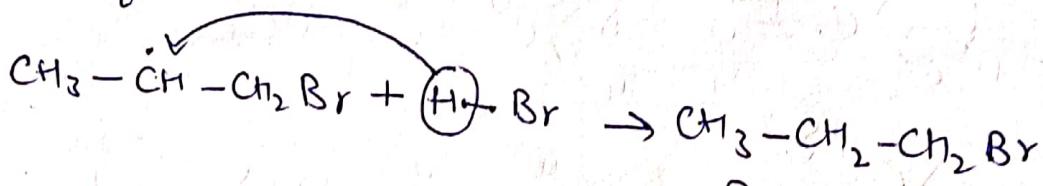
Bromine free radical

Step II : Br<sup>·</sup> radical attack propene.



Step III

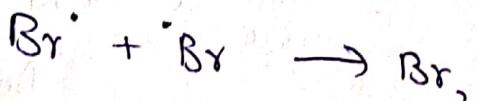
Propene free radical then attacked by another HBr to form product.



Product

Step IV → termination step:

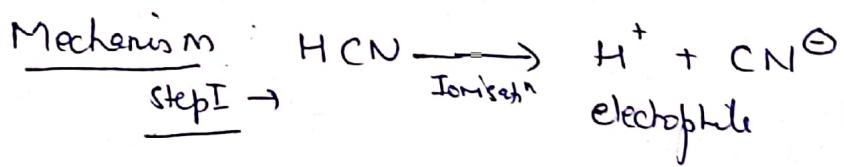
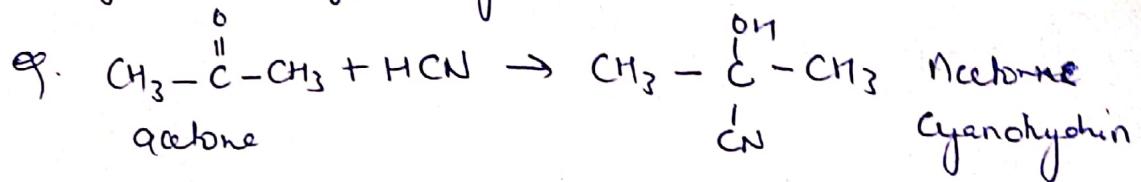
By comb<sup>n</sup> g Br<sup>·</sup> themselves.



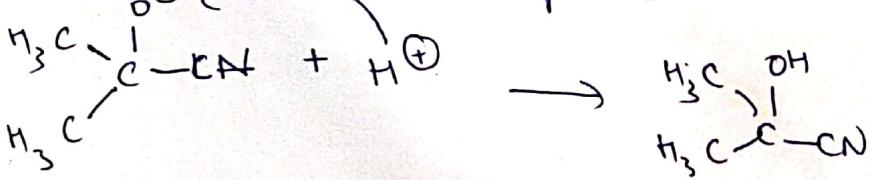
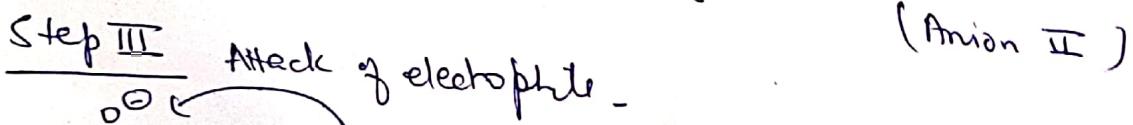
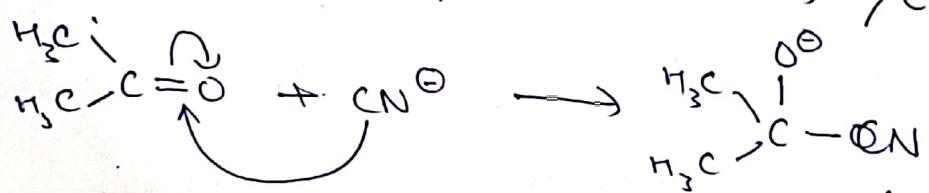
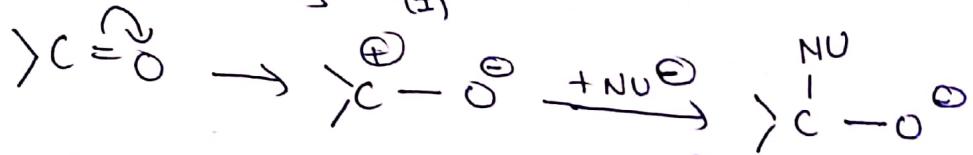
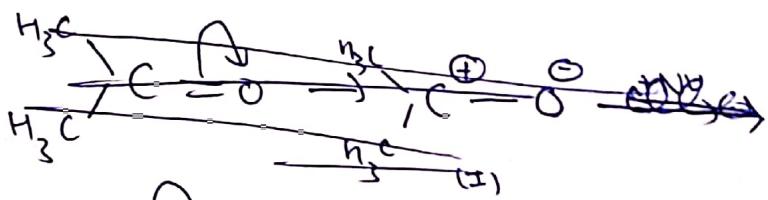
Nucleophilic Add<sup>n</sup> Reac: when add<sup>n</sup> rxn is initiated by a nucleophile followed by add<sup>n</sup> of electrophile

→ characteristic of carbon-hetero atom bond

→ typical rxns of aldehydes & ketones.



Step II → Attack of nucleophile on the charged carbonyl-carbon to form anion II, since {O is more electronegative than C}



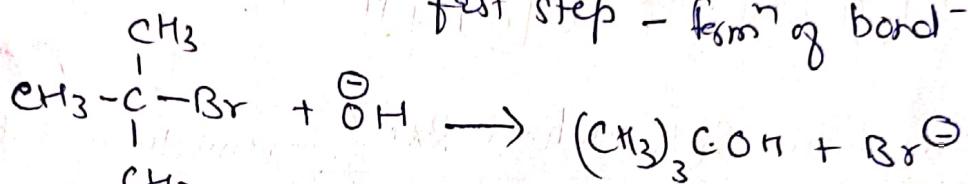
Acetone cyanohydrin

## OPTICAL ISOMERISM:

$S_N^1$  Rxn → When rate of nucleophilic substitution rxn depends upon the conc. of alkyl halide & independent of Conc. of nucleophile, the rxn is said to proceed via unimolecular mechanism.

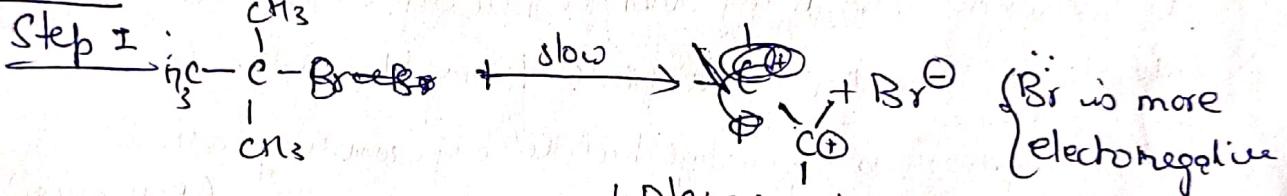
→ Involves two steps → slow step - bond breaking step

↓ fast step - form'g bond - bksplce

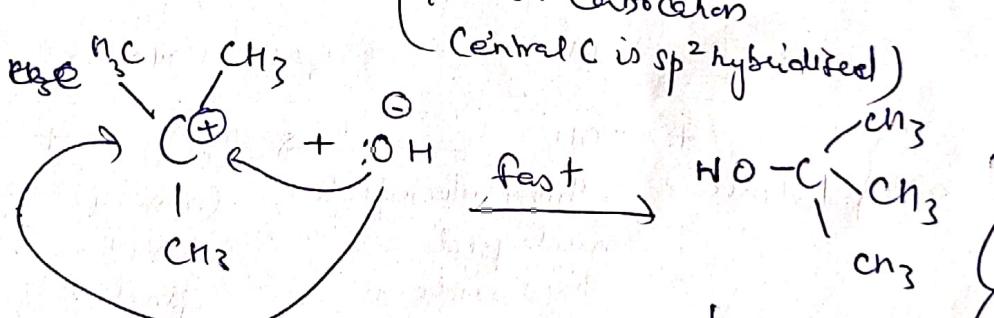


### Mechanism

#### Step I:

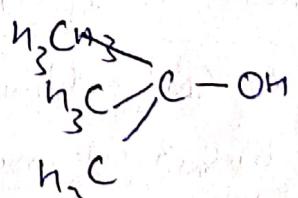


#### Step II



$$\text{Rate} \propto [(\text{CH}_3)_3\text{CBr}]$$

Rate order = 1



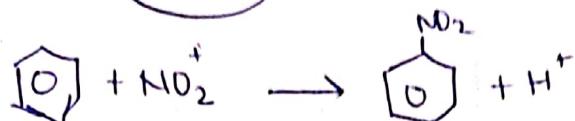
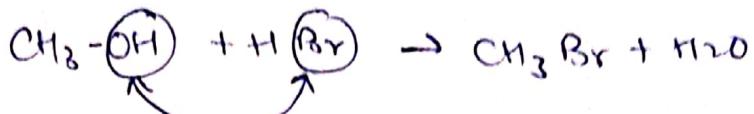
50/50 mix of  
enantiomers  
Racemic mixture

≡

Substitution Rxn : Replacement of an atom/gp from a molecule by other atom/gp.

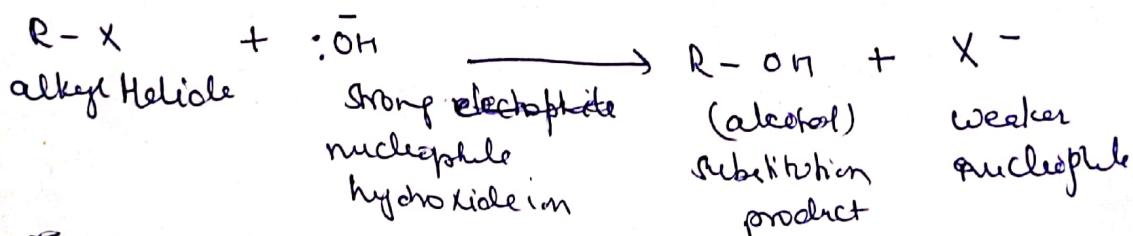


→ proceed via free radical/ionic mechanism.



Nucleophilic Substitution Rxn : - involves displacement rxn brought about by stronger nucleophile ( $e^-$ -rich), thereby displacing weaker nucleophile from the molecule.

e.g. Hydrolysis of alkyl halide by strong alkali ( $\text{KON}, \text{NaOH}$ )



These are of three types :

a)  $\text{S}_{\text{N}}^1$  : Unimolecular Nucleophilic substitution

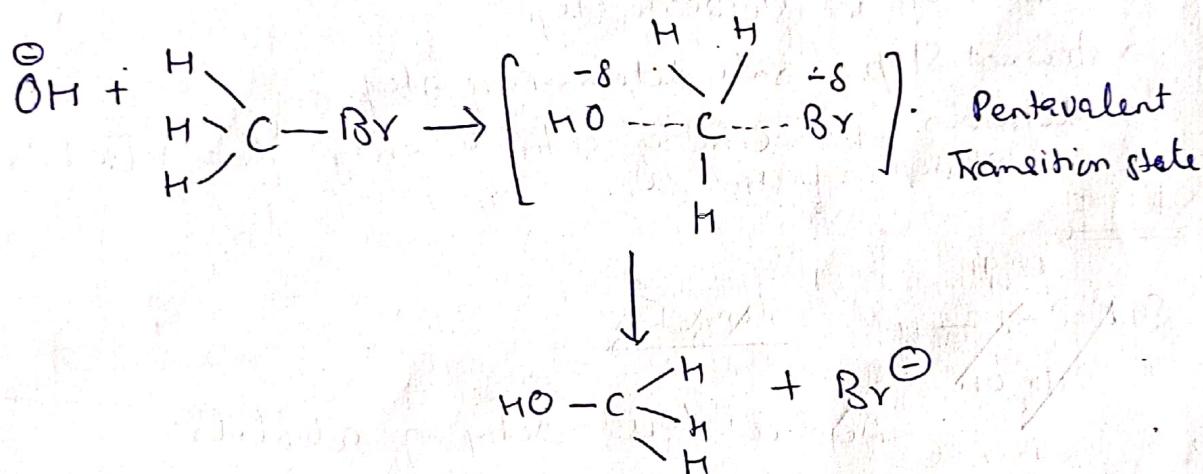
b)  $\text{S}_{\text{N}}^2$  : Bimolecular

c) ~~S<sub>N</sub>1, S<sub>N</sub>2~~, SNi

$S_N2$  Rxn → Rate of Rxn (nucleophilic substitution)  
depends upon ~~some~~ of both alkyl halide & nucleophile



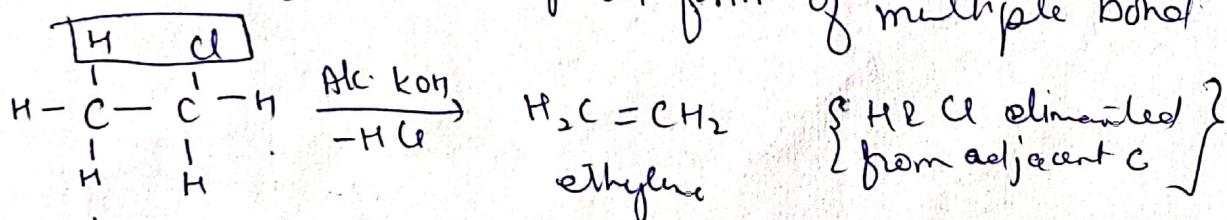
Mechanism: In  $S_N2$  rxn, breaking of bond & forming of bond takes place simultaneously. Such rxn proceed by via transition state in which C-atom appears to be pentavalent.



$$\text{Rate} \propto [CH_3-Br][OH^-]$$

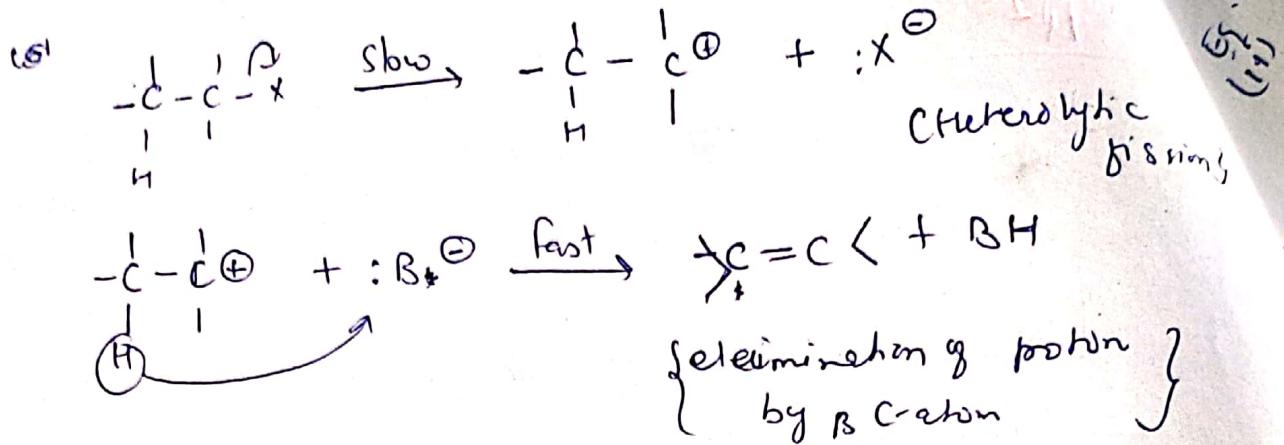
order = 2

Elimination Rxn's: Rxn in which two atoms are completely removed from a molecule (out being replaced by other atom/group resulting in form<sup>n</sup> of multiple bond)



→ Classified under three headings

- E1
- E2
- E1cB



Ques. EI Rxn  $\rightarrow$  Two step elimination Rx

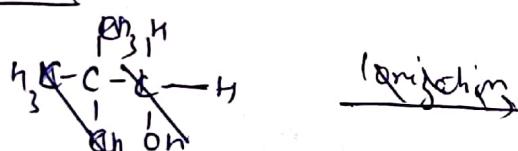
$\rightarrow$  Two step process

$\rightarrow$  first step is slowest step

$\rightarrow$  slowest step is rate determining step

$\rightarrow$  depends upon conc. of substrate only  $\{R = k[\text{substrate}]\}$

### Step I:

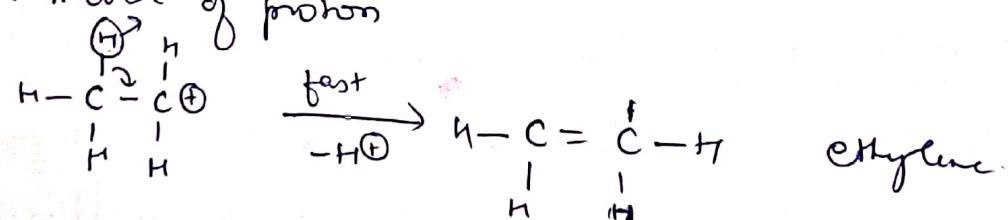


ethanol Acid catalyzed dehy. of alcohols.



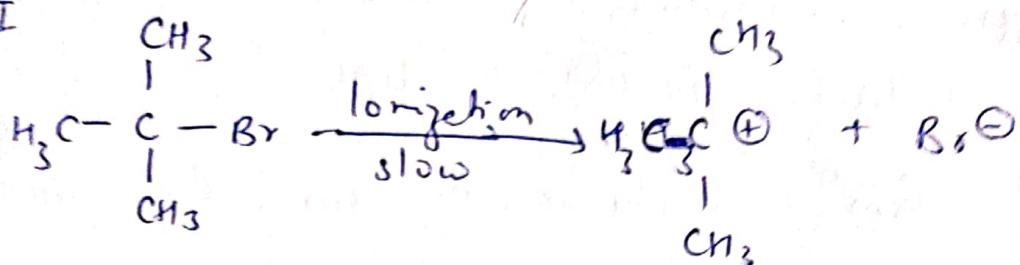
### Step II

Removal of proton



E<sub>1</sub>  
 (ii) Detachment of halogenation of 2-bromo-2-methylpropane

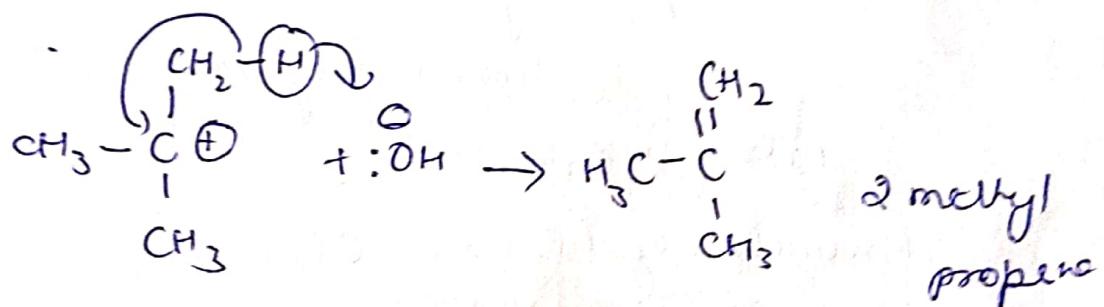
Step I



2-bromo-2-methyl  
propane

Tertiary  
carbocation

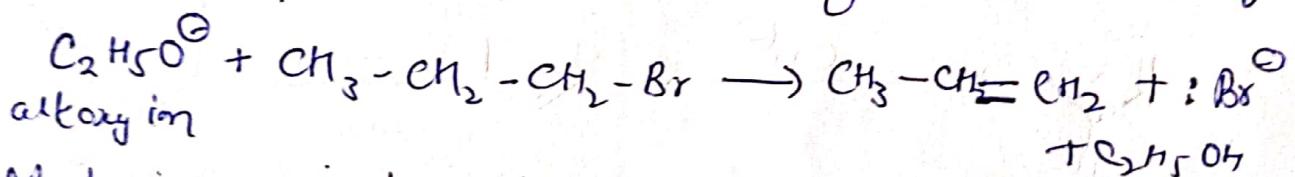
Step II



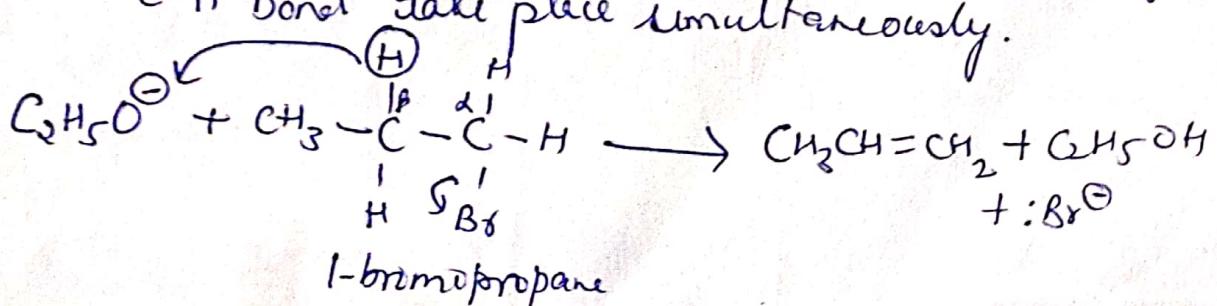
E2 Reaction : E2 stands for bimolecular elimination reaction

→ takes place in single step

→ rate depends upon the conc<sup>n</sup> of substrate & catalyst



Mechanism : involves abstraction of a proton by base from the β-carbon & simultaneous release of nucleophile of α-carbon of alkyl halide molecule i.e. breaking of C-X & C-H bond take place simultaneously.



E1CB Rxn is exceeding rarely.

Refers to elimination of first order from conjugate base. Mechanism involves 2 steps

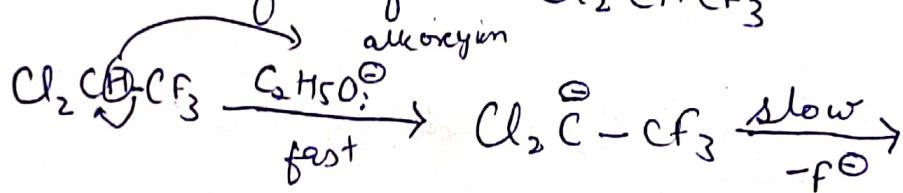
Step I: form<sup>n</sup> of carbocation by removal of proton from  $\alpha$ -carbon.

Step II: loss of halide ion from carbocation. This step is slowest step  $\rightarrow$  determines the rate of rxn  
 $\downarrow$

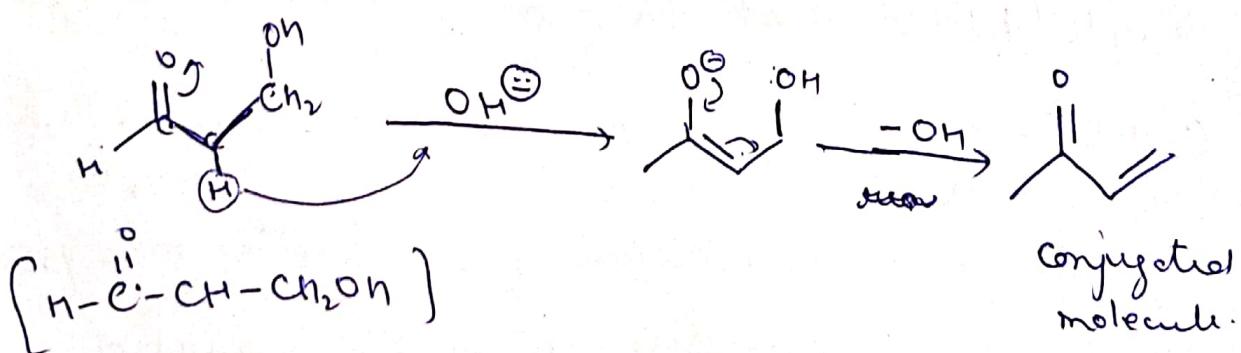
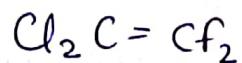
depends only upon conc<sup>n</sup> of carbocation

$$\text{Rate} \propto k[\text{Carbocation}]$$

e.g. Elimination of HF from  $\text{Cl}_2\text{CHCF}_3$



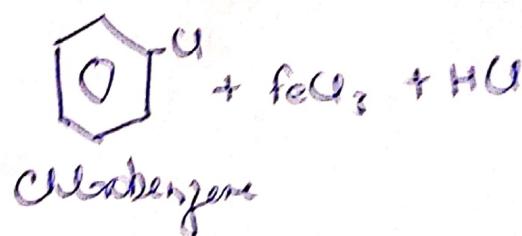
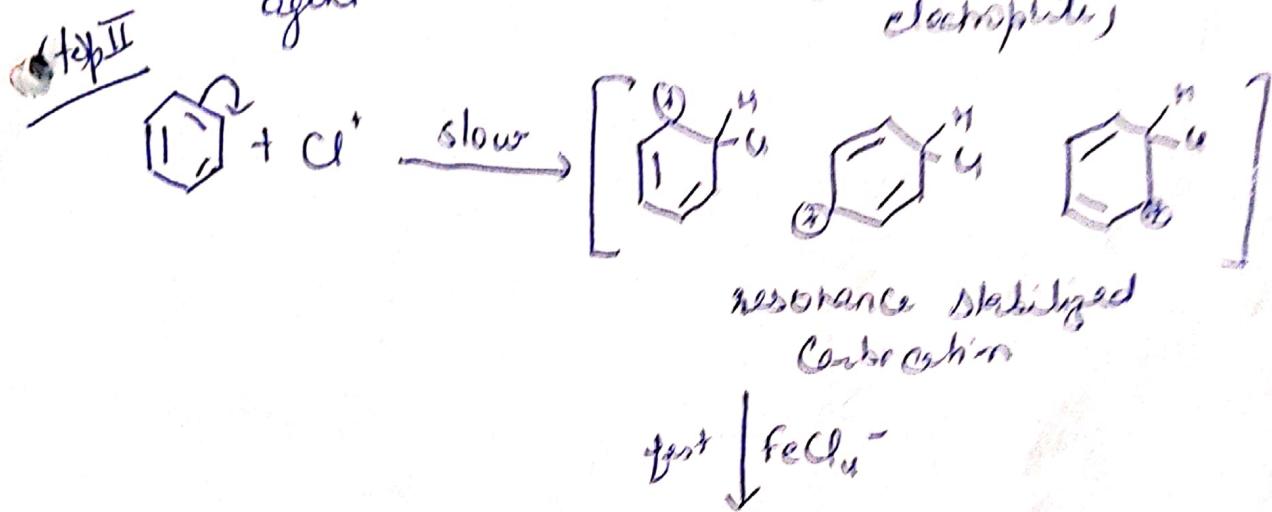
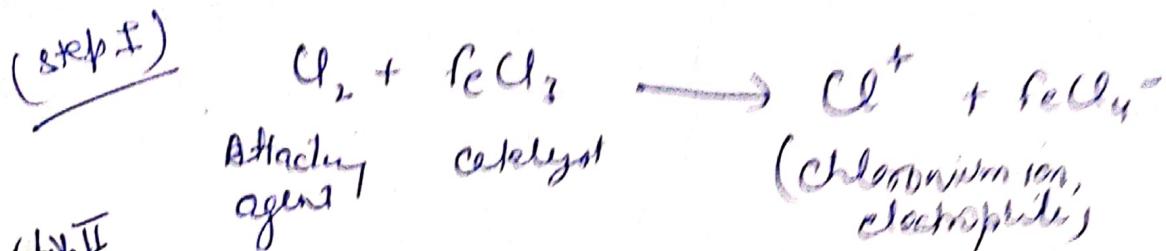
Mechanism



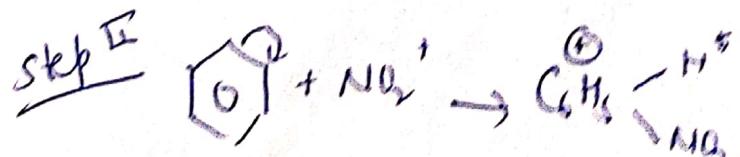
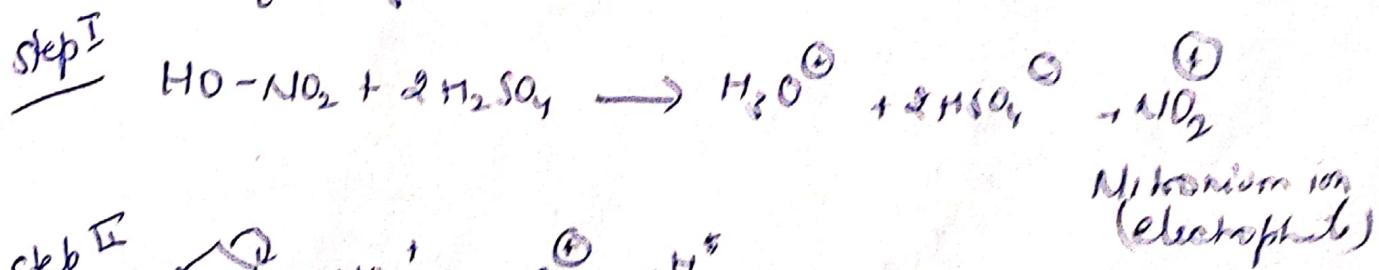
## Electrophilic substitution Reac.

Substitution reaction of a Halogen on the benzene ring brought about by an electrophile (C+ deficient species)

(i) Halogenation of arenes -



(ii) Nitration of benzene in conc  $\text{HNO}_3$  & conc  $\text{H}_2\text{SO}_4$



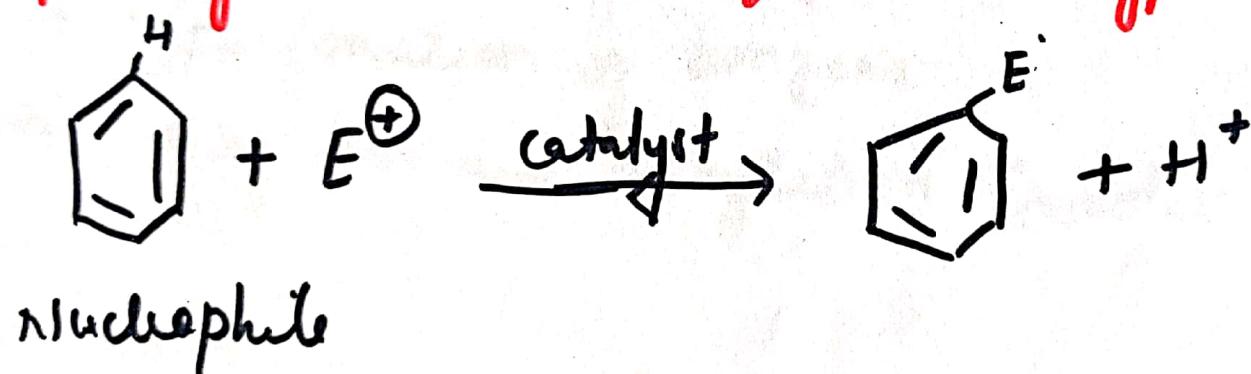
(Carbocation  
 resonance stabilized)

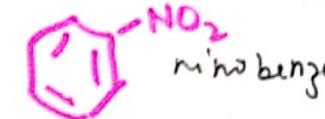
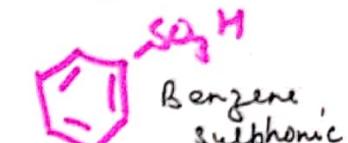
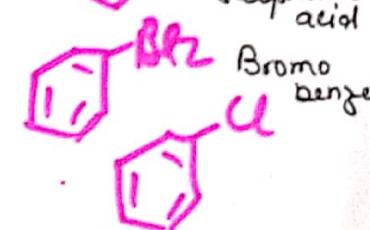


## Electrophilic Substitution Rxns:

Chemical Rxn in which electrophile displaces a functional group in a compound.

- typically but not always, a H-atom
- characteristics of aromatic compds
- Imp. way to introduce functional grp to benzene rings.



<u>Reaction Name</u>	<u>Reagent</u>	<u>Catalyst</u>	<u>Electrophile</u>	<u>Product</u>
Nitration	$\text{HNO}_3$	$\text{H}_2\text{SO}_4$	$\text{NO}_2^+$	 nitrobenzene
Sulphonation	$\text{SO}_3$	$\text{H}_2\text{SO}_4$	$\text{HSO}_3^+$	 Benzene sulphonic acid
Bromination	$\text{Br}_2$	$\text{FeBr}_3$	$\text{Br}^+$	 Bromobenzene
Chlorination	$\text{Cl}_2$	$\text{AlCl}_3$	$\text{Cl}^+$	
Friedel-Crafts alkylation	$\text{RX}$	$\text{AlCl}_3$	$\text{R}^+$	
Friedel-Crafts acylation	$\text{R}-\overset{\text{O}}{\underset{\text{C}}{\parallel}}-\text{C}-\text{Cl}$	$\text{AlCl}_3$	$\text{R}-\overset{\text{O}}{\underset{\text{C}}{\parallel}}-\text{C}^+$	

3 steps involved:

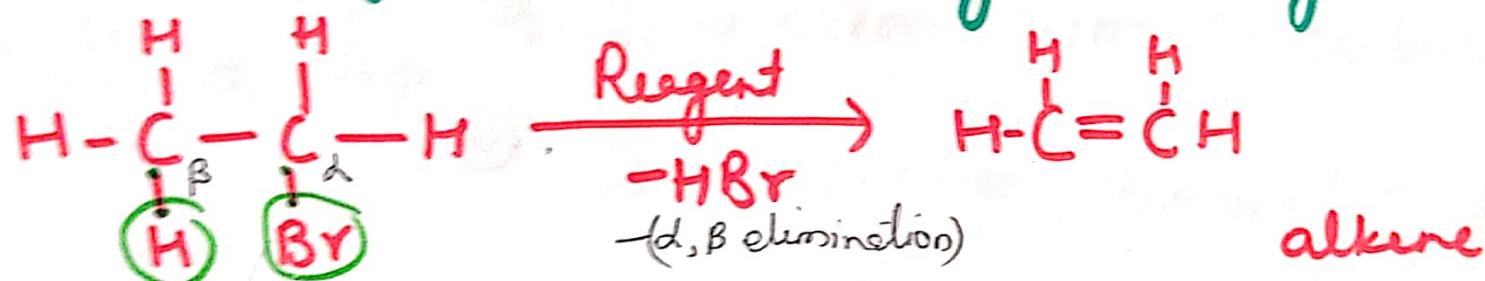
1. Formation of electrophile
2. Attack of formed electrophile
3. Removal of old electrophile or proton

Elimination Reactions : Transform sat. compd to unsaturated compd

Saturated  $\rightarrow$  Unsatuated (E/Z)

$\rightarrow$  Imp. way to prepare alkenes

$\rightarrow$  Dehydration & Dehydrohalogenation  $\rightarrow$  Imp. method



Types of elimination rxns ( $\alpha, \beta$  elimination)

$E^1$   
Unimolecular Rxn

$E^2$   
Bimolecular elim<sup>n</sup> Rxn

$E^1CB$   
Conjugate Base elim<sup>n</sup> Rxn

## E' Reaction Unimolecular elimination Rxn

Reaction rate of E'  $\propto$  conc of the substrate or substance to be transformed

→ exhibits first-order kinetics

Rate  $\propto$  [R-X]

Two steps

- ① Ionization / formation of carbocation (slow step)
- ② Deprotonation / Removal of proton

Slow step → Rate determining step

E' mechanism

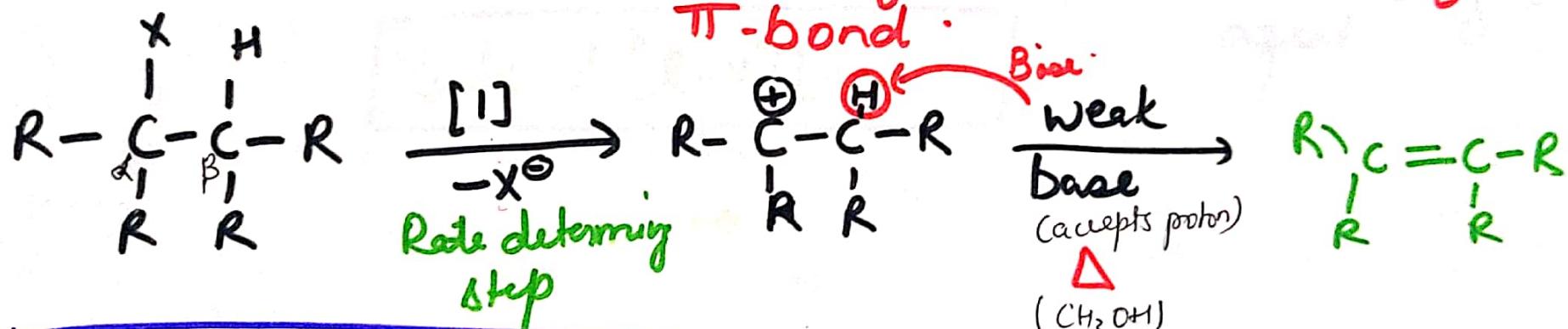
→ Shares the features of the S<sub>N</sub>I rxn, as also E' mech- also forms Carbocation intermediate through the loss of LG.

① Ionization involves, form<sup>o</sup> of carbocation as an intermediate

② In Deprotonation → proton ( $H^+$ ) lost from the Carbocation



due to presence of weak base  
which further leads to the forming  
 $\pi$ -bond.



Solvent → Polar Protic

$E^2$  Mechanism : refers to bimolecular elimination

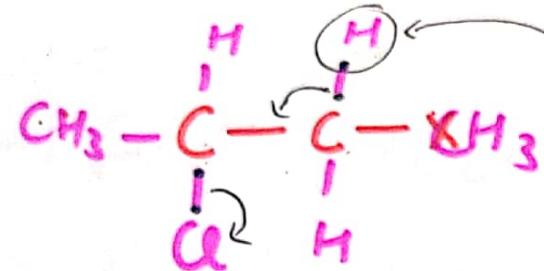
→ One step mechanism

→ (-H bond and C-X bond (Carbon-Halogen) break at same time to form a new = bond)

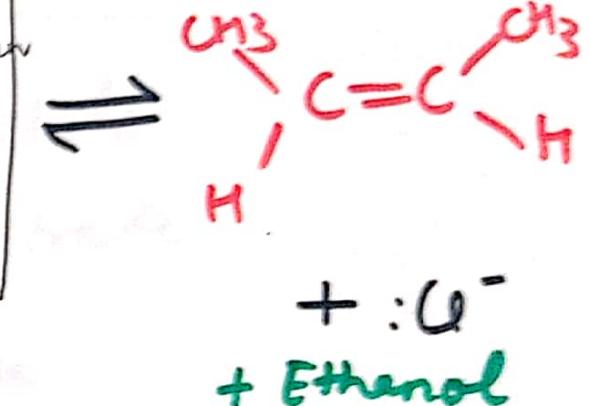
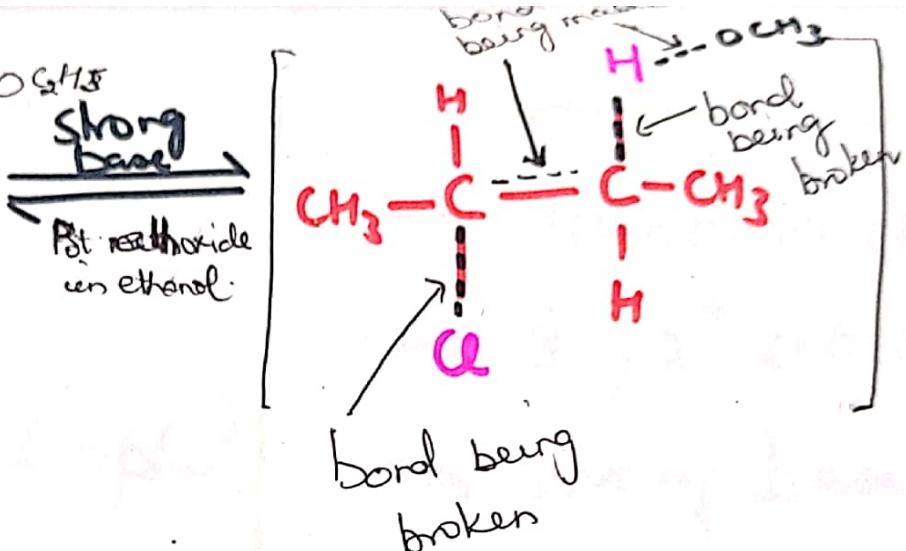
→ In  $E^2$  mechanism, a strong base is part of RDS

→ Rate of rxn of  $E^2$  mechanism of conc of substrate and conc. of eliminating agent.

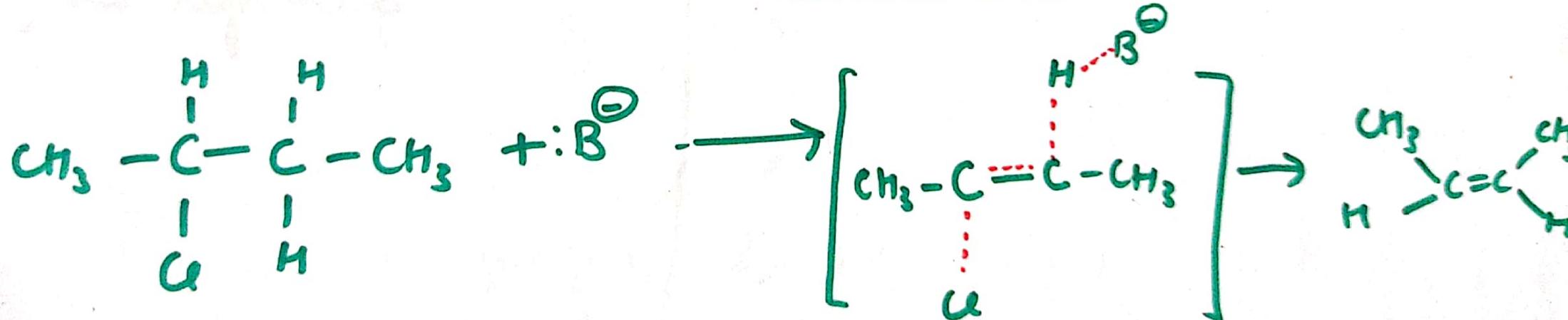
Rate  $\propto [R-X][Base]$



2-chloro butene



### Transition state



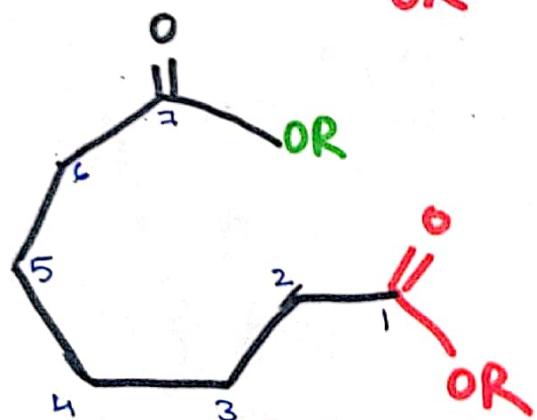
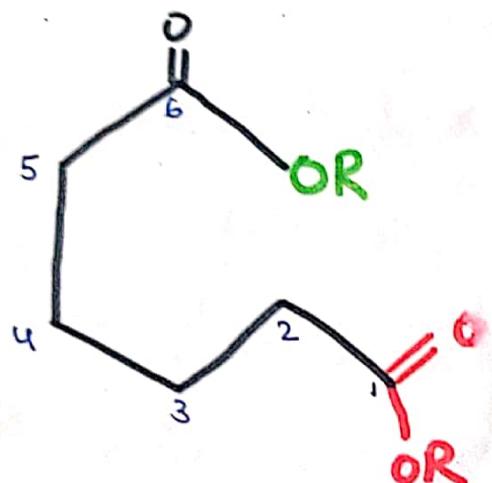
### E' mechanism

- form<sup>n</sup> of carbocation
- 3° / 2° substrate
- Weak base / nucleophile
- Protic solvent
- high temp.

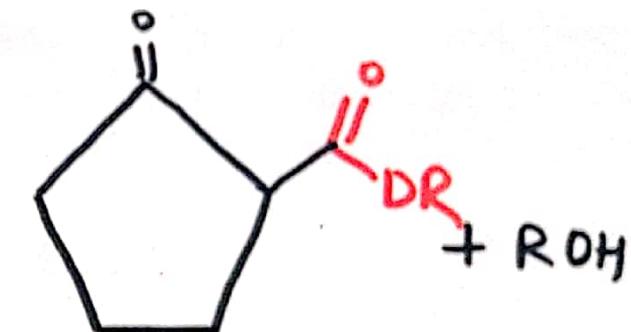
### E<sup>2</sup> Mechanism

- Transition state
- 3° / 2° substrate
- strong base
- Aprotic solvent

## Dieckmann Condensation Rxn:

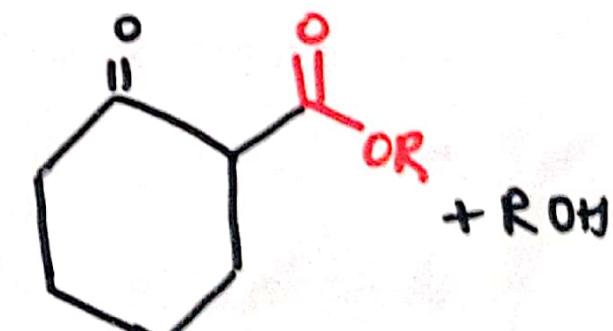


1. Na<sup>+</sup>OR, ethanol  
2. H<sub>3</sub>O<sup>+</sup>



5 membered ring

1. Na<sup>+</sup>OR, ethanol  
2. H<sub>3</sub>O<sup>+</sup>

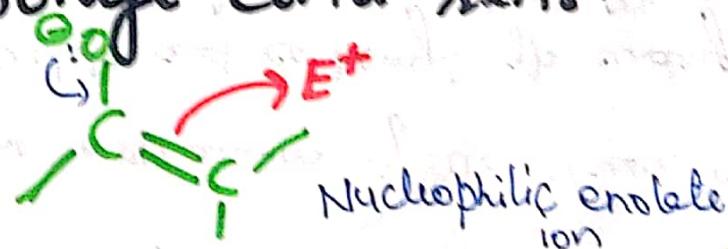
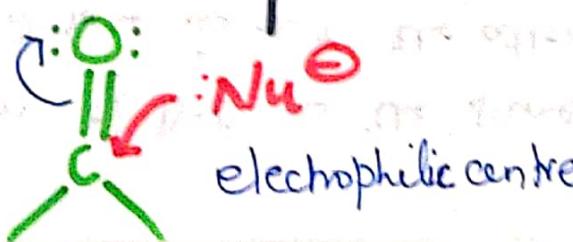


6 membered ring

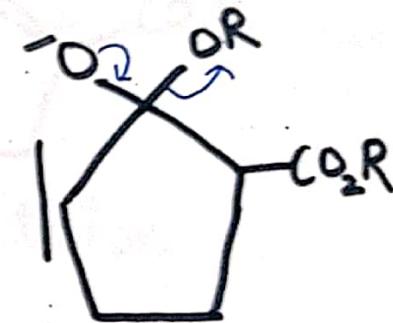
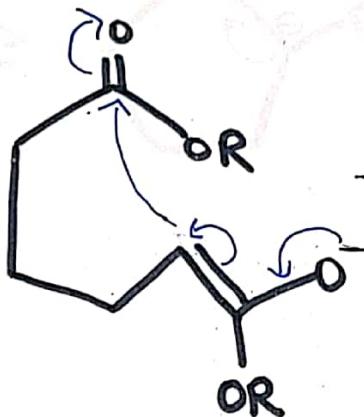
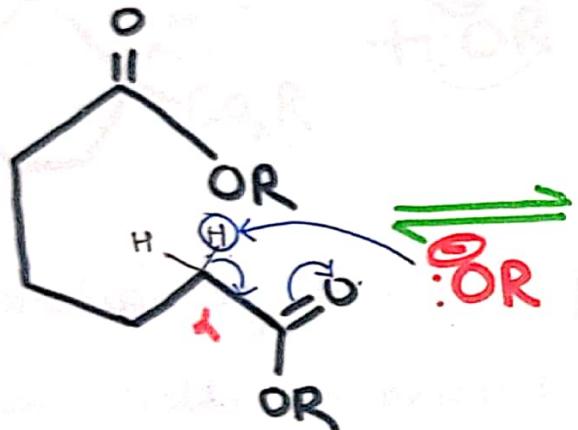
## → Dieckmann Condensation

- Intramolecular chemical reaction
- diesters with base →  $\beta$ -keto esters
- Intramolecular Variant of Claisen Condensation
- Used to prepare 5/6 membered ring of  $\beta$ -keto esters.

Carbonyl compds are both the electrophile & nucleophile in carbonyl cond<sup>n</sup> sxs.



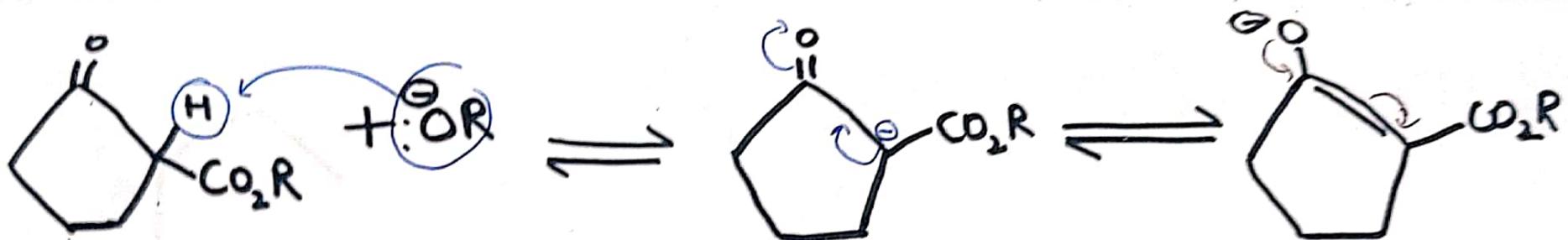
## Mechanism :



Base ( $\text{CO}_2\text{R}$ ) abstracts an ~~oxide~~ & proton from the C-atom next to one of the ester groups yielding enolate ion.

enolate ion, intramolecular nucleophilic add<sup>n</sup> of the ester enolate ion to the carbonyl end of the second ester (at the other end of carbon chain as a result cyclic intermediate (tetrahedral) is obt'd.

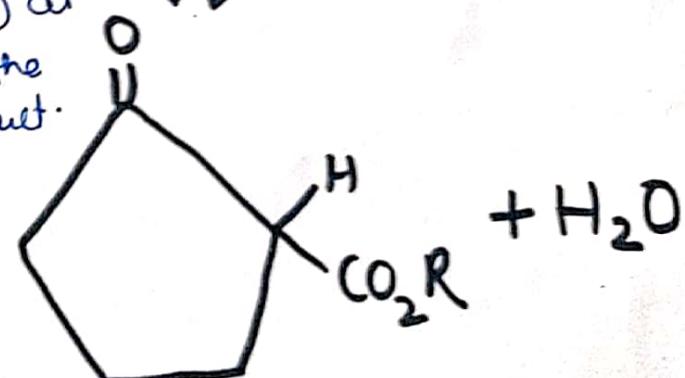
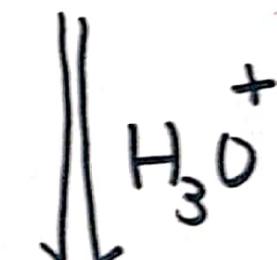
Cyclic tetrahedral intermediate, loss of alkoxide ion from the tetrahedral intermediate yielding cyclic  $\alpha$ -keto ester



Deprotonation of the acidic  $\beta$ -keto ester, yields an enolate ion.

enolate ion is protonated by ~~excess~~  
add' of aq. acid  
(Bronsted-Lowry acid) at  
the end of rxn to give the  
neutral  $\beta$ -keto ester product.

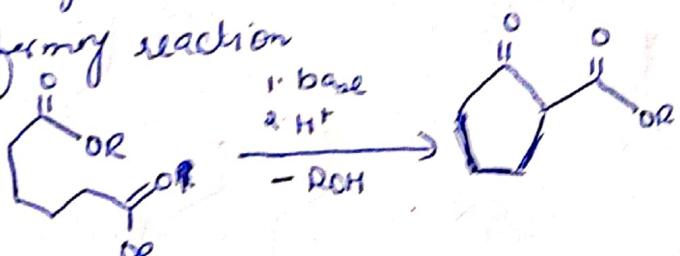
enolation



## Dieckmann Condensation: named after Walter Dieckmann

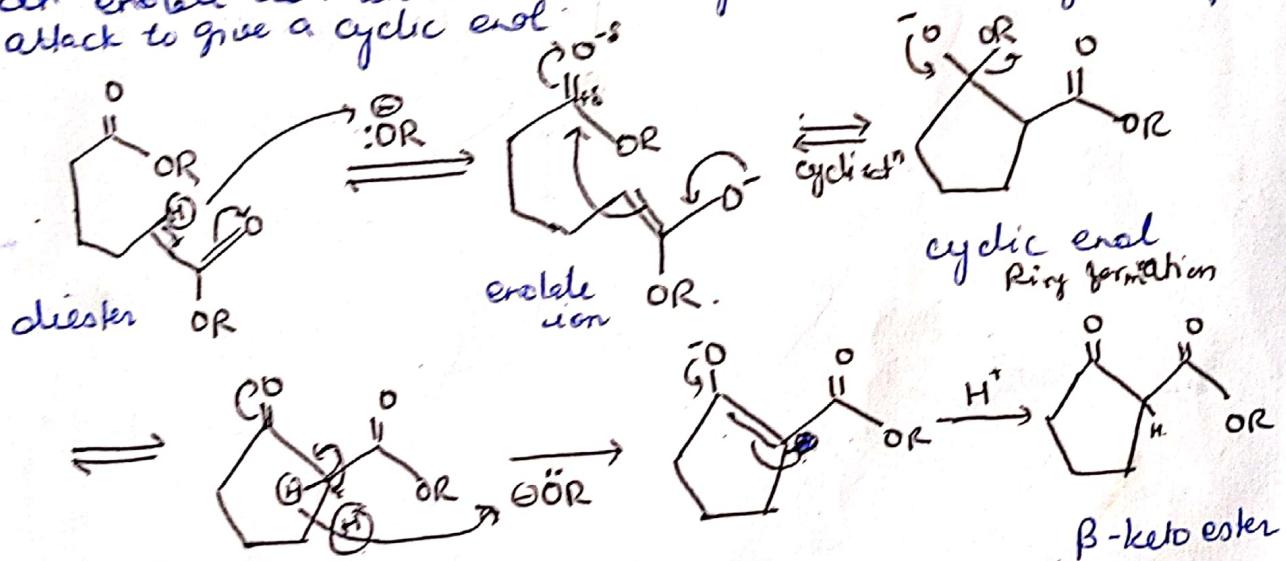
It is the intramolecular chemical rxn of diesters with base to give  $\beta$ -keto ester.

→ Ring forming reaction



### Mechanism:

Deprotection of an ester at the  $\alpha$ -position generates an enolate ion which then undergoes a 5-exo-trig nucleophilic attack to give a cyclic enol.



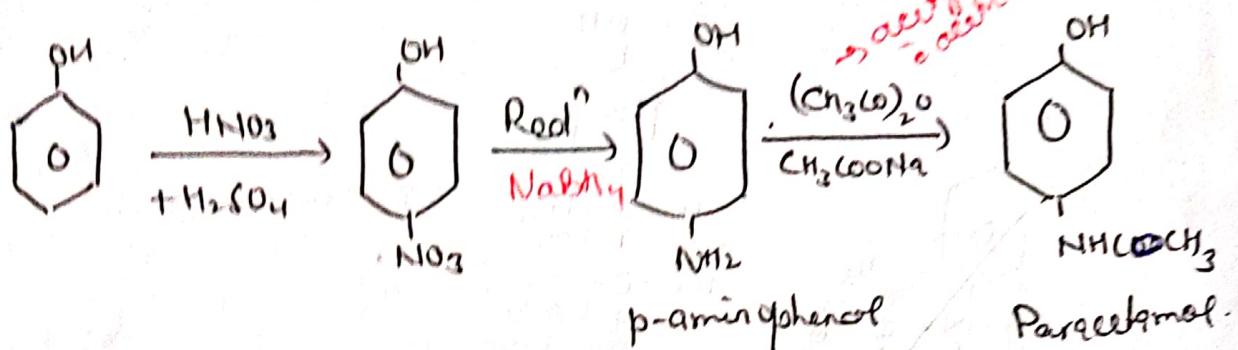
Protonation in a Brønsted-Lowry acid ( $\text{H}_3\text{O}^+$  for eg.) reforms  $\beta$ -keto ester. Due to steric stability of 5-2C-membered rings, these structures will preferentially be formed.

1,6-diesters will form 5-membered cyclic  $\beta$ -keto esters  
1,7-diesters " " 6- " " "

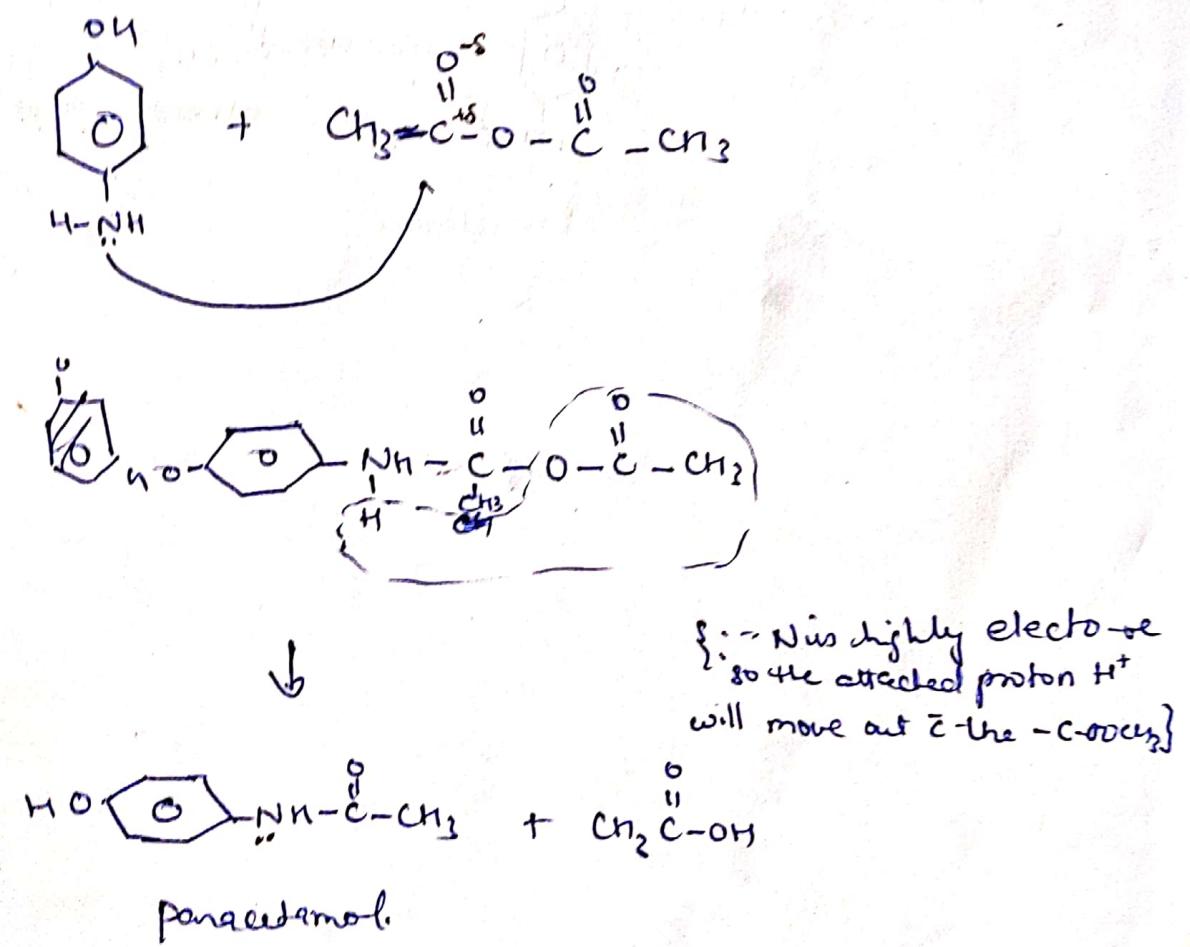
- This rxn is an intramolecular form of Claisen cond<sup>n</sup>.
- Mostly the base utilized would be the alkoxide  $\text{RO}^-$  matching the alcohol part of the ester.

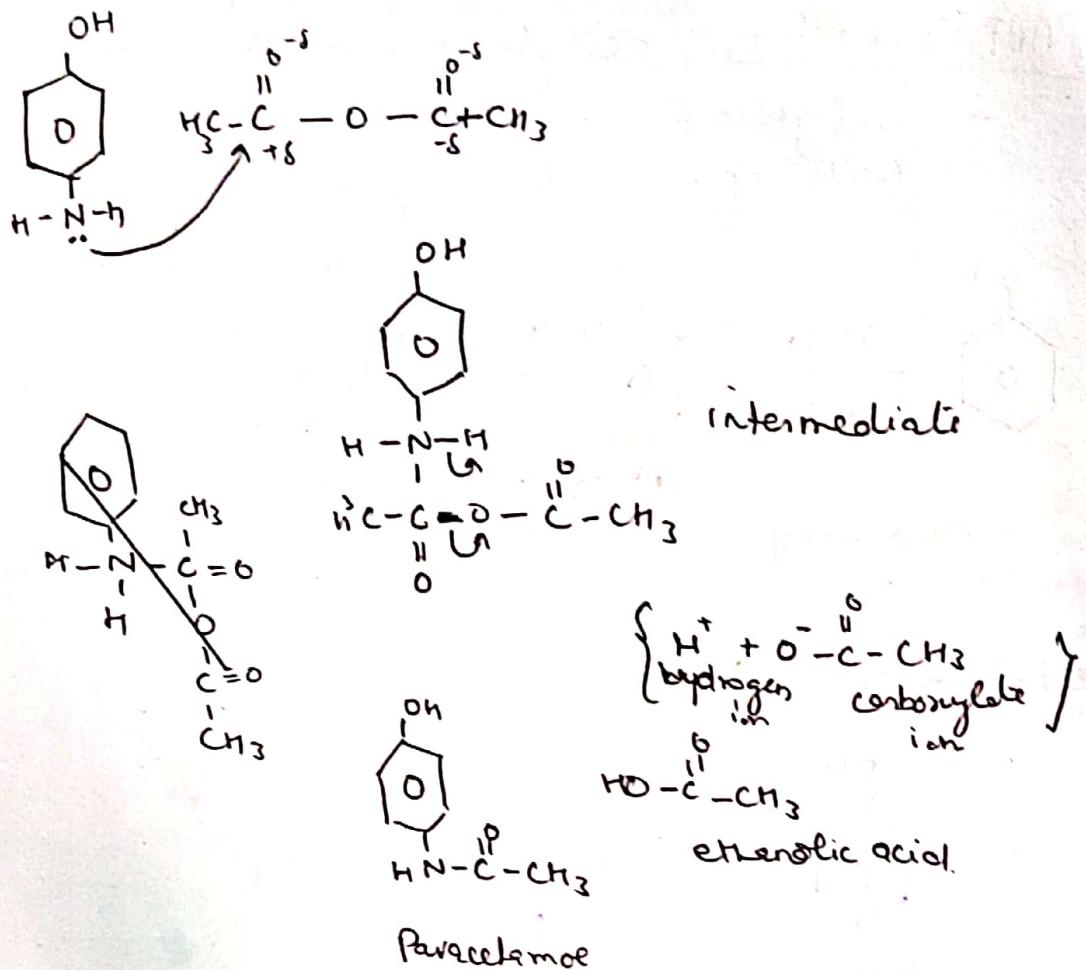
PARACETAMOL → acetyl derivative of p-aminophenol

analgesic & Antipyretic drug.  
(relieves pain) (decreases fever)



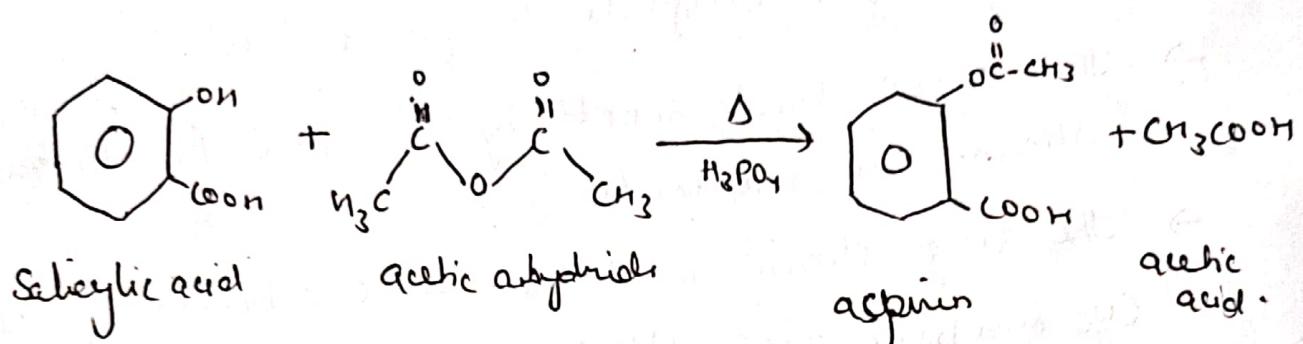
### Mechanism :



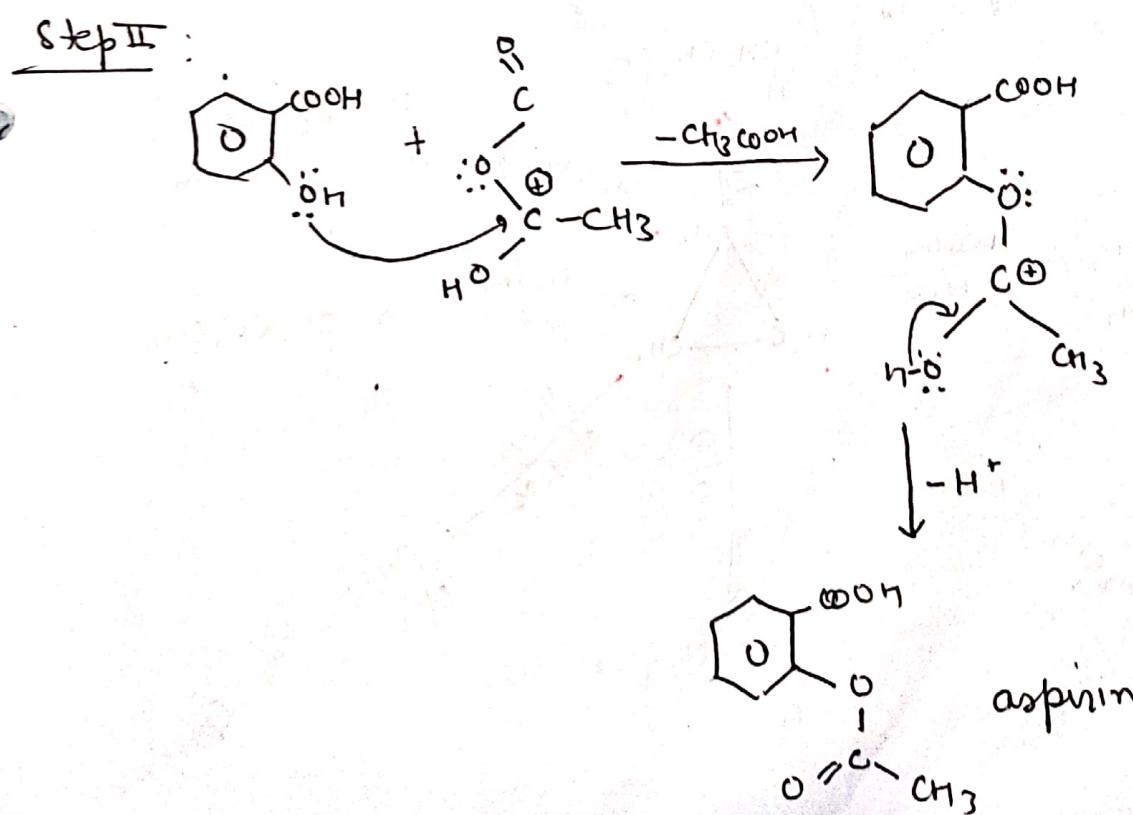
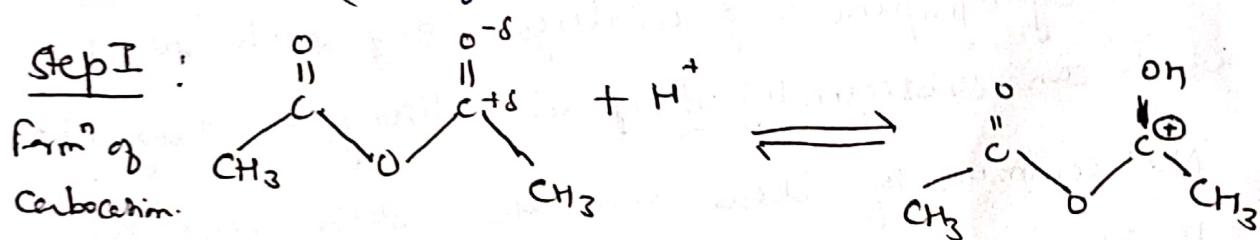


Aspirin: Acetyl Salicylic acid ( $\alpha$ -acetylbenzoic acid)

Chemicals used: salicylic acid, Acetic anhydride  
water (for precipitation) & phosphoric acid  
(as catalyst)

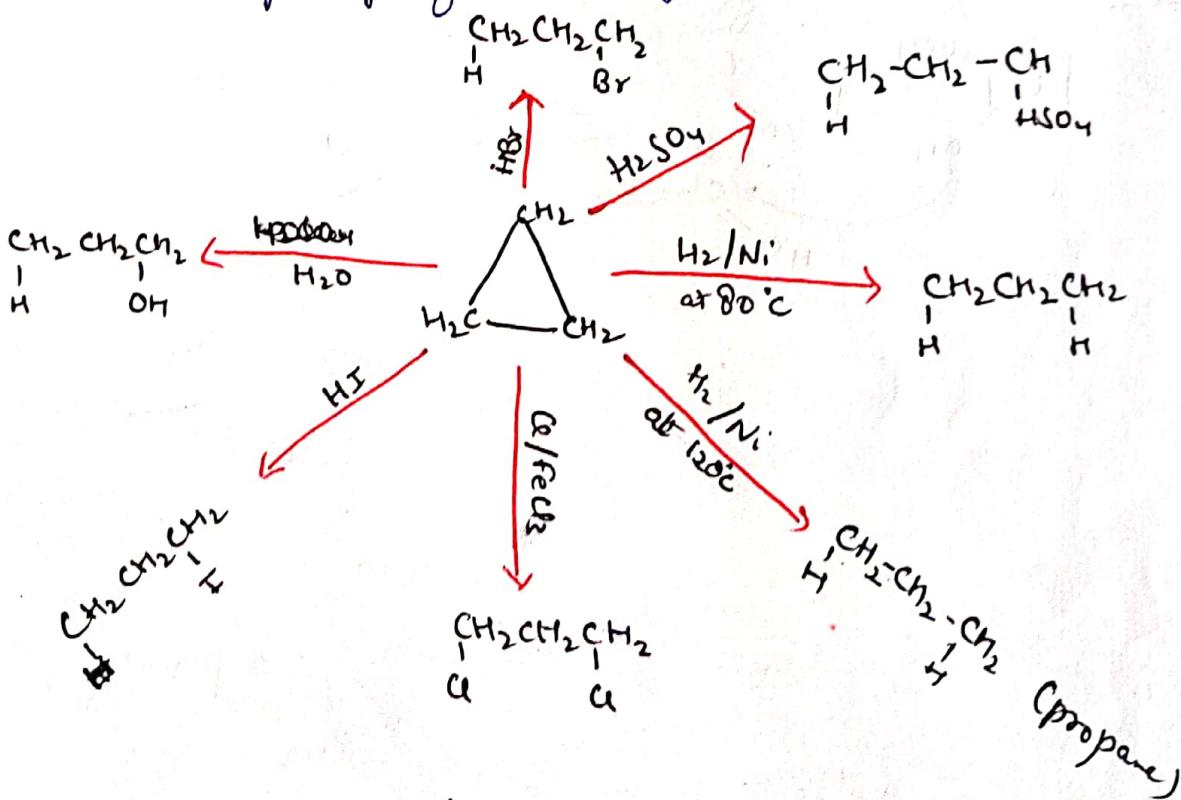


Mechanism: (Esterification/Nucleophilic acyl substitution)



## Addition Reactions of Cyclopropane:

- Cyclopropane ring (although an alkene) shows reactivity similar to alkenes towards various electrophiles, nucleophiles & free radicals.
- The above said reactivity is due to the ring strain in molecule.
- The ring strain weakens the C-C bonds of the cyclopropane ring. Hence cyclopropane is much more reactive than alkanes.
- Thus cyclopropane ring undergoes any such reaction which can subsequently help in relieving the ring strain.
- Most common of these are addition reactions leading to the opening of the ring.



In each of these rxn, a c-c bond is broken leading to ring fission & the atoms of the reagent (reacting species) attach at two terminals of the resulting propane chain.

→ The reagent (reacting species) must be able to polarize itself into nucleophilic & electrophilic centres for the addition to occur.



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Approved by AICTE, New Delhi

# Cycloalkanes

- ▶ Cycloalkanes are aliphatic saturated hydrocarbons.
- ▶ These are also commonly known as alicyclic compounds.
- ▶ Sometimes called carbocyclic compounds to differentiate them from heterocyclic compounds. They have general formula  $C_nH_{2n}$ , represented by polygons in skeletal drawing.



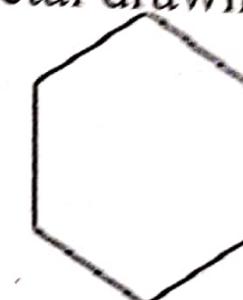
Cyclopropane



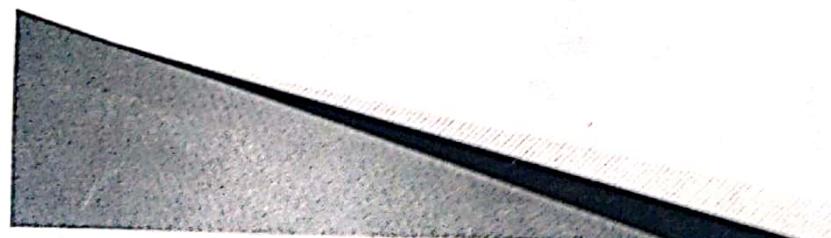
Cyclobutane



Cyclopentane

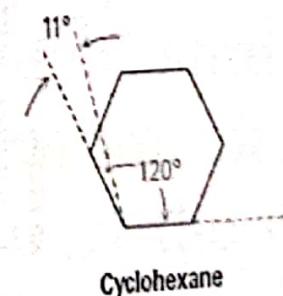
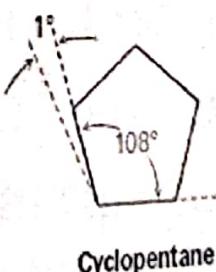
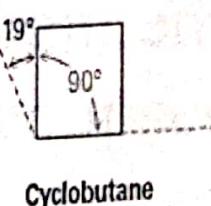
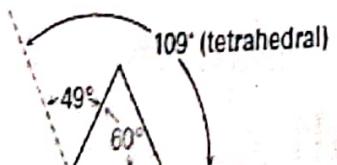


Cyclohexane



# Baeyer Strain Theory (Angle strain)

- ▶ According to this theory (adolf von Baeyer in 1885), any deviation from normal bond angle cause strain, called angle strain in the molecule, and greater the deviation from the normal angle, the greater the strain and less stability.
- ▶ In cycloalkanes, since each carbon atom is  $sp^3$  hybridized, the C-C-C bond angle should be tetrahedral ( $109.5^\circ$ )
- ▶ Angle strain- the strain due to expansion or compression of bond angles.
- ▶ Torsional strain- the strain due to eclipsing of bonds on neighboring atoms.
- ▶ Steric strain- the strain due to repulsion interactions when atoms approach each other too closely.



# Structure and Bonding in the Cyclopropane Ring



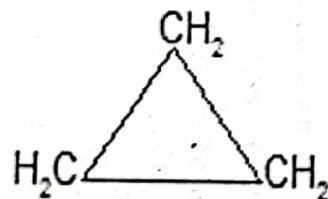
**SRM**  
INSTITUTE OF SCIENCE AND TECHNOLOGY  
*(affiliated to University of Delhi, U.G.C. & AICTE)*  
DEEHLI NCR CAMPUS, GHAZIABAD (U.P.)

- ▶ Cyclopropane has a triangular planar structure due to which , the bond angles between carbon-carbon bonds are expected to be  $60^\circ$ . This is far less than the thermodynamically stable angle of  $109.5^\circ$  as per the  $sp^3$  hybridisation of the carbon atoms. Due to this there is a considerable amount of ring strain in the cyclopropane molecule.
- ▶ In addition to this angular strain, cyclopropane also suffers additional torsional-strain. The torsional strain is due to the coplanar arrangement of the carbon atoms wherein leading to the eclipsed arrangement of the C-H bonds

## Addition reaction of cyclopropane

- ▶ Thus, it can be seen that ring strain substantially weakens the C-C bonds of the cyclopropane ring. Hence, cyclopropane is much more reactive than alkanes or other higher ring systems.
- ▶ Cyclopropane being the most strained ring and more reactive undergoes addition reactions like alkenes (addition reactions (electrophilic, nucleophilic or free-radical)).
- ▶ Cycloalkanes are relatively inert towards the action of common reagents at room temperature.
- ▶ Cyclopropane and cyclobutane compounds are exceptions and show a tendency to react with opening of the ring.

► Cyclopropane forms addition products with ring fission, as shown :



$\text{Cl}_2 / \text{Dark}$	$\rightarrow \text{Cl}(\text{CH}_2)_3\text{Cl}$ Addition reaction
$+ \text{Br}_2$	$\rightarrow \text{Br}(\text{CH}_2)_3\text{Br}$ 1,3-dibromo propane
$+ \text{HBr}$	$\rightarrow \text{CH}_3 - \text{CH}_2 - \text{CH}_2\text{Br}$ 1-bromopropane
$+ \text{Ni}, \text{H}_2$ $120^\circ\text{C}$	$\rightarrow \text{CH}_3 - \text{CH}_2 - \text{CH}_3$ Propane
$+ \text{H}_2\text{SO}_4$	$\rightarrow \text{CH}_3 - \text{CH}_2 - \text{CH}_2\text{HSO}_4$
$+ \text{KMnO}_4$	$\rightarrow$ No reaction
$\text{HI}$	$\rightarrow \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{I}$

# deterioration of a material over time

Page No.  
Date:

## CORROSION

When the metals are exposed to the atm. environment, they react with the air or water <sup>in</sup> of the environment to form undesirable compds usually oxides.

This process is called corrosion. The environment could be of any type such as air, atm., water, seawater, acids, alkalies, steam, gases, soils & liquid metals. etc. The interaction of metal with the environment could take place at any temp.

Almost all metals except the less reactive metals such as gold, palladium, Pt, undergo corrosion.

Example: → Rusting of Iron ( $Fe_2O_3$ )  $Fe_3O_4$

→ Rn of chlorine gas in Mg or Tin

→ form of green layer of basic carbonate [ $CaCO_3 + CuCO_3$ ]

Definition: It is the destruction or decay or deterioration of material under the influence of environment due to the chemical rxn. reactions.

Most common <sup>OR</sup> kind of corrosion is <sup>32</sup>  $Oxidation$  (Scientifically defined as "corrosion of metallic materials by metal oxide by the influence of oxygen of the atm. metal + oxygen  $\leftrightarrow$  metal oxide".

Reverse of the above eq<sup>n</sup> is the principle of extract metallurgy. (extraction of metals)

INTEGRATION:

palladium  
platinum  
iridium  
osmium  
ruthenium

## Consequences of corrosion:

The economic & social consequences of corrosion include -

- 1) Plant shutdown due to failure.
- 2) Replacement of corroded equipment.
- 3) Preventive maintenance (such as painting).
- 4) Necessity for overdesign to allow for corrosion.
- 5) Loss of efficiency.
- 6) Contamination or loss of the product (e.g. from a corroded container).
- 7) Safety (e.g. from a fire hazard or explosion or release of a toxic product or a collapse of construction bco. of a sudden failure).
- 8) Health (e.g. from pollution due to a corrosion product or due to an escaping chemical from a corroded equipment).

**CAUSE:** In nature, most metals exist as found in chemically combined state known as ore. All the metals except gold, pt & <sup>other</sup> palladium, exist in nature in the form of sulfides, oxides, sulphates, carbonates, etc. These combined forms of metals represent their thermodynamically stable state (low energy state). The metals are extracted from these ores after supplying a large amount of energy. Metals in the combined state have higher energy than in a metallic state. It is their natural tendency to go back to the low energy state i.e. combined state by recombining with the elements that are present in the environment. This is the reason for corrosion.

Angstrom

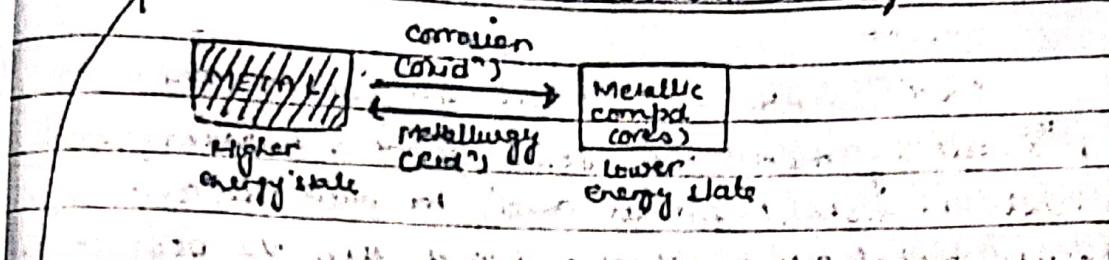
porous oxide film

Li, Be alk.

Na

Efficiency decreased  
Safety concern  
Aesthetically displeasing  
Penalty offical, Repairing cost

For e.g. Chlorine or iodine attack on silver, generating a protective film of silver halide on the surface. On the other hand, stannic chloride formed on tin is volatile and hence corrosion is not prevented.



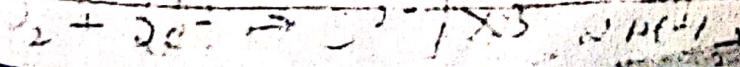
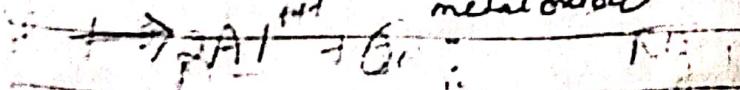
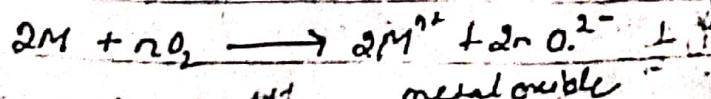
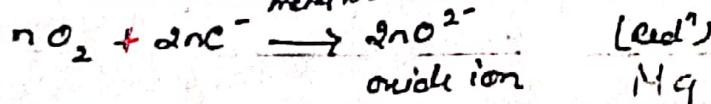
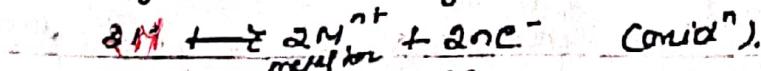
### CHEMICAL CORROSION / DRY CORROSION / DIRECT CHEMICAL ATTACK THEORY

This type of corrosion occurs mainly due to the action of atm. gases such as oxygen, halogens, sulphur dioxide, hydrogen sulphide, Nitrogen, etc. on the metal surfaces. In this type of corrosion generally a solid film of the corrosion product is formed on the surface of the metal which resists further corrosion. However, if a soluble or liquid corrosion product is formed, then the metal is exposed to further attack.

Dry or chemical corrosion is of three main types:

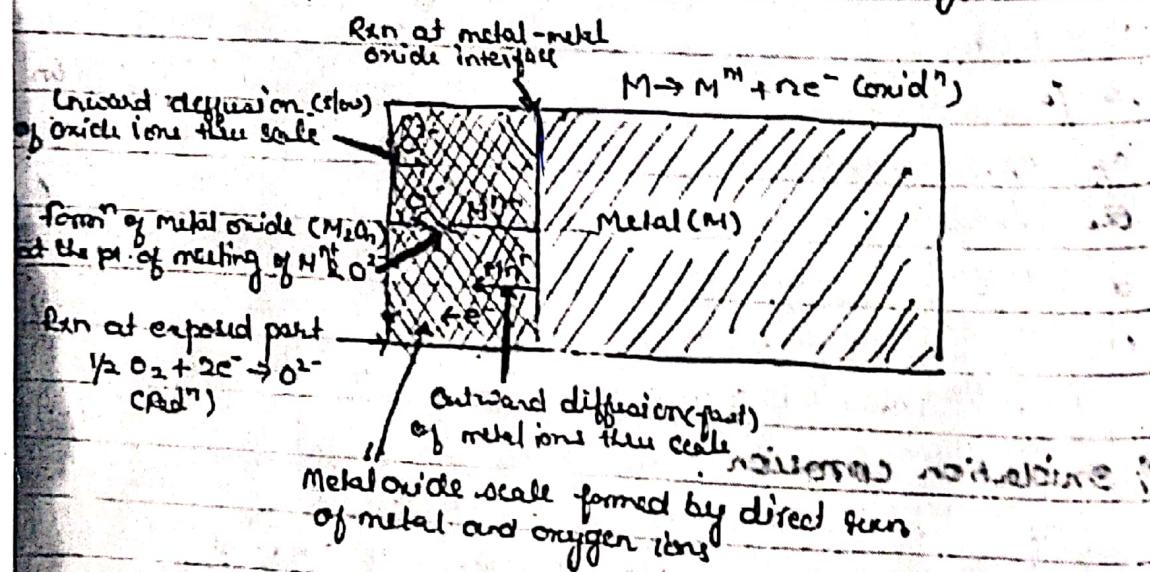
#### Oxidation corrosion:

This type of corrosion is one of the most common ways in which metals are attacked by direct action of oxygen; generally in absence of moisture. Alkali & alkaline earth metals (e.g. Na, Mg, Ca, etc) suffer extensive oxidn even at low temps whereas at high temps, practically all metals except Au, Ag & Pt are oxidized. The ions involved are:



Mechanism:

"Oxid" occurs first at the surface of the metal. The resulting metal oxide scale forms a barrier that tends to restrict further "oxid". For oxid to continue, either metal must diffuse outwards through the scale to the surface or the oxygen must diffuse inwards through the scale of the underlying metal. Both transfers occur, but the outward diffusion of metal ions generally, is more rapid than the inward diffusion of oxygen since the metal ion is appreciably smaller than the oxygen ion and consequently, of much more mobility.



Nature of the oxide film formed is very imp. in oxid<sup>2</sup> corrosion.

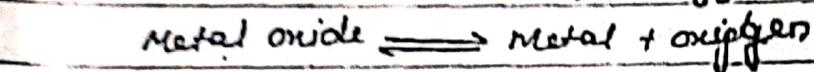
Metal + oxide → mixed oxide (corrolier product)  
When oxid<sup>2</sup> starts, a thin layer of oxide is formed on the metal surface and the nature of this film decides the further action. The film may be:

{ "n" layer is called film, when its thickness is less than about  $300 \text{ \AA}$   
( $1 \text{ \AA} = 10^{-8} \text{ cm}$ ); and it is called scale, when its thickness exceeds this value.

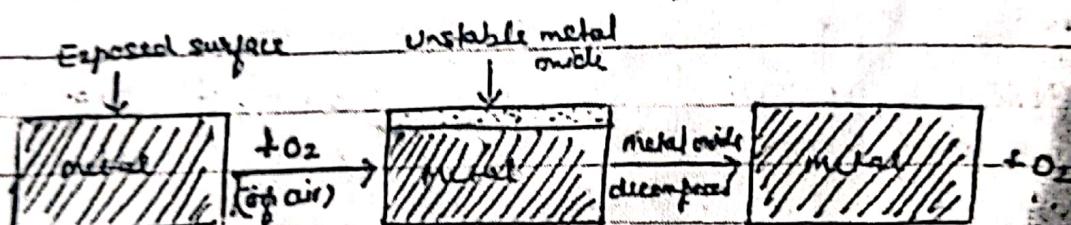
i) Stable: A stable layer has fine-grained ir structure and can get adhered tightly to the parent metal surface. Hence, such a layer can cut-off penetration of attacking oxygen to the underlying metal. Such a film is protective in nature; thereby shielding the metal surface.

The oxide films on  $\text{Al}$ ,  $\text{Ti}$ ,  $(\text{Sn})$ ,  $\text{Pb}$ ,  $\text{Cu}$ ,  $\text{Re}$  etc., are stable, tightly adhering & impervious in nature. Consequently, further oxidation corrosion is prevented.

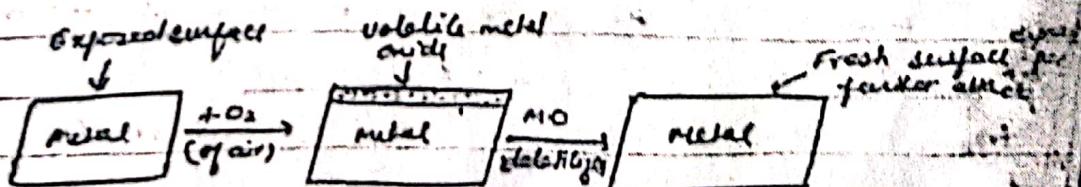
Ex:  $\text{Al}_2\text{O}_3$  is stable.  $\text{Al} \rightarrow \text{Al}_2\text{O}_3$  is stable.



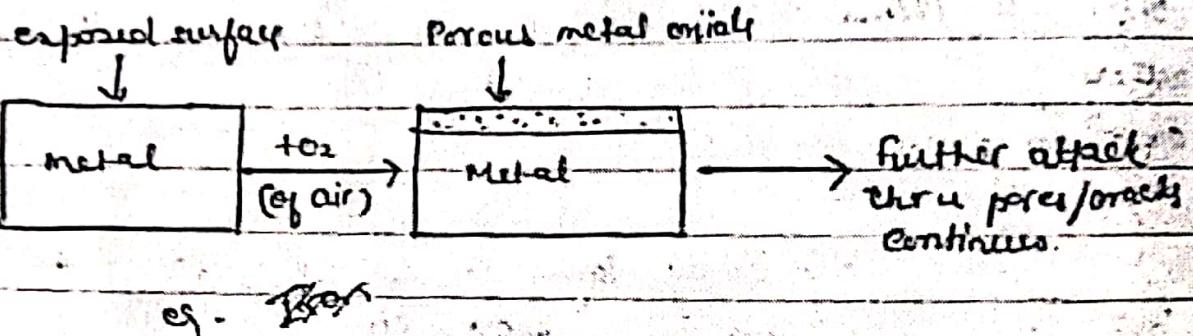
Consequently,  $\text{oxide}^n$  corrosion is not possible in such a case. Thus  $\text{Ag}$ ,  $\text{Au}$  &  $\text{Pt}$  do not undergo  $\text{oxide}^n$  corrosion.



ii) Volatile film: The oxide layer volatilizes as soon as it is formed, thereby leaving the underlying metal surface exposed for further attack. This causes rapid and continuous corrosion, leading to excessive corrosion e.g., molybdenum oxide ( $\text{MoO}_3$ ) is volatile.



(iv) Porous: The oxide film formed is having pores or cracks. In such a case, the atmospheric  $O_2$  have access to the underlying surface of metal, through the pores or cracks of the layer, thereby the corrosion continues unabated, till the entire metal is completely converted into its oxide.



PILLING-BEDWORTH RULE: Acc. to it,

→ If vol. of the oxide is at least as great as the vol. of the metal from which it is produced; then oxide is protective or non-porous. e.g. -

If vol. of the oxide is less than vol. of metal, the oxide layer is porous & non-protective. bcos it cannot prevent the access of  $O_2$  to the fresh metal surface below.

Thus,

Alkali & Alkaline-earth metals (like Li, K, Na, Mg) form oxide of vol. less than the vol. of metals. This results in the form<sup>n</sup> of a porous layer thru which  $O_2$  can diffuse to bring about further attack on the metal.

On the other hand, Aluminium, tungsten and molybdenum form layer oxide layers of greater volume than the metal from which they are produced. Consequently, an extremely tightly-adhering non-porous layer is formed. Due to the absence of any pores or cracks in the oxide film, the rate of rust rapidly decreases to zero.

2) CORROSION BY OTHER GASES: Gases like  $\text{SO}_2$ ,  $\text{Cl}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{F}_2$  etc. The extent of corrosive effect depends mainly on the chemical affinity b/w the metal and gas involve. The degree of attack depends upon "form" of protective (non-porous) or non-protective (porous) films on the metal surface.

e.g. The  $\text{AgCl}$  layer formed from the attack of chlorine on silver metal is protective & non porous. So, the intensity of attack decreases and protects the Ag metal from further attack whereas, when  $\text{Cl}_2$  attack tin, forming  $\text{SnCl}_4$  layer which get volatilized from the surface of the tin & leaving thereby the fresh metal for further attack.

~~3) LIQUID METAL CORROSION:~~ This type of corrosion is due to the chemical action of flowing liquid at metal at high temp on solid metal or alloy. It occurs in device used for nuclear power. The corrosion involves dissolution of a solid metal or internal penetration of the liquid metal into solid metal.

### Wet corrosion / Electrochemical corrosion.

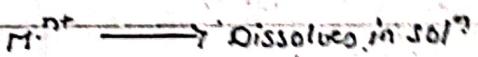
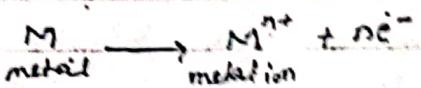
Electrochemical corrosion, as its name goes, involves electrochemical cell (anode - cath.) It takes place when moisture or a liquid is present. The following two cond's must be satisfied generally in order that this type of corrosion to take place.

- 1) Availability of two different metals partly or completely immersed in a soln (electrodes)
- 2) Availability of a conducting medium (an electrolyte).

This corrosion occurs due to the existence of adjacent 'anodic' and 'cathodic' areas/parts, b/w which current flows through the conducting solution.

At anodic area, Red<sup>n</sup> rxn i.e., liberation of free electrons takes place, so anodic metal is destroyed by either dissolving or assuming combol state (such as oxide etc). Hence corrosion always occurs at anodic area.

At anode:



→ forms compd such as oxide.

At cathodic area, Red<sup>n</sup> rxn (i.e. gain of electrons) takes place usually cathodic rxns do not affect the cathode; hence most metals cannot be further reduced i.e. at cathodic part, dissolved constituents of the conducting medium accepts the electrons to form some ions (like  $\text{OH}^-$ ,  $\text{O}_2^-$ ).

The metallic ion (at anodic part) and non-metallic (formed at cathodic part) diffuse towards each other in conducting medium and form the corrosion product, no where b/w anode & cathode the electrons set free at the anode flow through the metal and are finally consumed in the cathodic rxn. Thus essential requirements for electrochemical cell corrosion involve: i) form<sup>n</sup> of anodic & cathodic areas or parts in conti with each other.

Corrosion of anodic areas only

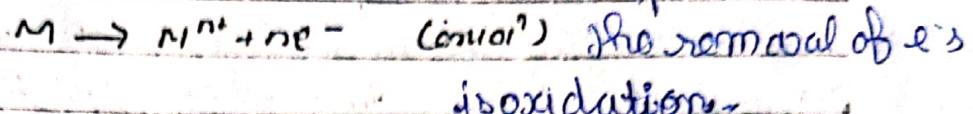
- a) form<sup>n</sup> of corrosion product somewhere b/w anodic & cathodic areas.

Mechanism: Electrochemical corrosion involves flow

of electron-current b/w the anodic and cathodic areas.

At anode  $\rightarrow$

The addition of hydrogen is also oxidized OR



At cathode  $\rightarrow$  Cathodic rxn consumes  $e^-$ 's with

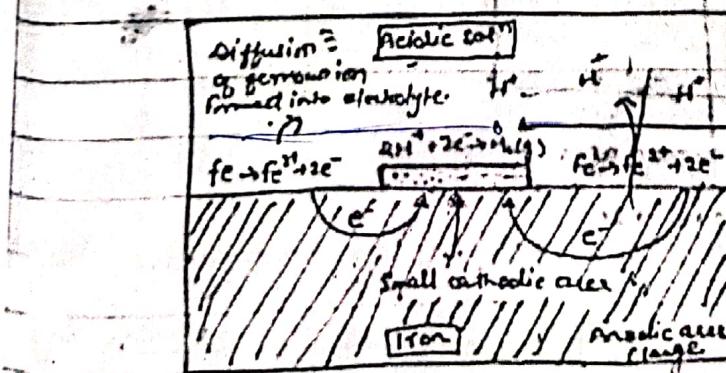
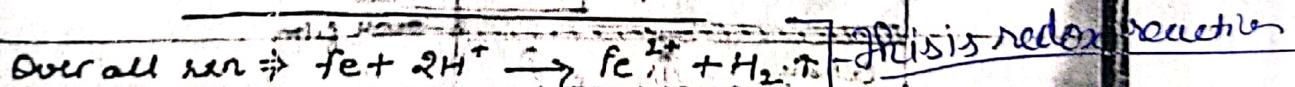
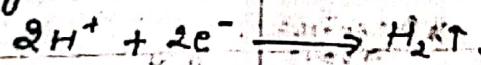
either by:

a) evolution of  $H_2$  b) absorption of  $O_2$ , depending upon the nature of the corrosive environment.

a) Evolution of hydrogen: It occurs, usually, in acidic environments. Consider metal like Fe. Anodic reaction is



ferrous ion. On this removal of  $e^-$ 's, it is dissolution of iron as ferrous ions & the liberation of  $e^-$ . These  $e^-$ 's flow thru the metal, from anode to cathode, where  $H^+$  ions (in acidic soln') are eliminated as hydrogen gas.



Oxidation and reduction both take place

Thus this type of corrosion causes displacement of hydrogen ions from the acidic soln' by metal ions.

very large area whereas the cathodes are small areas.

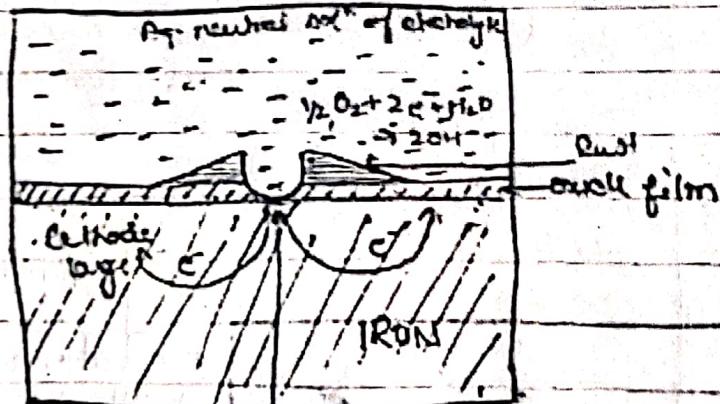
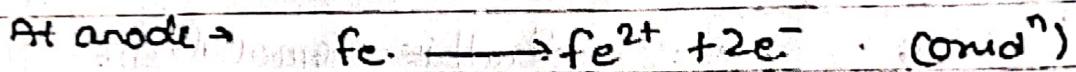
### b) Absorption of Oxygen:

→ takes place when a metal comes in contact with a basic (containing  $\text{OH}^-$  ions) or a neutral (say,  $\text{NaCl}$ ) salt.

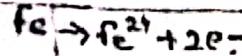
e.g. Rusting of iron in neutral soln. soln. of electrolytes ( $\text{NaCl}$ ) in the presence of atm oxygen.

The surface of iron is, usually, coated with a thin film of iron oxide. However, if this iron oxide film develops some cracks, anodic areas are created on the surface; while the well metal parts act as cathodes.

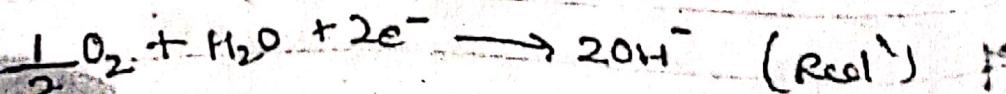
1. In this anodic areas are small surface parts
2. Cathodic areas are large surface part.



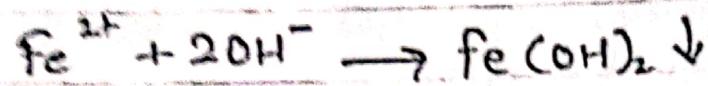
• All anodic areas



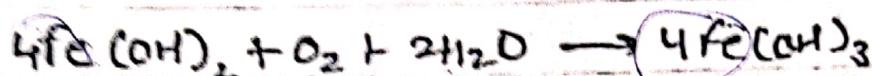
At cathode - Liberated e-s flows from anodic to cathodic steel iron metal, where e-s are intercepted by the dissolved  $\text{O}_2$  as:



ferrous hydroxide is pptd.

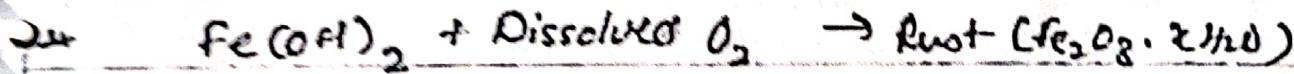


(i) if enough  $\text{O}_2$  is present,  $\text{Fe(OH)}_2$  is easily oxidised to ferric hydroxide.

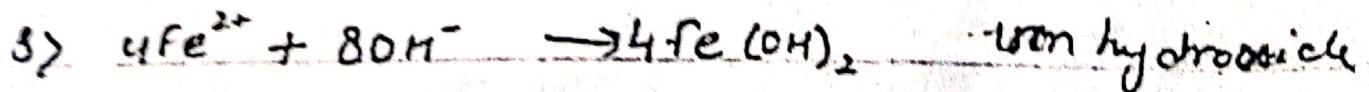
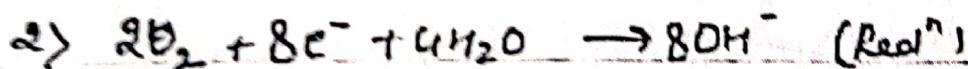
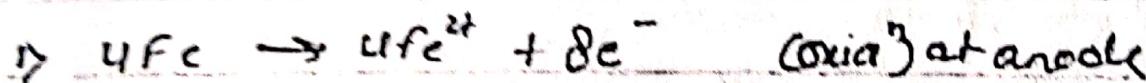


This product is called yellow rust, actually correspond to  $\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ .

(ii) if supply of  $\text{O}_2$  is limited, the corrosion product may be even black anhydrous magnetite,  $\text{Fe}_3\text{O}_4$ .



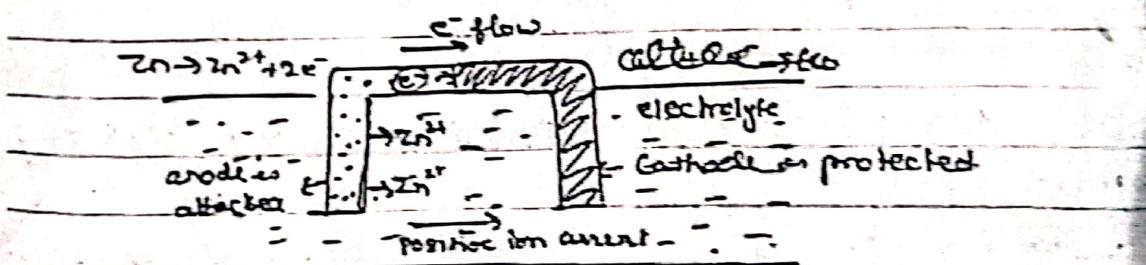
rxn involved -



## GALVANIC (OR BIMETALLIC) CORROSION :

When two dissimilar metals (e.g., Zinc & Copper) are electrically connected and exposed to an electrolyte, the metal higher in electrochemical series undergoes corrosion. This type of corrosion is called Galvanic Corrosion.

Zinc (higher in electromf series) forms the anode & is attacked & get dissolved; whereas Cu acts as cathode.



### Mechanism:

In acidic sol<sup>n</sup> → Hydrogen evolution corrosion occurs  
In neutral or basic sol<sup>n</sup> → O<sub>2</sub> absorption occurs.

The electron-current flow from Zinc to Cu. Thus it is evident that the corrosion occurs at the anodic metal; while the cathodic part is protected from the attack.

- Eg → 1) Steel screws in a brass marine hardware  
2) Lead-Antimony solder around Cu wire  
3) A steel propeller shaft in bronze bearing  
4) Steel pipe connected to Cu plumbing.

Brass      Cu & Zn  
bronze → Cu & Sn  
steel - Fe & C

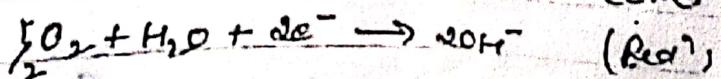
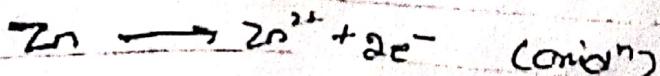
## Mild (anodic) cell corrosion (or) differential aeration corrosion

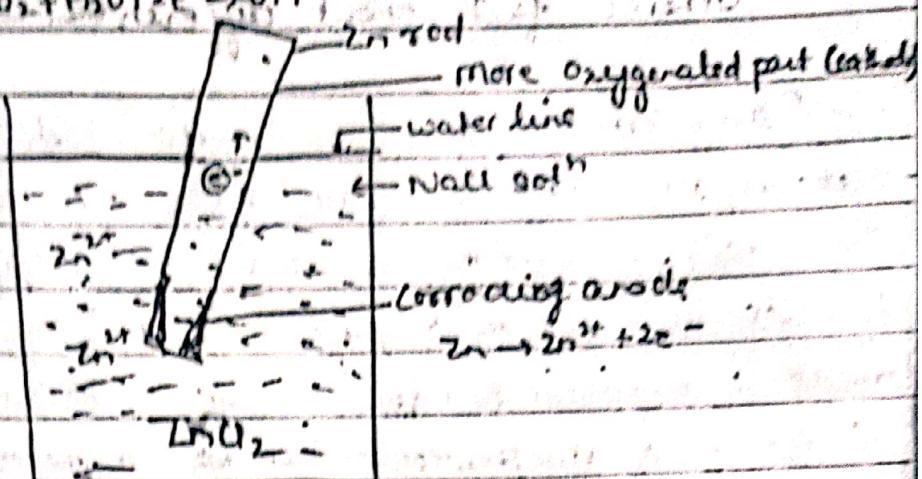
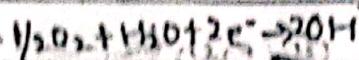
→ Also comes under the name "Differential aeration corrosion".

When a metal surface is exposed to air atmosphere of different air conc' or different  $O_2$  conc'; the part that is exposed to low oxygen conc' acts as anode & the other part that is exposed to high  $O_2$  conc' acts as cathode.

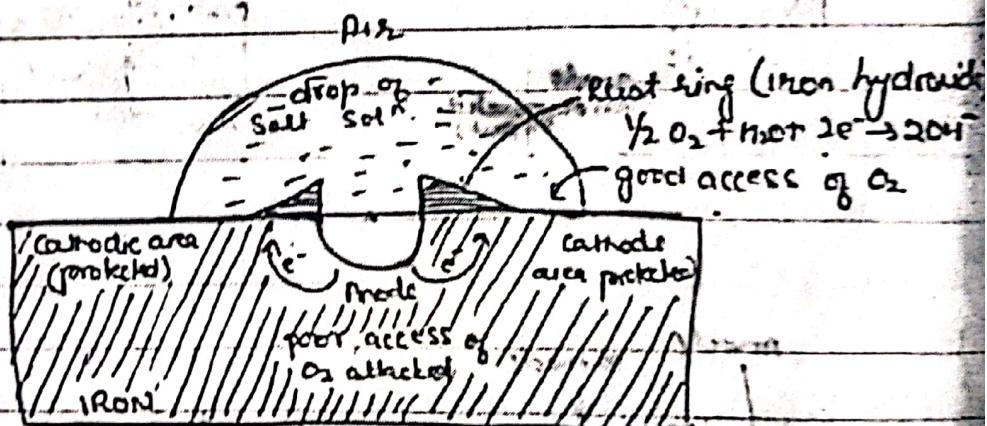
As we know, electrons flow from anode to cathode. This flow of  $e^-$  is caused by the difference in the air conc' and that is why it is called "differential aeration conc'".

Differential aeration accounts for the corrosion of metals, partially immersed in a sol' just below the water line. Thus, if a metal (say Zn) is partly immersed "in a sol' (e.g. salt), in a dil. sol' of neutral salt (NaCl) & the sol' is not agitated properly. Then the parts above & closely adjacent to the waterline are more strongly aerated (bcos of easy access of  $O_2$ ) & become cathodic. On the other hand, parts immersed to greater depth (which have less access of  $O_2$ ) now become anodic. So a diff. of potential is created, which causes a flow of current b/w two differentially aerated areas of the same metal. Zn will dissolve at the anodic areas &  $O_2$  will take up the  $e^-$ s at the cathodic areas to form hydroxyl ions.





In a similar way, iron corrodes under water drops (as salt salt'). Area covered by droplets, having no access of  $O_2$ , become anodic w.r.t respect to the other areas, which are freely exposed to air.



from the above oxygen conc' all increases corrosion, but it occurs where the oxygen conc' is lower.

## General facts about differential aeration corrosion

Pitting corrosion: It is a localized accelerated attack, resulting "the form" of cavities around which the metal is relatively unattacked. Thus pitting corrosion results in "the form" of pinholes, pit & cavities in the metal. Pitting is usually the result of breakdown or cracking of the protective film on a metal at specific pts. This give rise to "the form" of small anodic and large cathodic areas. On the

