

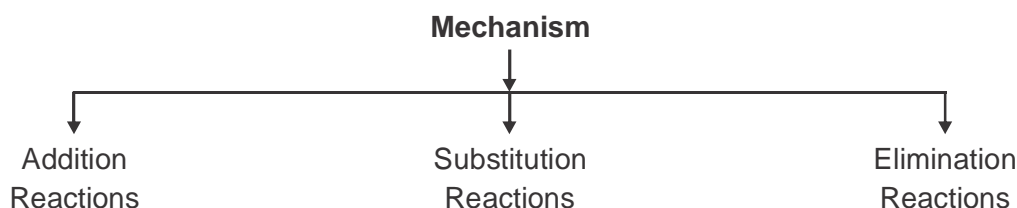
**UNIT-8**

# Organic Reaction Mechanism and Synthetic Applications

## 1. ORGANIC REACTION MECHANISM

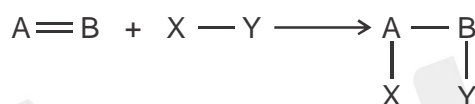
A detailed and stepwise description of pathway by which reactant is converted into product is called reaction mechanism.

**Types of Reaction Mechanism :**



### Addition Reaction

Addition reaction are the characteristics property of the multiple bond. (e.g. alkenes and alkynes).

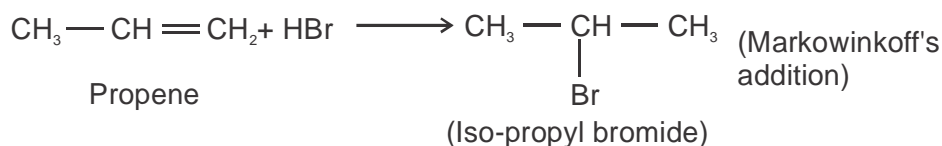


The addition reaction can be divided into four types i.e

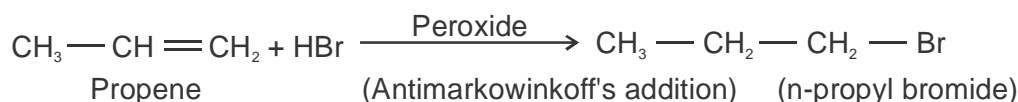
1. Electrophilic additions
2. Nucleophilic additions
3. Free Radical additions
4. Concerted additions

**1. Free Radical Addition :** In general, the addition of halogen acid to unsymmetrical alkenes give Markownikoff's addition product.

**Markownikoff's Addition :** When an unsymmetrical reagent added to an unsymmetrical multiple bond (alkene or alkyne) the negative part of reagent attached to that carbon atom which has lesser no. of H atom.



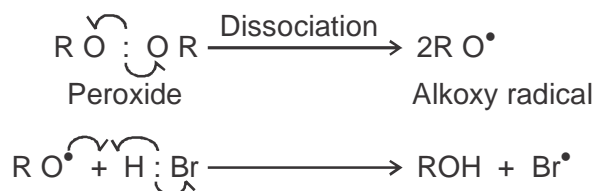
However, this is not always the case. Addition of HBr to unsymmetrical alkenes in presence of a peroxide gives a product which is different from the Markownikoff's product this is known as Antimarkownikoff's addition. This is also known as peroxide effect or Kharasch effect.



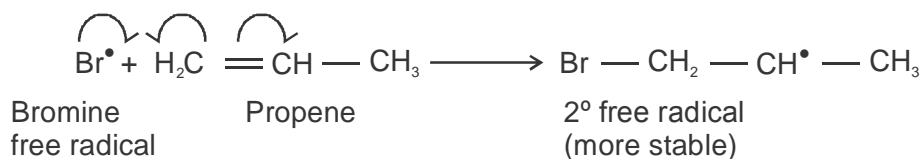
Free radical addition reactions occurs either in the gas phase or in inert non polar solvents in the presence of UV light or sunlight, heat or catalytic amount of radical initiators such as peroxide, azo compounds like AIBN (Azo isobutyronitrile) etc.

Following steps are involved in the free radical mechanism.

**(1) Chain Initiation Step :** Peroxide dissociates into two free radicals called alkoxy radicals.

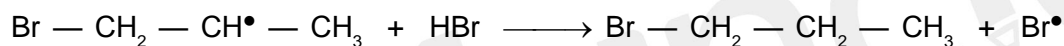


**(2) Chain Propagation Step :** Bromine radical adds to a double bond, forming a new free radical with the odd electron on the carbon atom.

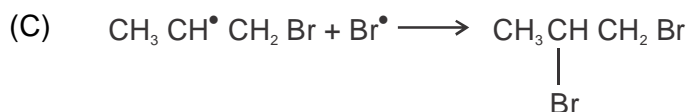
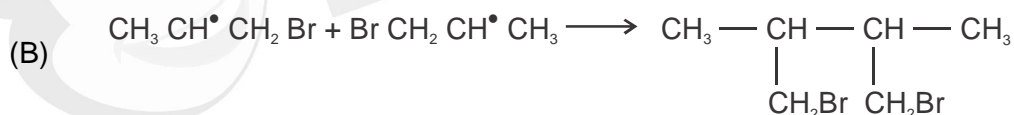


Since secondary free radical is more stable than the primary free radical, only the secondary free radical is formed.

The alkyl free radical (secondary free radical) reacts with an HBr molecule to generate another bromine radical.

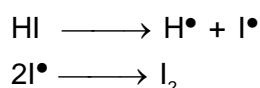


**(3) Chain Termination Step :** Termination occurs by any or all of the reactions which use up species involved in the propagation steps.

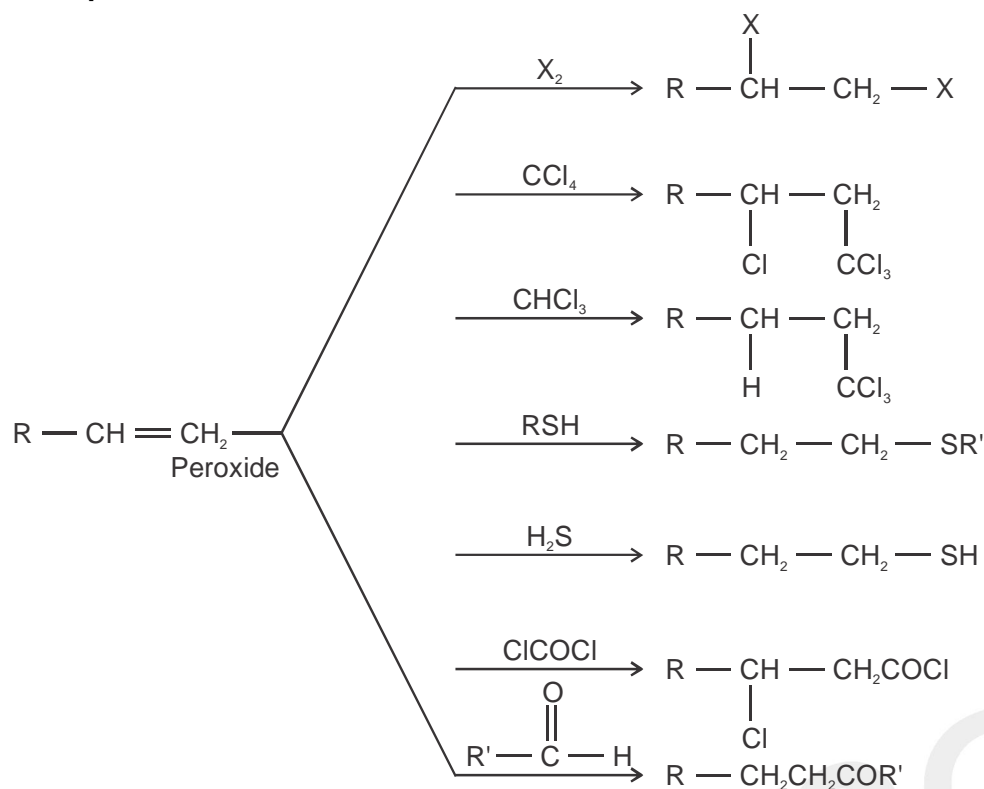


- Only HBr gives free radical addition reaction in the presence of Peroxide. HF, HCl and HI do not give free radical addition. This is because HCl and HF have large bond energy so do not give free radicals.

While HI has minimum bond energy so it is very reactive.



Examples :



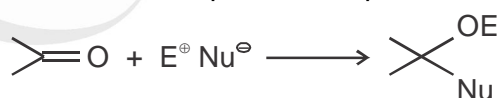
**2. Nucleophilic Addition :** Such reaction are usually encountered in compound containing Polar functional groups e.g., carbonyl,  $-\text{C} \equiv \text{N}$ ,  $\text{C} = \text{S}$  etc.

The most important examples are encountered in compounds containing carbonyl group.

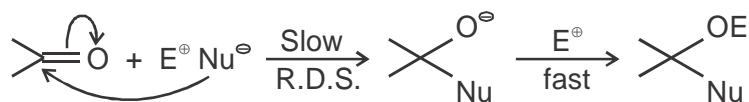


The heteroatom i.e. oxygen in the case of aldehyde or ketone, reduce the electron density on carbonyl carbon.

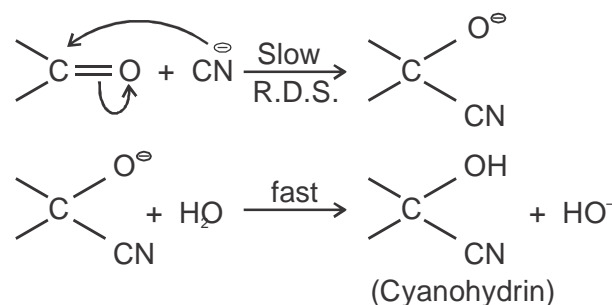
Thus, attack of nucleophile takes place at carbonyl carbon.



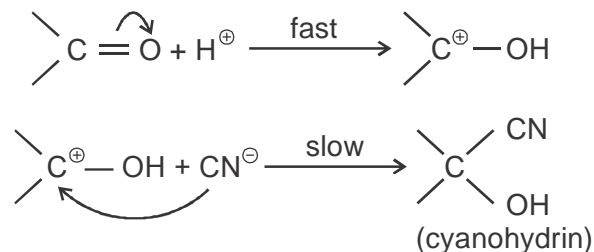
**Mechanism :**



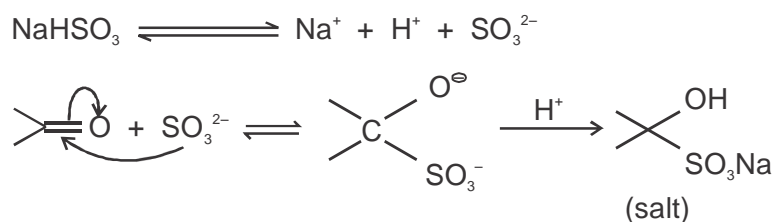
**(i) Addition of HCN to Carbonyl Group :** The addition is catalysed by acid or base. The base increases the concentration of  $\text{CN}^-$ . So the base catalysed nucleophilic additions are common.



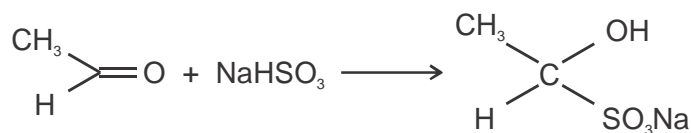
Acid catalysed addition of HCN  $\Rightarrow$



**(ii) Bisulphite Addition :** In the case of Bisulphite, the effective nucleophile in this case is  $\text{SO}_3^{2-}$   
The Product is Bisulphite Crystalline adduct



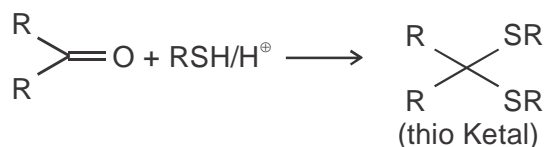
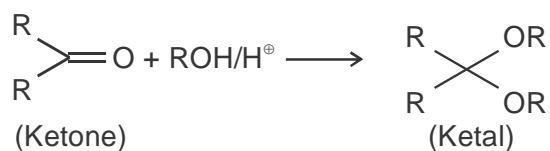
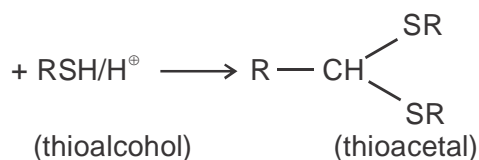
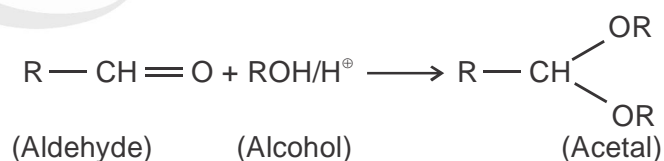
**Examples**

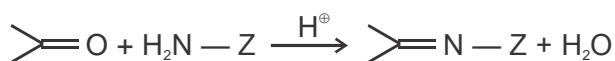
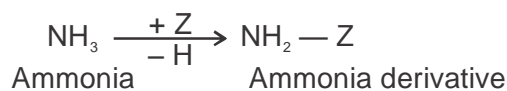
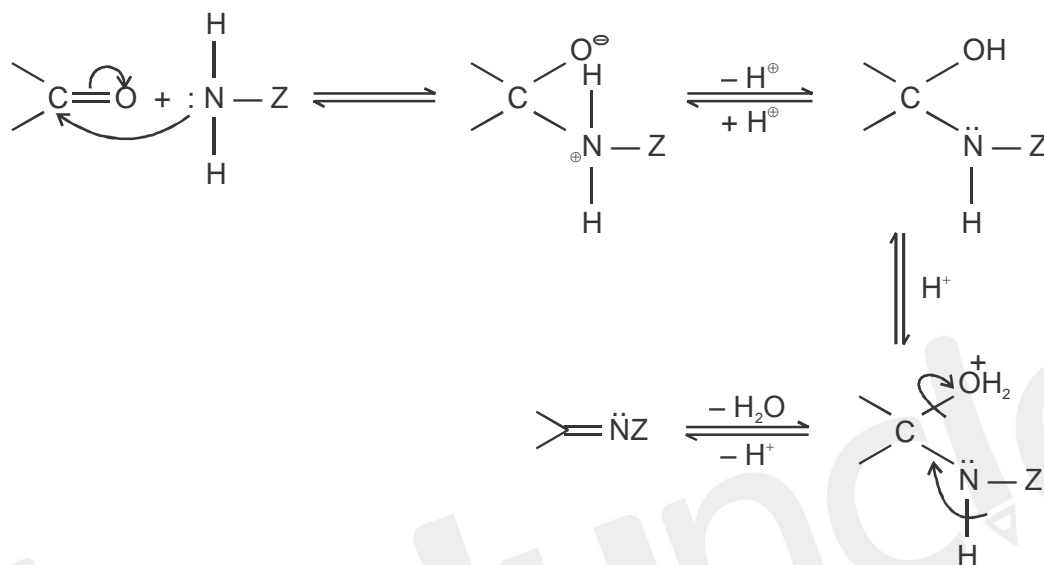


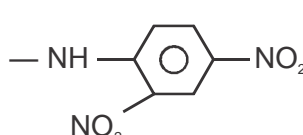
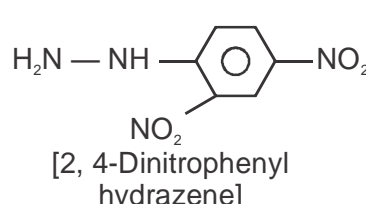
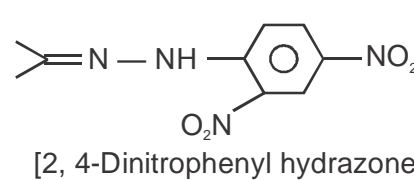
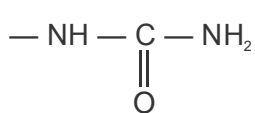
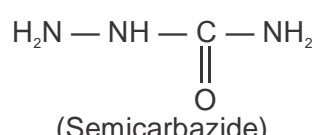
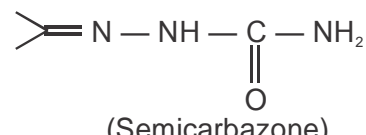
**(iii) Addition of Grignard Reagents :** Addition of Grignard reagent to Carbonyl compound gives the adduct, which can be hydrolyzed to alcohols.



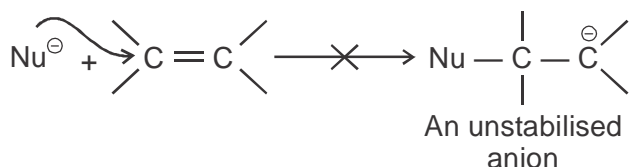
**(iv) Addition of Alcohol and Thioalcohol :**



**(v) Addition of Derivatives of Ammonia :**

**Mechanism :**


S.No.	Group (Z)	Reagent (NH <sub>2</sub> — Z)	Product (>C=N — Z)
1.	— OH	NH <sub>2</sub> OH (Hydroxylamine)	>C=N — OH (oxime)
2.	— NH <sub>2</sub>	NH <sub>2</sub> — NH <sub>2</sub> (Hydrazine)	>C=N — NH <sub>2</sub> (Hydrazone)
3.	PhNH —	H <sub>2</sub> N — NH — Ph (Phenylhydrazine)	>C=N — NH — Ph (Phenyl hydrazone)
4.		 [2, 4-Dinitrophenyl hydrazine]	 [2, 4-Dinitrophenyl hydrazone]
5.		 (Semicarbazide)	 (Semicarbazone)

**(vi) Nucleophilic Addition to Activated Carbon-Carbon Bond :** We know that simple double bond undergo electrophilic addition reactions. Carbon-Carbon double bonds are unreactive towards nucleophiles, so addition is not observed because it would require formation of an unstabilised anion, the conjugate base of an alkane.

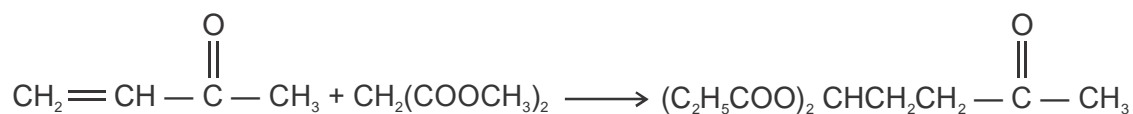


However, compounds containing carbon-carbon double bonds conjugated with electron withdrawing substituent (such double bonds are called activated carbon-carbon double bonds) undergo nucleophilic addition reaction. Such reactions are catalysed by base.

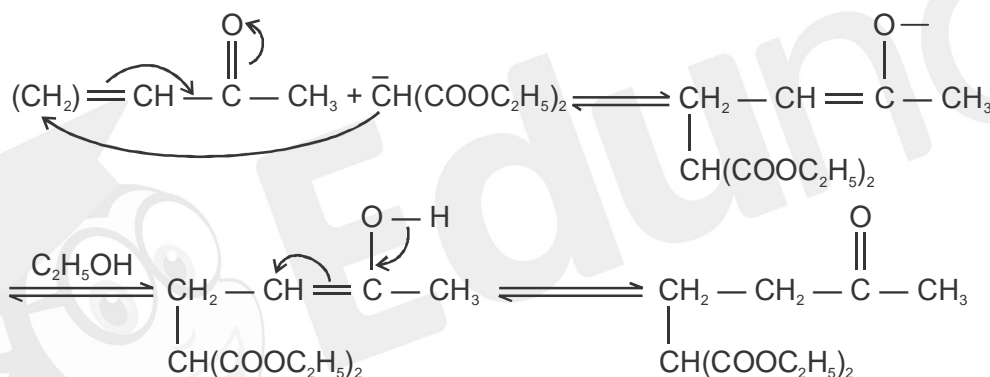
The most important reaction of this category is the Michael addition reaction.

**Michael Addition :** Also known as Conjugate addition, Michael addition is the 1,4 addition of a nucleophile to an  $\alpha, \beta$ -unsaturated Carbonyl compounds.

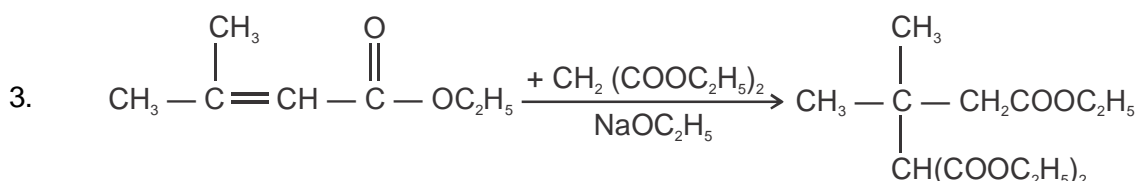
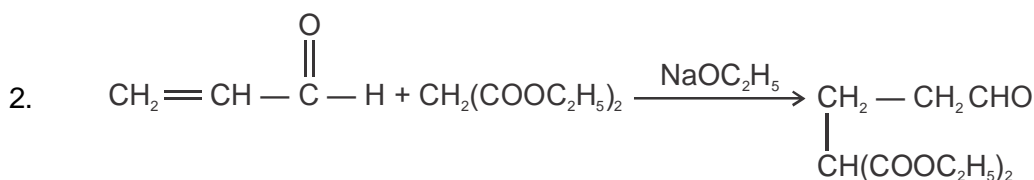
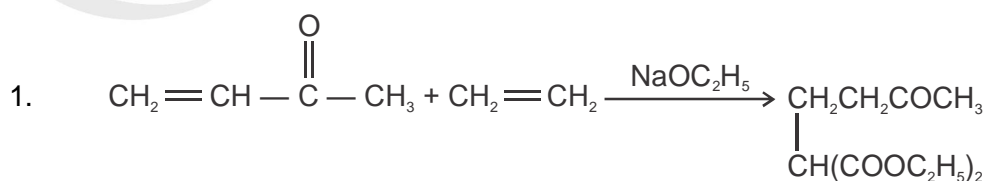
**Example-**



**Mechanism :**



**Applications :** Some typical applications of Michael addition are given below :

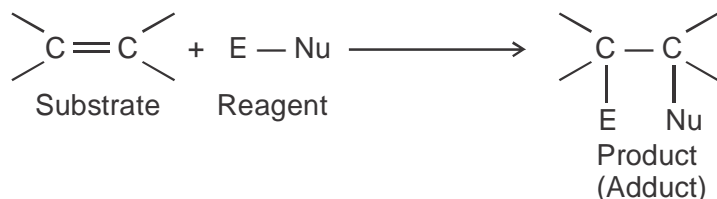


**3. Electrophilic Addition Reactions :** It takes place in the following substrate

1. Alkene
2. Alkyne
3. 1,3-Butadiene
4. Isocyanide

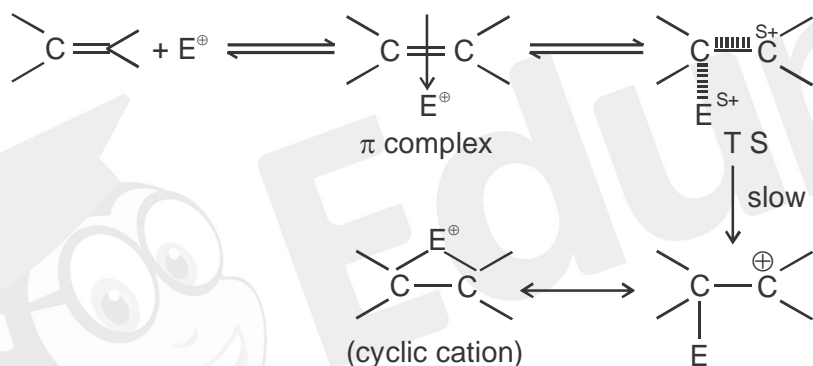
Pi-bonds have tendency to act as Lewis acid. Thus, Pi-bond is particularly susceptible to electrophile. Electrophiles include positive electrophiles such as Proton, Neutral Electrophiles such as bromine and the Lewis acid,  $\text{BF}_3$  and  $\text{AlX}_3$ , metal ions that contain vacant d-orbitals  $\text{Ag}^+$ ,  $\text{Hg}^{+2}$  and  $\text{Pt}^{+2}$  also act as electrophiles.

**Electrophilic Addition reactions in Alkenes :** Let us consider the following general reaction:



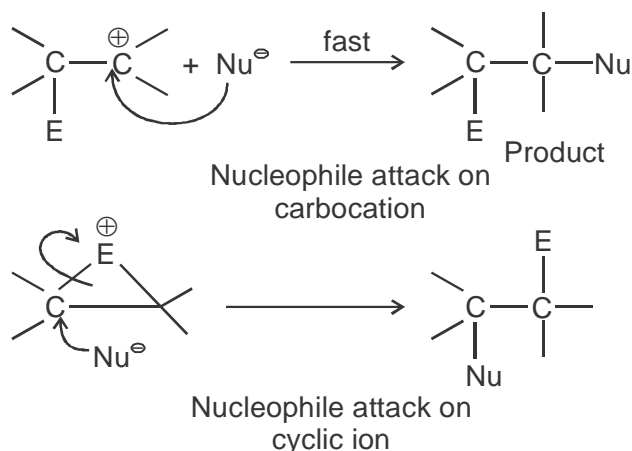
**Mechanism :**

**Step 1 :** The initial step of an electrophilic addition is the formation of a Pi-complex.



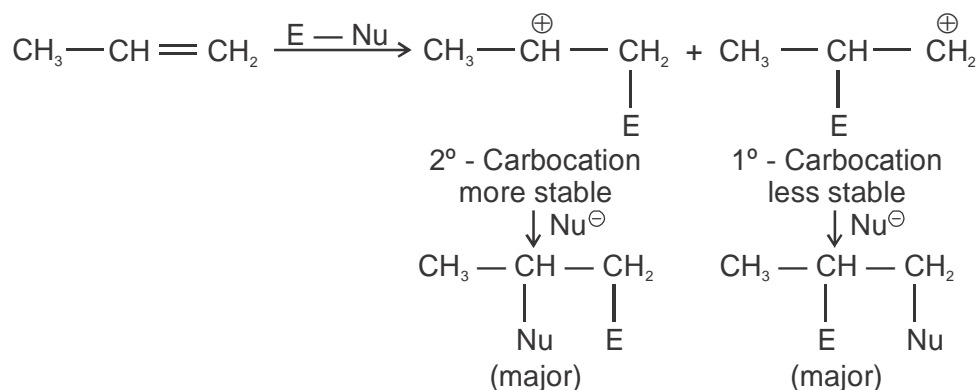
If the electrophile has a lone pair of electrons, then a three membered cyclic cation is formed. The cyclic cation may either be an intermediate (e.g. in the case of polar addition of  $\text{Br}_2$ ) or a true cyclic product (e.g. addition products of Carbene, nitrene etc.)

**Step 2 :** Second step involve the attack of nucleophile

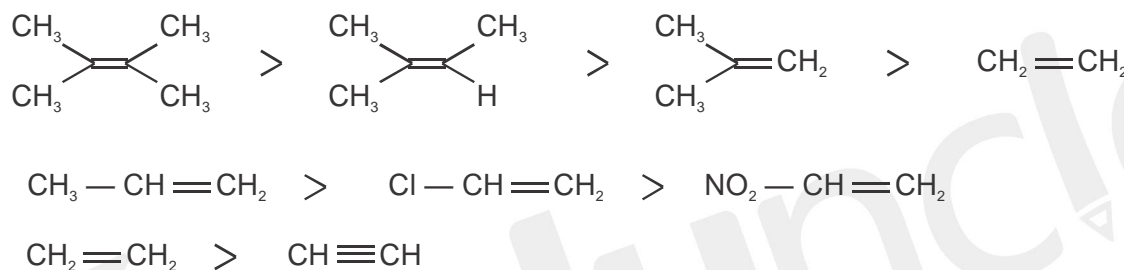


- Rate  $\propto [\text{>C=C}] [\text{E}^+]$
- Follow second order kinetics.

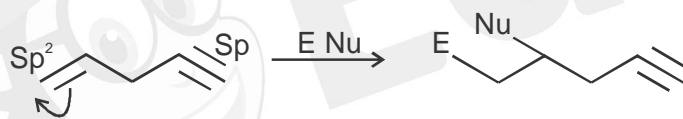
Since intermediate carbocation is formed so if possible rearrangement should be takes place.



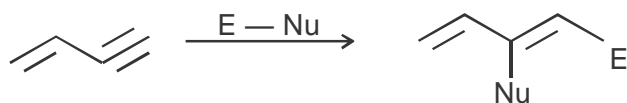
Since alkene behaves as nucleophile, so as well as nucleophilicity of alkene increases; their reactivity towards electrophilic addition reaction increase.



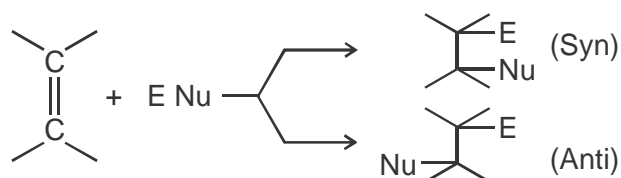
If in the substrate both double as well as triple bonds are present then electrophilic addition reaction take place at C = C first.



If both double and triple bonds are in conjugation then Electrophilic addition will be takes place at triple bond because to maintain conjugation.



**Stereochemistry of Addition Reaction :** If E<sup>⊕</sup> and Nu<sup>⊖</sup> attacks from the same side of the double bond, the addition will be syn; when as if they attacks from the opposite sides of double bond, the addition will be Anti.

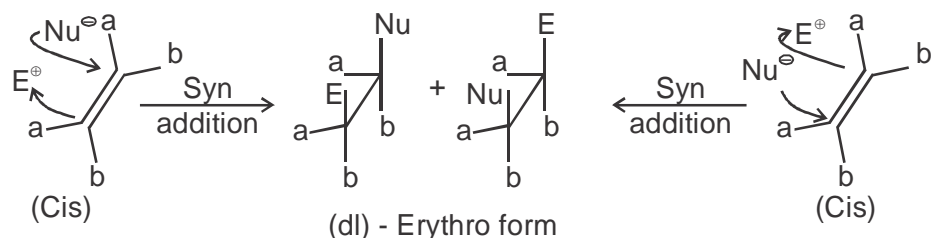


The nature of addition syn or anti of a particular reagent (E-Nu), ⇒

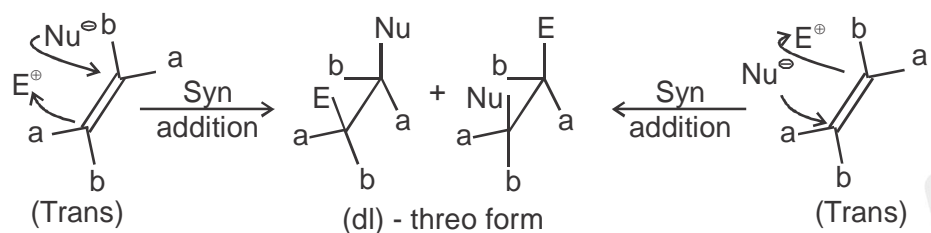


**Case 1 :** If  $E \neq Nu$  and addition is syn

(i) Syn addition to Cis alkene given (dl)-erythro form

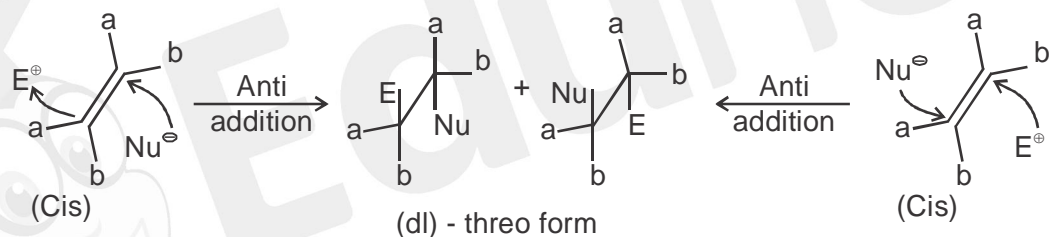


(ii) Syn addition to trans alkene given (dl)-threo form

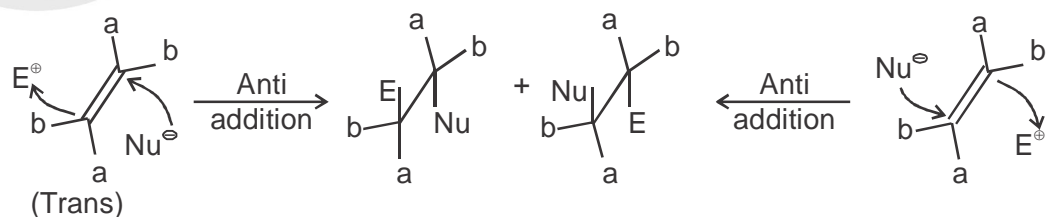


**Case 2 :** When  $E \neq Nu$  and addition is anti

(i) Anti addition to cis-alkene gives (dl) threo form



(ii) Anti-addition to a trans compound form (dl) erythro form

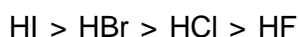


**Case 3 :** When  $E = Nu$ , the (dl)-erythro form becomes a meso but the (dl)-threo form remains the same.

(i) Addition of Hydrogen halide :



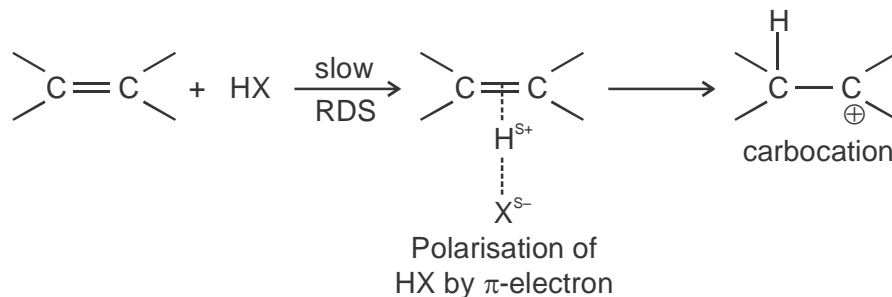
The reactivity of HX in this reaction is :



The strongest acid is the most reactive while the weakest acid is the least reactive.

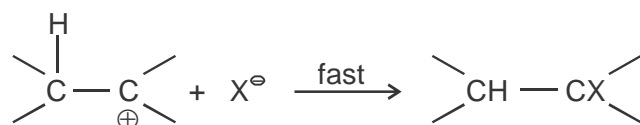
Addition of HX takes place in two steps :

**Step 1** : Electrophile  $\text{H}^{\oplus}$  attacks on alkene to form more stable carbocation.



Hydrogen halide do not form bridge ion with alkene because there is no bonded electron pair on a Proton.

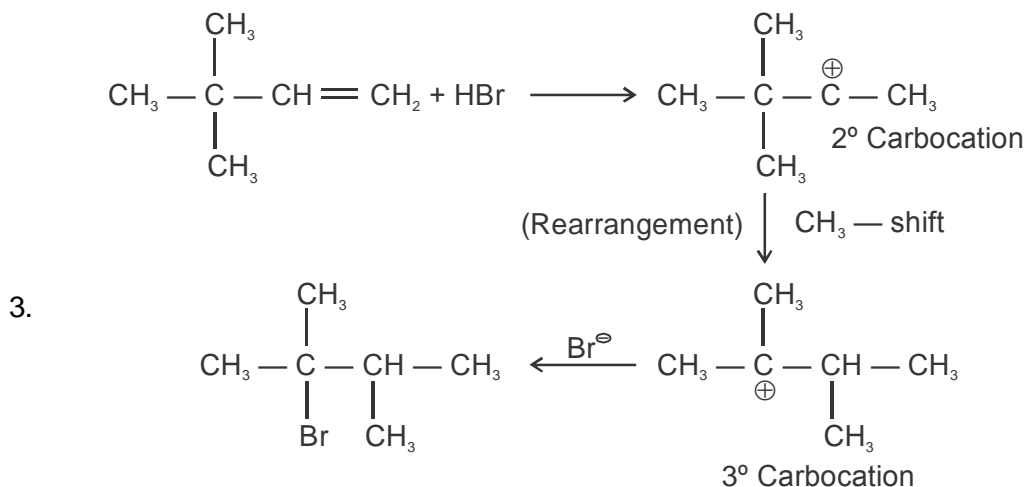
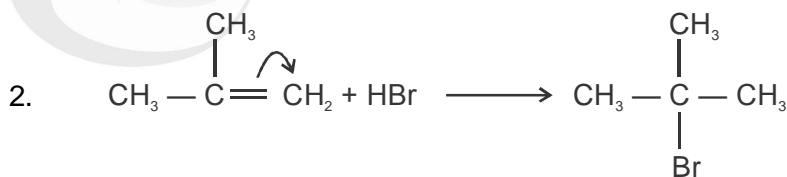
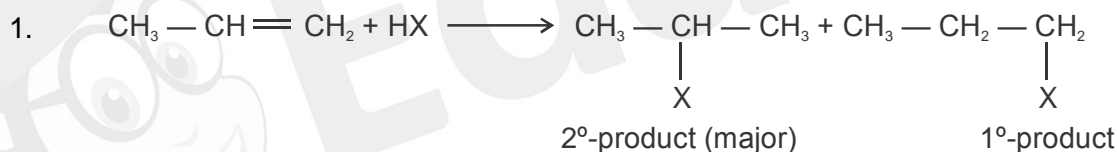
**Step 2** : It involves the rapid attack of the carbocation by the nucleophile  $\text{X}^{\ominus}$  to give addition product.



Since rate determine step involves the substrate and the reagent, the reaction is expected to follow the second order kinetics.

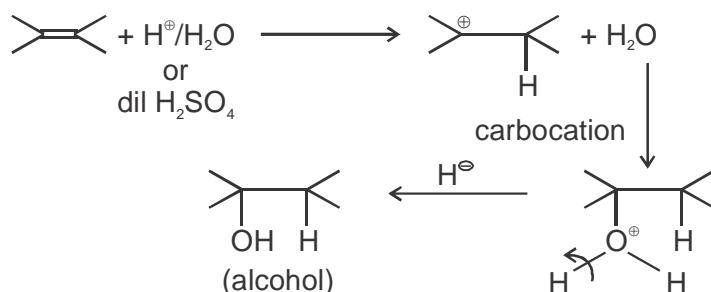
$$\text{Rate} = k [\text{Alkene}] [\text{HX}]$$

**Examples :**

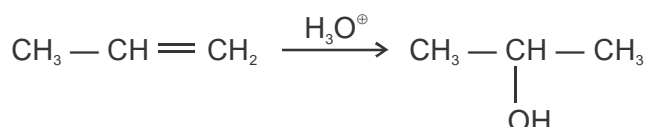


(ii) Addition of H<sub>2</sub>O :

## (A) Direct Addition :

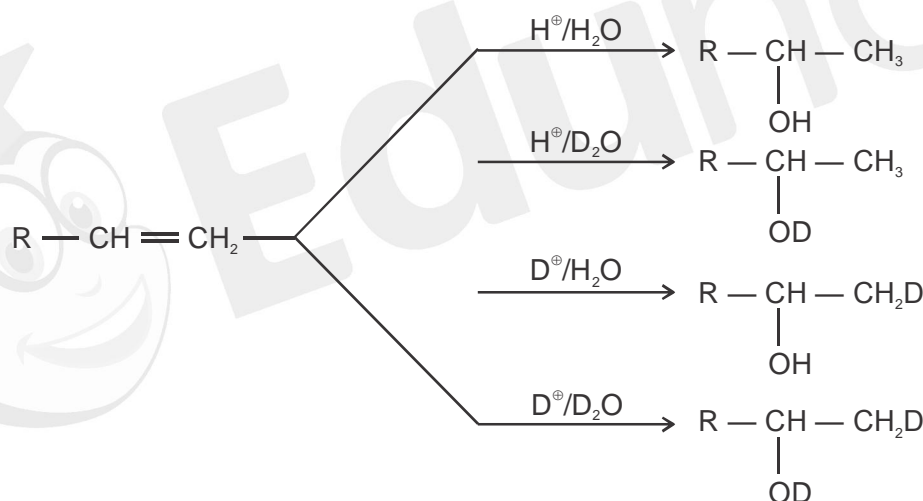


## Example



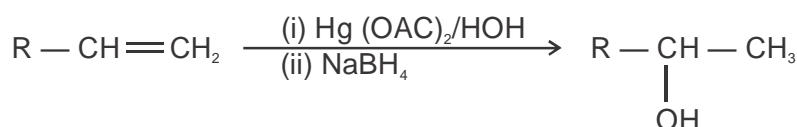
## Note :

- Hydration of alkene are usually regioselective and it follows Markownikoff's rule.
- Here intermediate carbocation is form so if possible rearrangement should be takes place.



## (B) Electrophilic addition involving metal ions (Oxymercuration-Demercuration) :

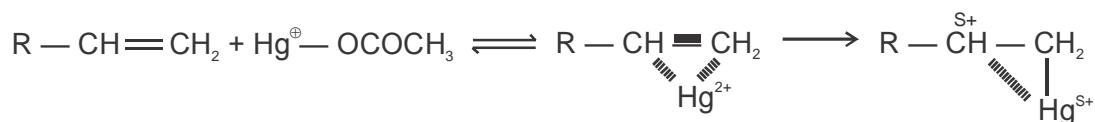
- Several metal cations are capable of electrophilic attack on alkenes e.g., Hg<sup>++</sup>, Pd<sup>++</sup> etc.
- Mercuric acetate and water add to alkenes in a reaction is called oxymercuration.
- Unlike the hydration reaction, oxymercuration proceeds without rearrangement.
- The product of the oxymercuration is usually reduced with sodium borohydride (NaBH<sub>4</sub>) is called demercuration



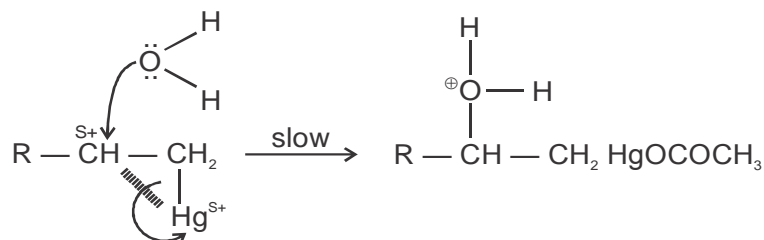
## Mechanism :



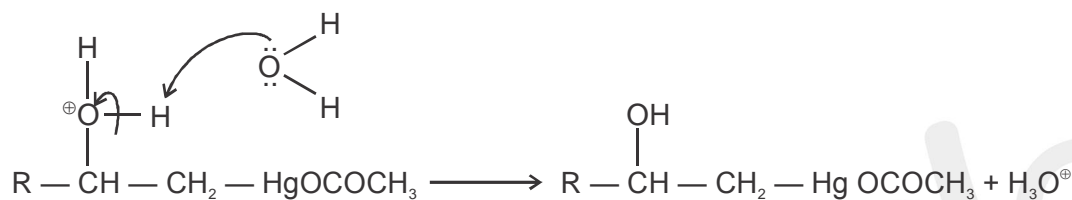
**Step 1 :** Attack of Electrophile -



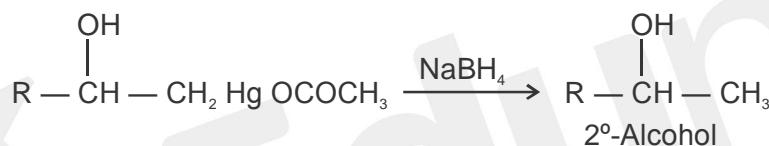
**Step 2 :**



**Step 3 :**

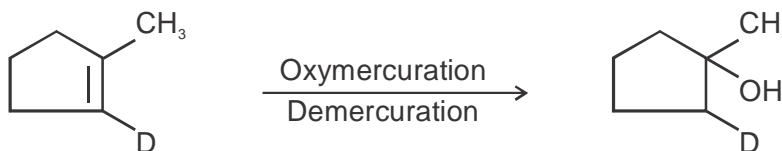
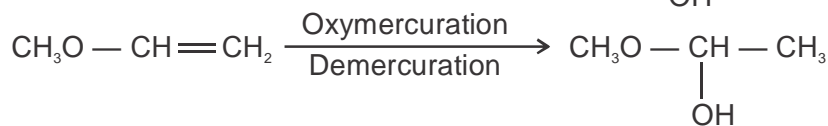
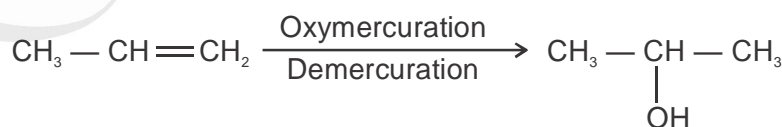
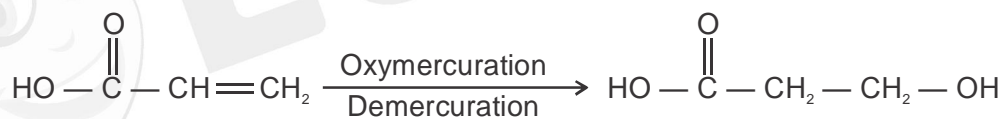


**Step 4 :**



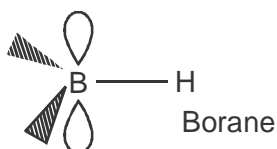
Here Markownikoff's addition of H and OH will be takes place.

**Examples**



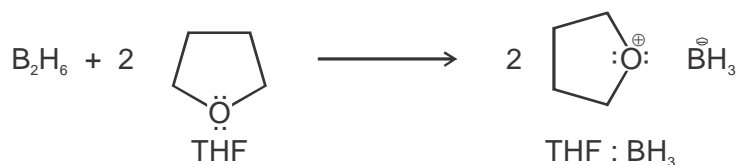
**(C) Addition of BH<sub>3</sub> :**

**Hydroboration-Oxidation :** Borane is neutral strong electrophile because it has empty p-orbital.



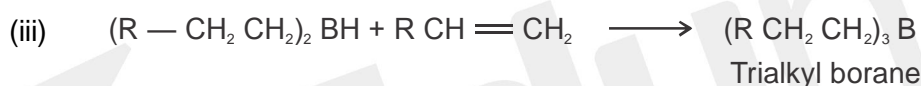
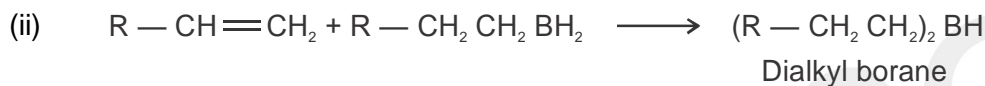
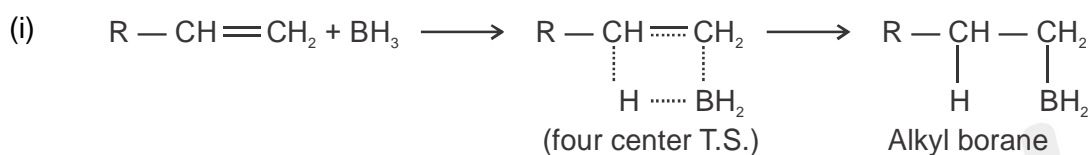
Free borane is unavailable as it spontaneously dimerises to diborane ( $B_2H_6$ ).

Diborane is commercially in the form of complex with THF

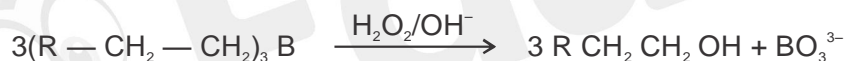


**Hydroboration** : Hydroboration is the process in which alkyl and alkenyl borane are prepared by the addition of borane to olefins and acetylenes.

Normally, reaction of borane with olefins does not stop after the addition of one  $BH_3$  molecule, because resulting  $RBH_2$  adds to another molecule of olefin to give  $R_2BH$ , which in turn adds to a third olefin molecule, thus the final product is trialkyl borane ( $R_3B$ )

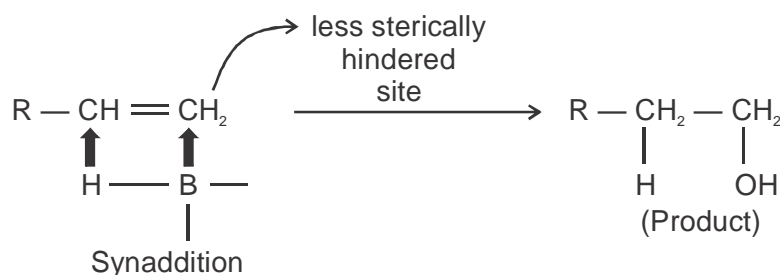


**Oxidation** : Organoboranes are easily oxidized to alcohols by alkaline hydrogen peroxide.

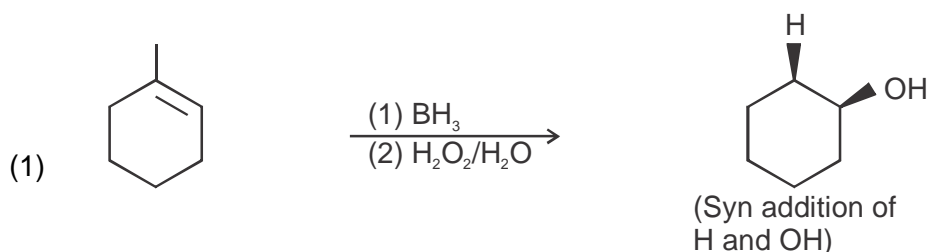


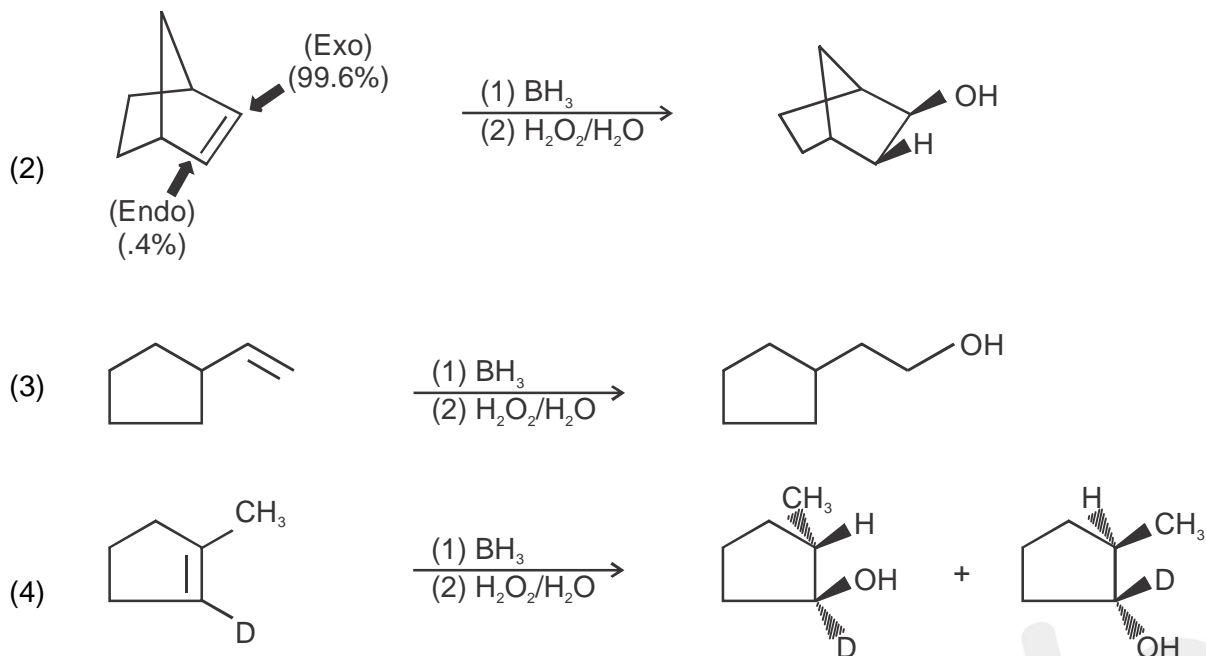
Here antimarkownikoff's product will be obtained.

**Stereochemistry** : The boron attacks from the less hindered side and overall addition is syn and is stereospecific.

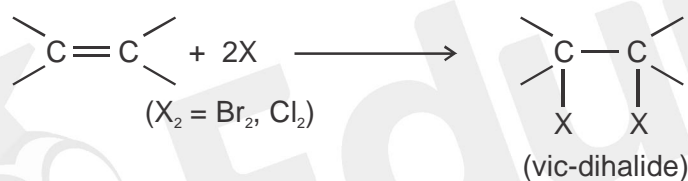


### Examples

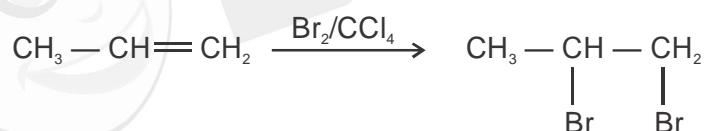




**(iii) Addition of Halogens :** Alkenes react with solutions of halogen in an inert solvent to produce vic-dihalide



**Example :**

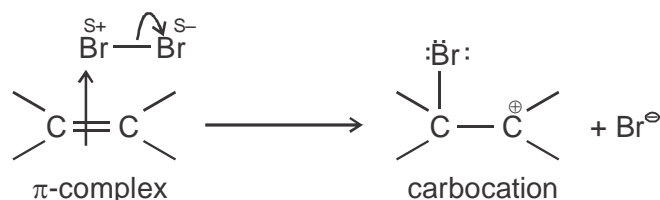


**Mechanism of Bromination :**

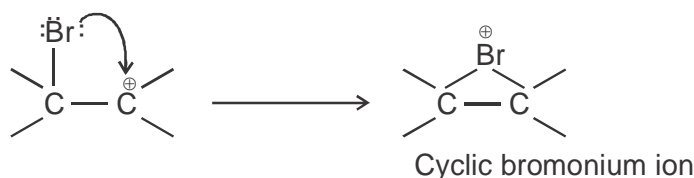
**Step 1 :** Formation of  $\pi$ -Complex.



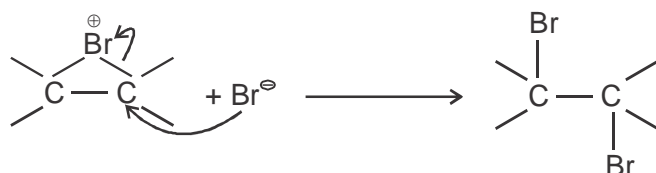
**Step 2 :** The  $\pi$ -Complex formed above breakdown to form a carbocation and bromide ion.



**Step 3 :** Formation of cyclic bromonium ion- Bromonium ion is a cation in which the bulk of the positive charge is on the bromide.

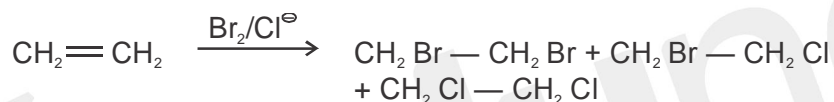


**Step 4 :** The cyclic bromonium ion thus produced reacts with the nucleophilic bromide ion leading to the formation of addition product.

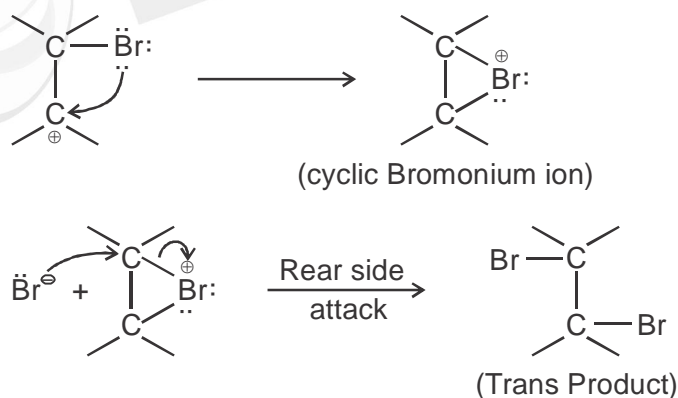


- The above mechanism is supported by the observation that mixed products are obtained when an alkene is treated with bromine water in presence of other nucleophiles such as chloride or nitrate ion.

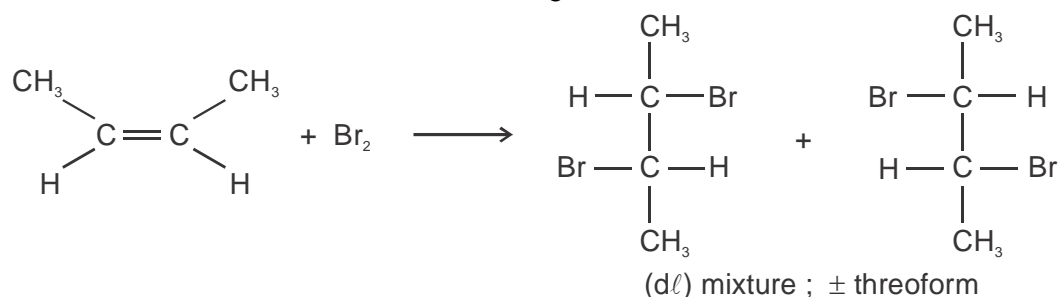
In these cases the stepwise addition takes place and not the direct addition of a halogen molecule to an alkene.

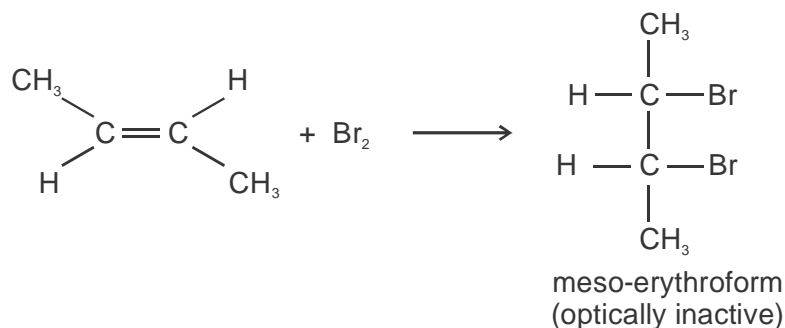


- Formation of  $\text{CH}_2\text{Br}-\text{CH}_2\text{Cl}$  confirm that reaction intermediate is positively charged intermediate which is trapped by the nucleophiles,  $\text{Cl}^\ominus$
- It has been found that the addition reaction of alkenes usually give trans-addition products. The above reaction mechanism can be explained by the formation of cyclic bromonium ion intermediate

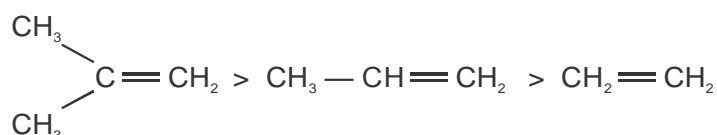


- When Cis-2-butene is treated with bromine, gives racemic mixture (pair of enantiomers) where as bromination of trans-2-butene gives meso dibromide.

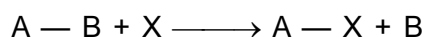




The rate of addition of halogen increase with increasing alkylation at the double bond. Thus reactivity of given alkenes in decreasing order is as follows :



**Substitution Reaction :** The replacement of one group by another is called substitution reaction.



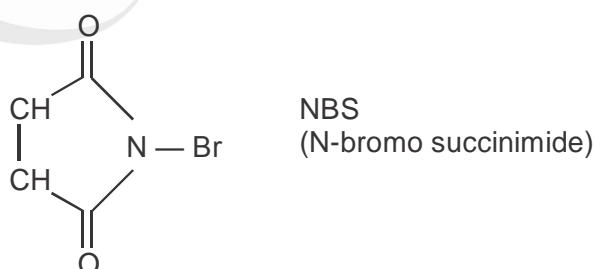
There are three main types of these reactions

- (i) Free Radical Substitution
- (ii) Electrophilic Substitution
- (iii) Nucleophilic Substitution

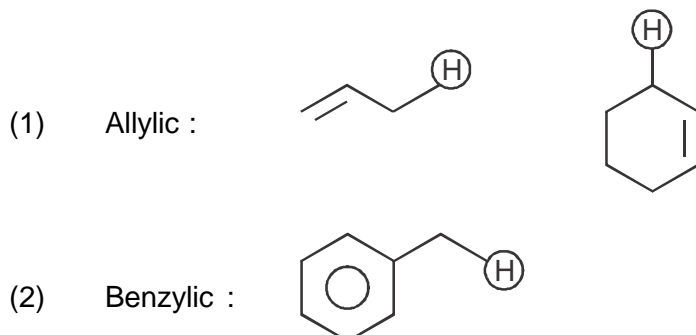
**(i) Free Radial Substitution Reaction :**

- (A) Bromination by NBS
- (B) Halogenation of alkane
- (C) Gomberg reaction
- (D) Wartz reaction
- (E) Hunsdieker reaction

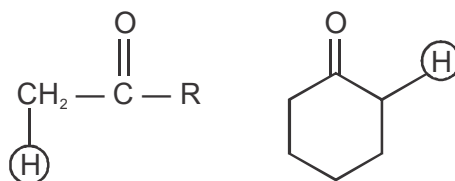
**(A) Bromination by NBS :**



NBS causes bromination at the following active positions -



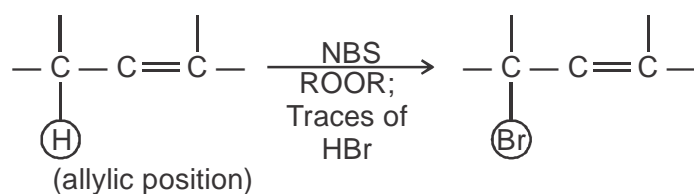
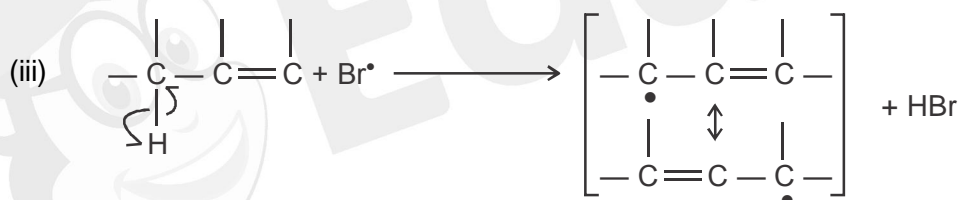
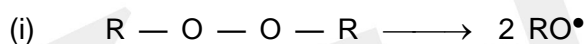


(3)  $\alpha$ -position with respect to carbonyl :

 (4) Propargylic position :  $\begin{array}{c} \text{CH}_2 - \text{C} \equiv \text{CH} \\ | \\ \text{H} \end{array}$ 

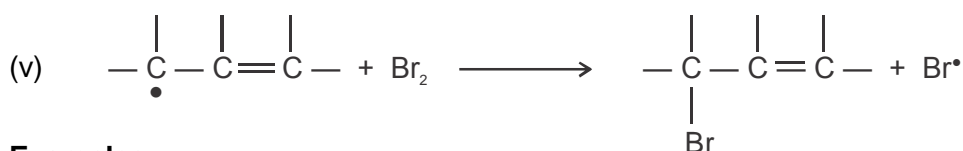
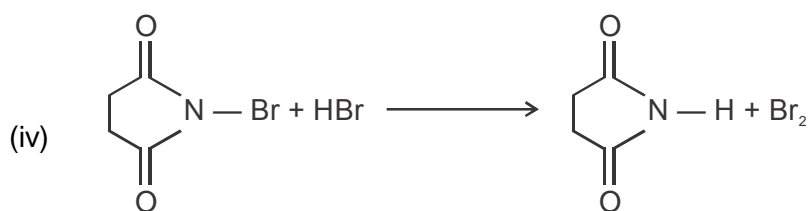
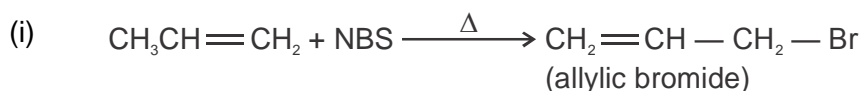
NBS also causes the oxidation of alcohol

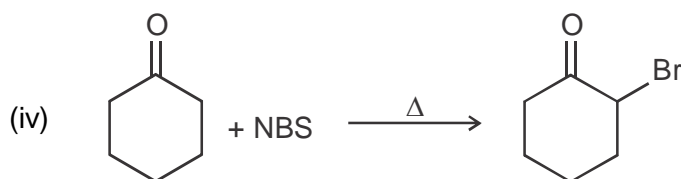
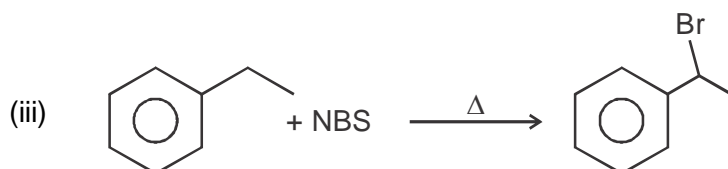
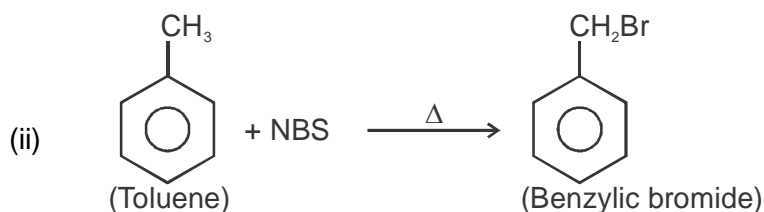
 $1^\circ$ -Alcohol  $\longrightarrow$  Aldehyde

 $2^\circ$ -Alcohol  $\longrightarrow$  Ketone

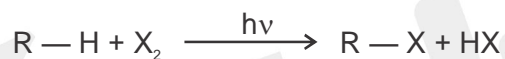
 $3^\circ$ -Alcohol  $\longrightarrow$  No oxidation

**Mechanism :**


Mostly stable resonating structure gives major product


**Examples :**




### (B) Halogenation of Alkane :



#### Mechanism :

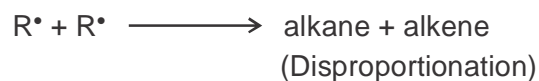
##### (1) Chain Initiation Step :



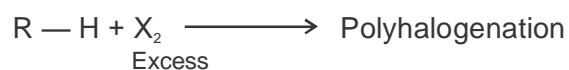
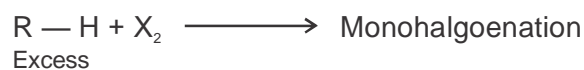
##### (2) Chain Propagation Step :



##### (3) Chain Termination Step :

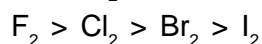


#### Important Points :

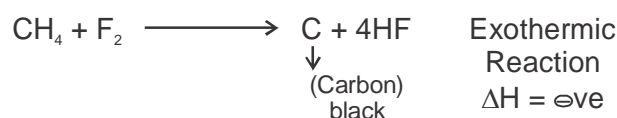


**Reactivity and Selectivity :**

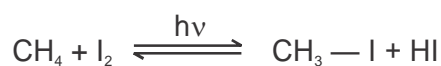
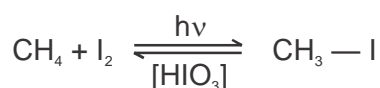
$$\text{Reactivity} \propto \frac{1}{\text{Selectivity}}$$

 Reactivity of  $X_2$  :


- $F_2$  is maximum reactive so fluorination does not takes place



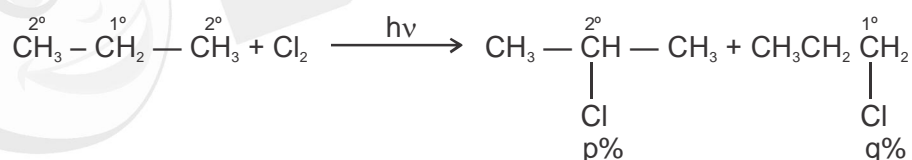
- $I_2$  is least reactive so iodination is reversible reaction


 Here  $HIO_3$  is used to remove HI

 Relative reactivity of  $Cl^\bullet$  and  $Br^\bullet$  radicals towards  $1^\circ$ ,  $2^\circ$  and  $3^\circ$  H atom :

	$1^\circ$ H	:	$2^\circ$ H	:	$3^\circ$ H
$Cl^\bullet \Rightarrow$	1	:	3.8	:	5.0
$Br^\bullet \Rightarrow$	1	:	82	:	1600

Relationship between % yield of product and relative reactivity of H atom :

$$\frac{\text{yield of } 2^\circ \text{ Product}}{\text{yield of } 1^\circ \text{ Product}} = \frac{\text{no's of } 2^\circ \text{ H's}}{\text{no's of } 1^\circ \text{ H's}} \times \frac{\text{relative reactivity of } 2^\circ \text{ H's}}{\text{relative reactivity of } 1^\circ \text{ H's}}$$

**Examples :**

 here,  $p\%$  = yield of  $2^\circ$  Product

 $q\%$  = yield of  $1^\circ$  Product

$$\frac{p\%}{q\%} = \frac{2}{6} \times \frac{3.8}{1.0} = \frac{7.6}{6} = 1.266$$

$$\frac{p\%}{q\%} = 1.26$$

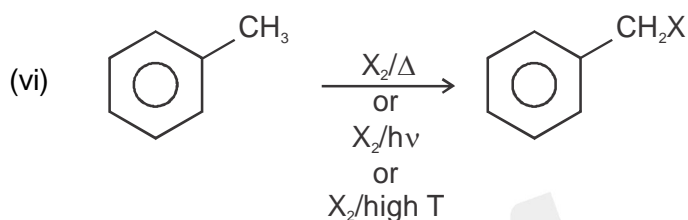
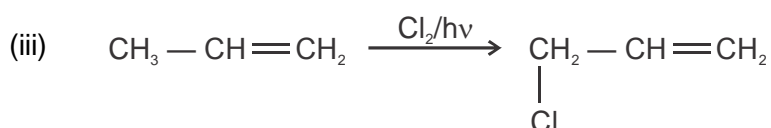
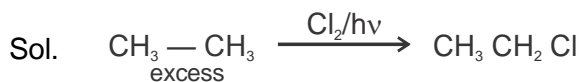
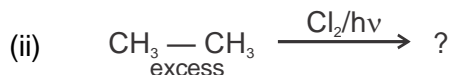
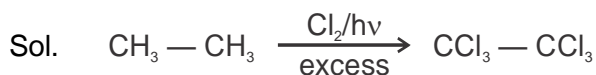
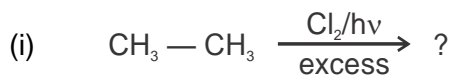
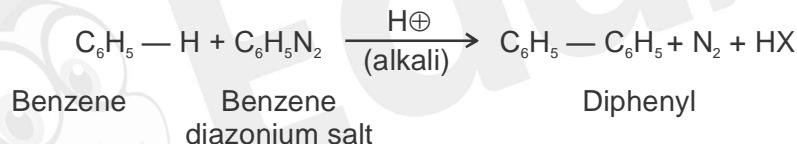
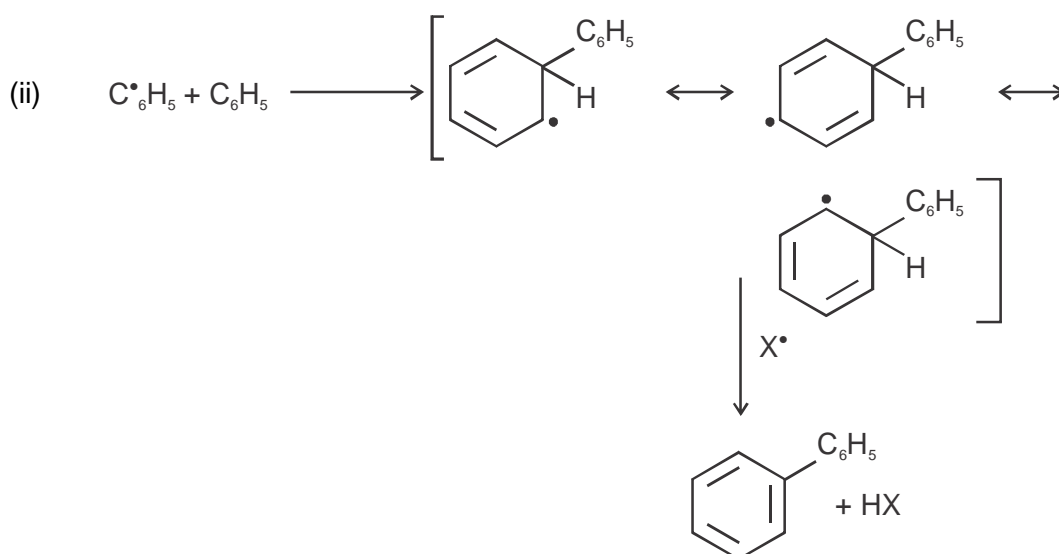
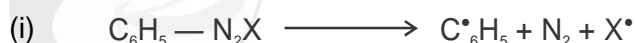
$$\frac{p}{(100 - p)} = 1.26$$

$$p = 126 - 1.26p$$

$$2.26p = 126$$

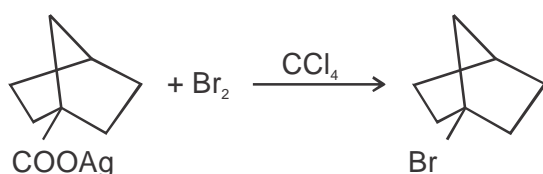
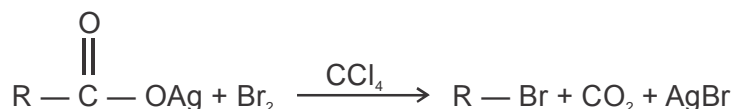
$$p = \frac{126}{2.26} = 55\%$$

$$q = (100 - 55) = 45\%$$

**Questions :**

**(C) Gomberg Reaction : Acylation of aromatic compounds.**

**Mechanism :**


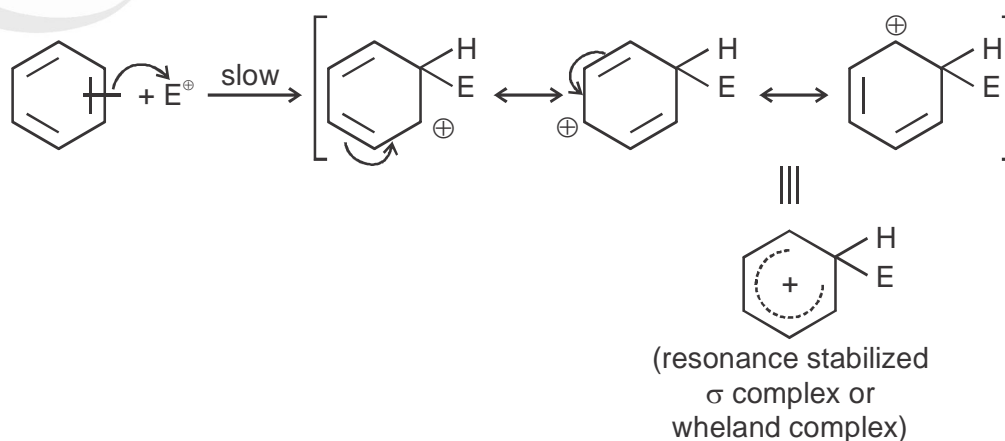
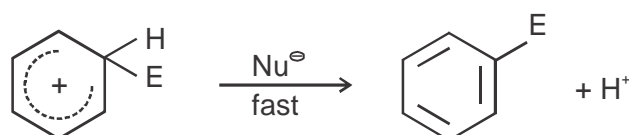
**(D) Wartz Reaction :**

**Mechanism :**

**(E) Hunsdiecker Reaction :**

**(ii) Electrophilic Substitution Reaction :**
**Aromatic Electrophilic Substitute Reactions :**

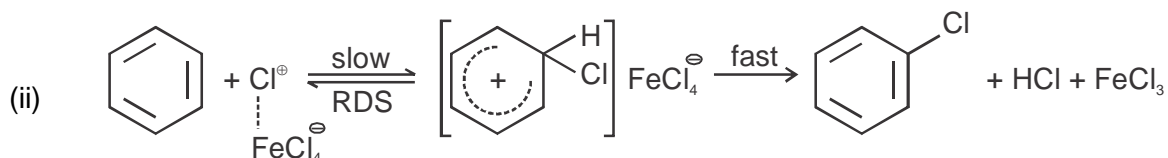
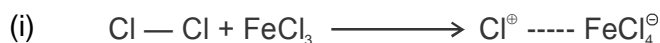
- Electrophilic substitutes are characteristics reactions of aromatic compounds.
- Aromatic Electrophilic substitution reactions follow second order kinetics, and rate of this type of reactions depends on the concentration of both the substrate and the attacking electrophile.

Generally accepted mechanism for such reactions designed as  $\text{ArS}_{\text{E}^2}$ , is suggestive two discrete steps :

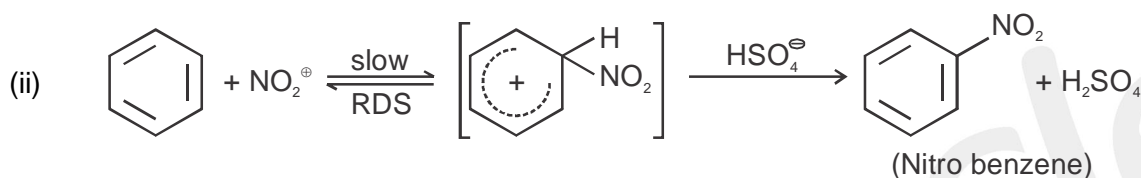
**Step 1 : Formation of  $\sigma$  Complex (or Wheland complex)**

**Step 2 : Loss of a Proton gives the substituted aromatic derivative.**


**Mechanism of Some Typical Aromatic Electrophilic Substitution Reactions :**

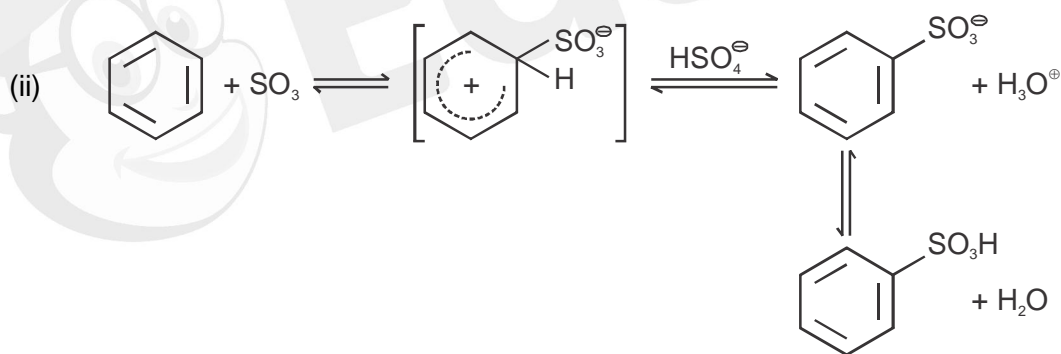
**(1) Halogenation :** Aromatic compounds can be halogenated with halogen in the presence of a catalyst often called as a halogen carrier, for ex.  $\text{FeCl}_3$ ,  $\text{FeBr}_3$ ,  $\text{AlCl}_3$  or  $\text{AlBr}_3$  etc. For example,



**(2) Nitration :** The introduction of a Nitro ( $\text{NO}_2$ ) group into an aromatic system is called nitration. The most common reagent for the nitration of aromatic compounds is a mixture of nitric acid.



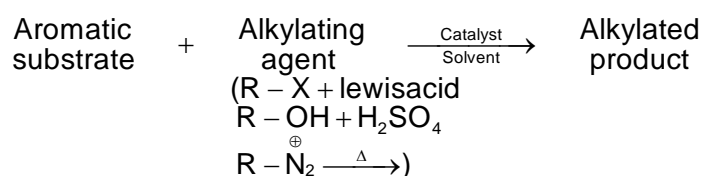
**(3) Sulphonation :** Sulphonation is usually done with fuming sulphuric acid (oleum) or concentrated sulphuric acid. In these case the active electrophile is  $\text{SO}_3$ .



**(4) Friedel-Crafts-Reactions :** The introduction of an alkyl or acyl group into an aromatic ring is called friedel crafts reaction.

**(A) Friedel Crafts Alkylation :** The introduction of an alkyl group into an aromatic ring is called Friedel Crafts alkylation.

The reaction is usually brought about by alkyl halide, olefins and alcohols in the presence of a lewis acid catalyst e.g.  $\text{AlCl}_3$ ,  $\text{AlBr}_3$ ,  $\text{BF}_3$ ,  $\text{HF}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{ZnCl}_2$  etc.

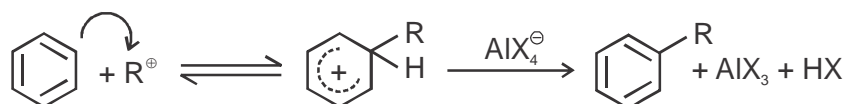
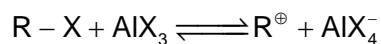


- The solvent used are  $\text{CS}_2$ ,  $\text{CCl}_4$ , diethyl ether and nitrobenzene.

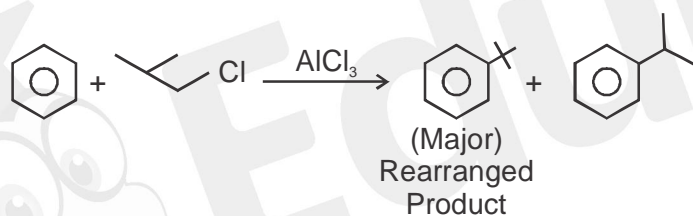
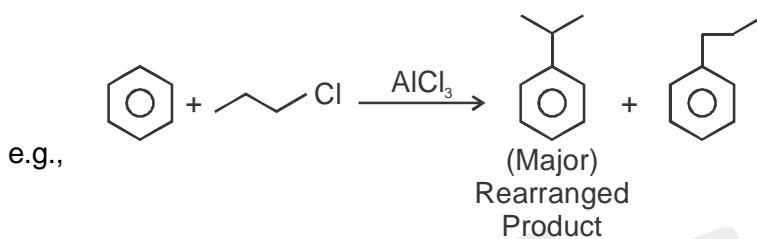
**Example :**



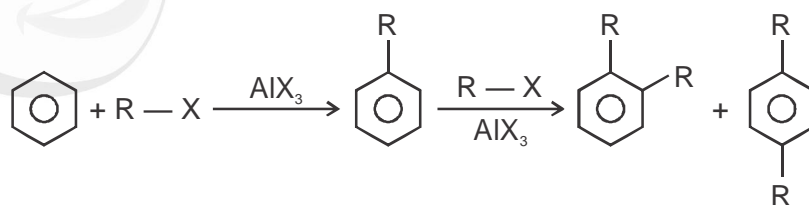
**Mechanism :**



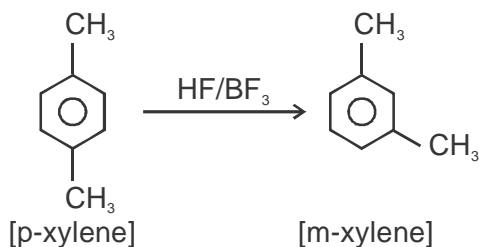
- Since intermediate carbocation is formed by the alkylating agent, if possible then rearrangement should be takes place.



- In friedel crafts alkylation, polyalkylation also takes place

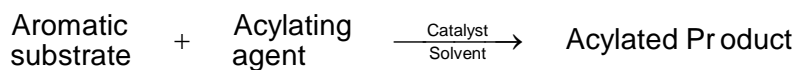


- Some time isomerisation also takes place

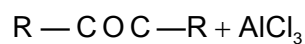


**Friedel-Crafts Acylation :** The introduction of an acyl group into an aromating ring is called friedel crafts acylation.

The reaction is brought about by acylhalide, carboxylic acids, anhydrides and ketones in presence of lewis acid catalyst similar to that in friedel crafts reaction.



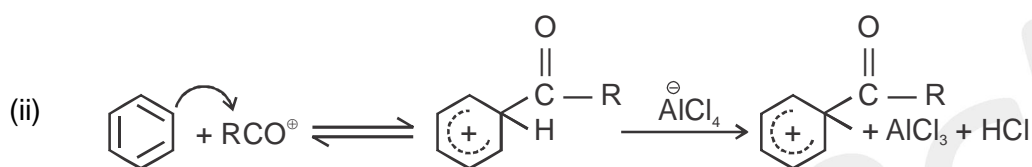
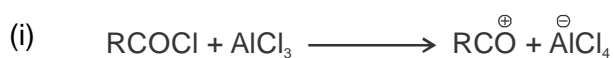
e.g. -



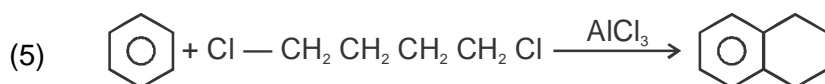
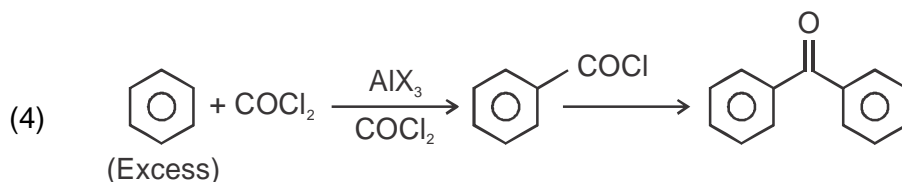
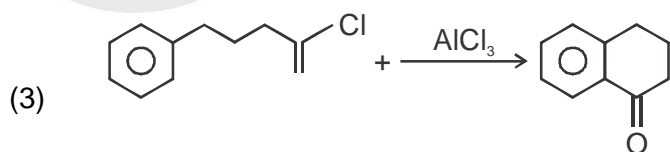
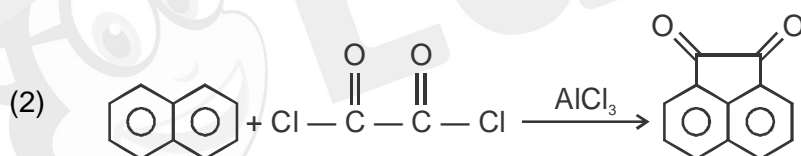
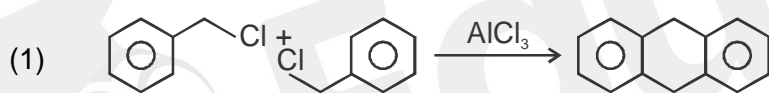
**Example :**



**Mechanism :**



Some other examples are :



**Orientation and Reactivity in Mono Substituted Benzene :** When a mono substituting benzene undergoes an electrophilic substitution, then the rate of reaction and the position taken up by the incoming group are determined by the substituent already present on the benzene ring.



On this basis, various substituents can be divided into following three categories :

**(1) Ortho, Para-directing and Activating Groups :** All the groups which are electron releasing such as  $-OH$ ,  $-OR$ ,  $-NH_2$  etc are ortho-para directing and activating groups.

The benzene ring contains a group of this category is more reactive towards electrophilic substitution, this is called activation of the benzene ring.

**Example :**  $O^\ominus$ ,  $NH_2$ ,  $NHR$ ,  $OH$ ,  $OR$ ,  $NHCOR$ ,  $OCOR$ ,  $SR$ ,  $Ar$  etc.

**(2) Meta-Directing and Deactivating Group :** All the groups which are electron withdrawing, decrease the electron density of benzene ring are known as deactivating groups.

Due to decrease in electron density of the ring, the rate of Electrophilic substitution decreases.

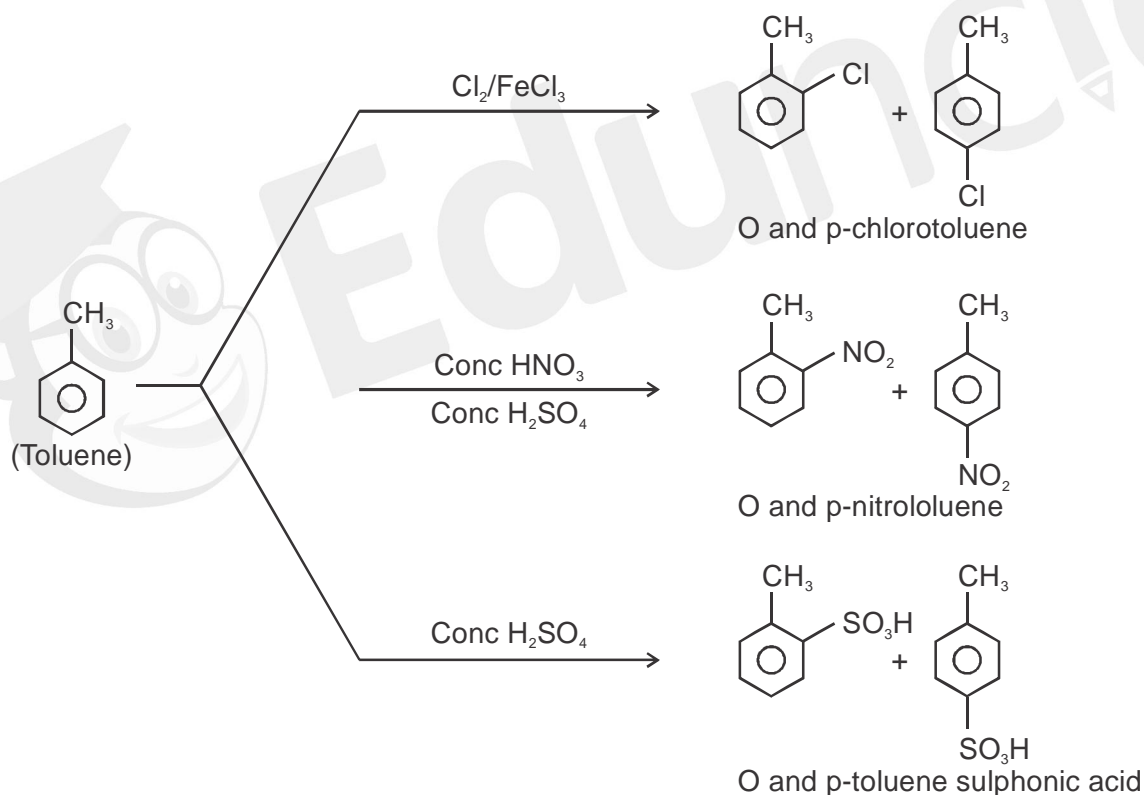
If a group of this category is already present on the benzene ring then the incoming group is attached to the meta position.

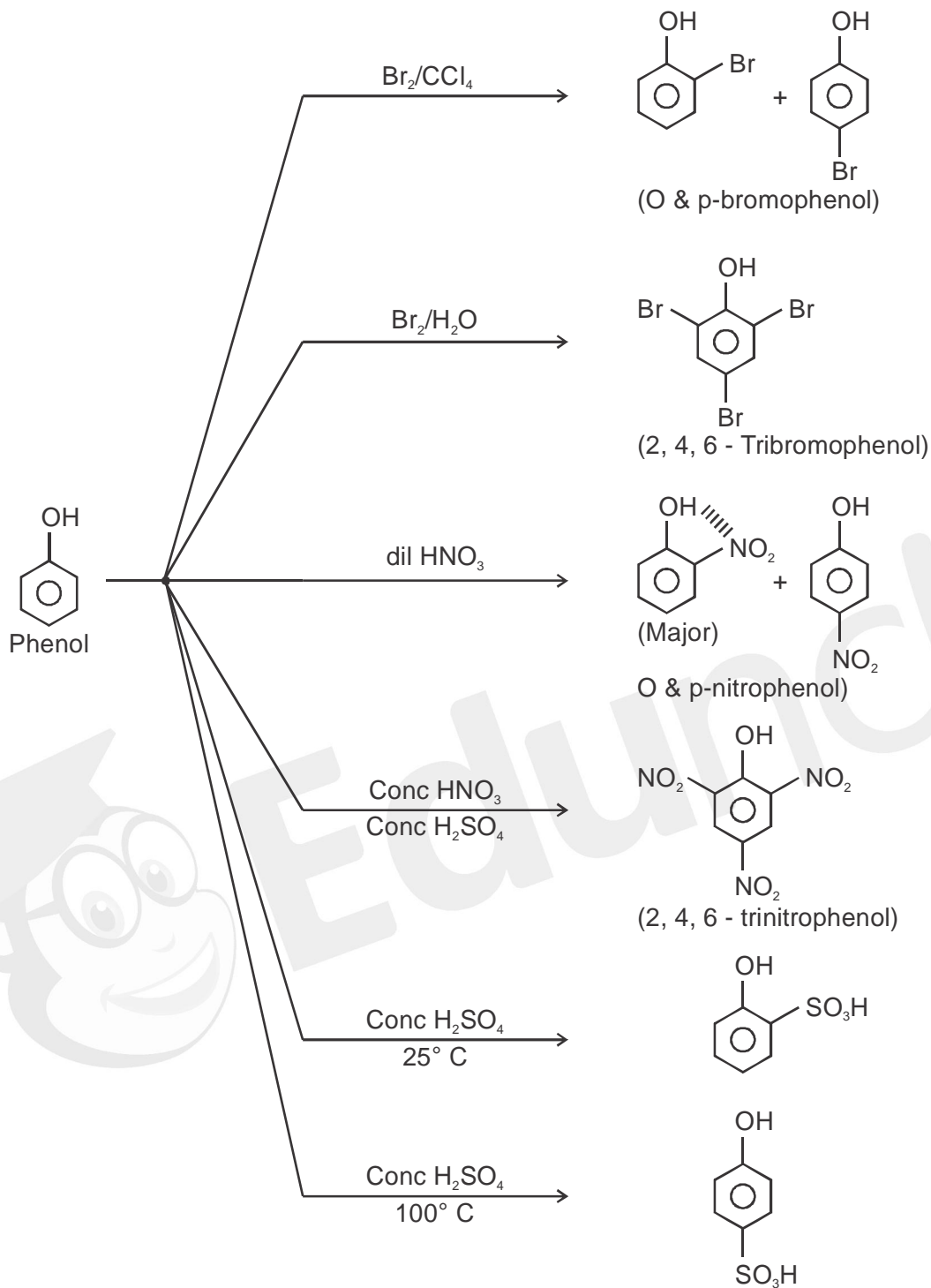
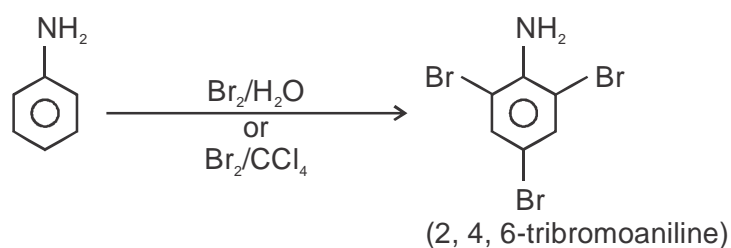
**Example :**  $NR_3^\oplus$ ,  $NO_2$ ,  $CF_3$ ,  $CN$ ,  $SO_3H$ ,  $CHO$ ,  $COR$ ,  $COOH$ ,  $CONH_2$ ,  $CCl_3$  and  $NH_3^\oplus$ .

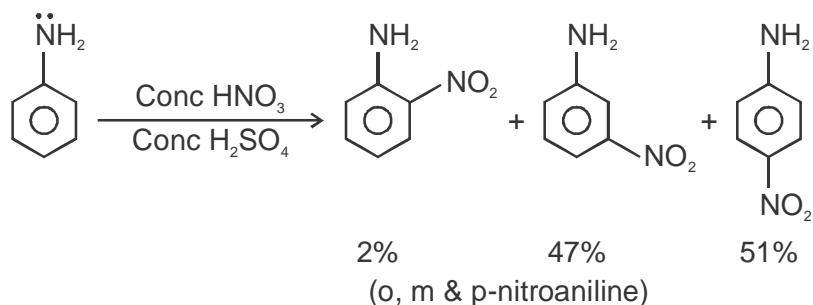
**(3) Ortho-Para Directing and Deactivating Groups :**

**Example :** Halogens (F, Cl, Br, and I)

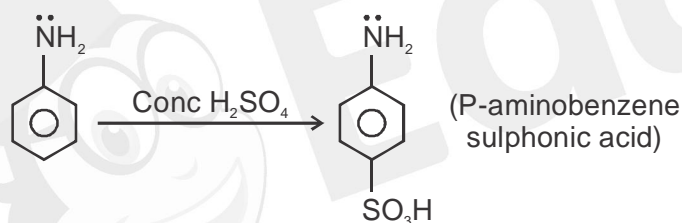
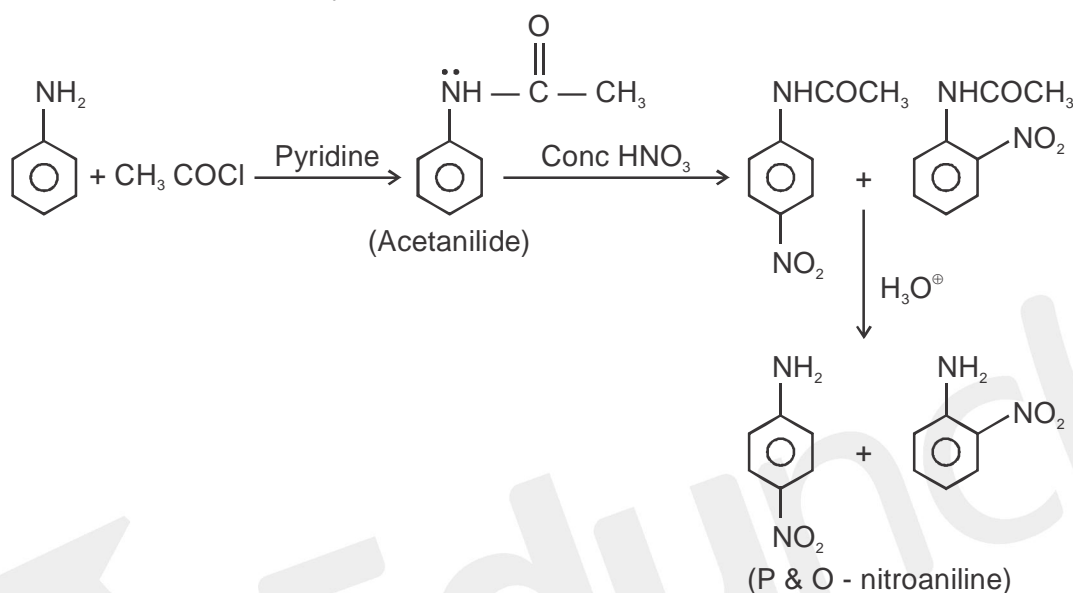
**Aromatic Electrophilic Substitution in Toluene :**



**Aromatic Electrophilic Substitution in Phenol :**

**Aromatic Electrophilic Substitution in Aniline :**




In order to increase the yield of Para-Aniline first of all converted into acetanilide.



**(iii) Nucleophilic Substitution Reaction :** Replacement (Displacement) of an atom or group by a nucleophile is known as Nucleophilic substitution reaction.

The group that is replaced (leaving group) carries its bonding electron.



The compound on which substitution takes place is called the substrate and the group that becomes displaced from carbon, taking the electron pair with it, is called leaving group.

The leaving group often leaves as an anion but may also be a neutral molecule. The substrate consists of two parts, alkyl group and leaving group.

**Example :**



Substitution reactions at saturated carbon can be mechanistically categorized as unimolecular ( $\text{S}_{\text{N}}1$ ) and ( $\text{S}_{\text{N}}2$ ) Bimolecular.

**(1) S<sub>N</sub>1 (Substitution Nucleophilic Unimolecular) :** A nucleophilic substitution reaction at a saturated carbon involving only one species in the transition state of the rate determining step is said to follow mechanism.

Such a reaction takes place in two steps :

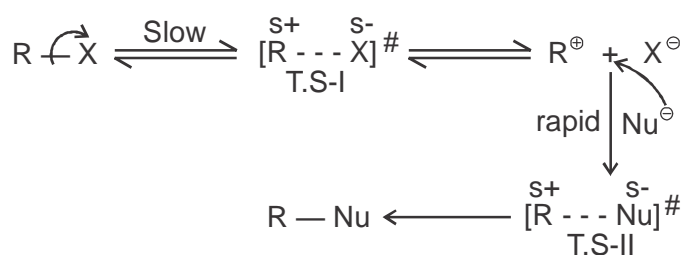
**Step 1 :** Formation of carbocation



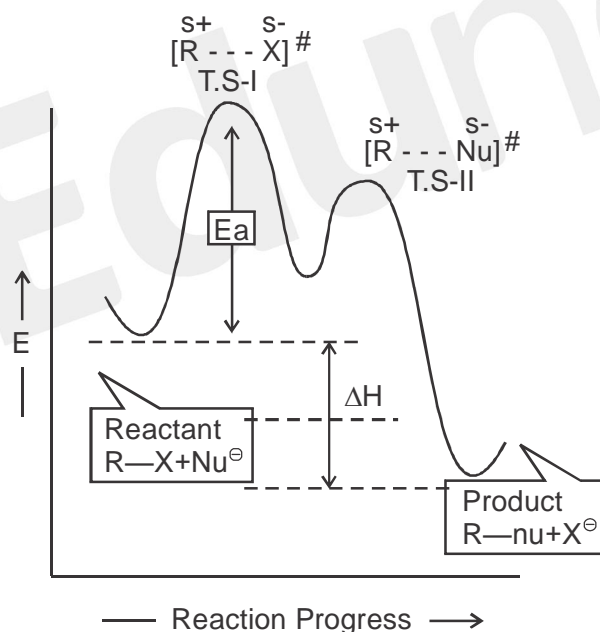
**Step 2 :** Capture the carbocation by the nucleophile



The overall reaction may be represented as :



The first step is endothermic, while the second step is exothermic. The energy profile diagram for the process may be drawn as :



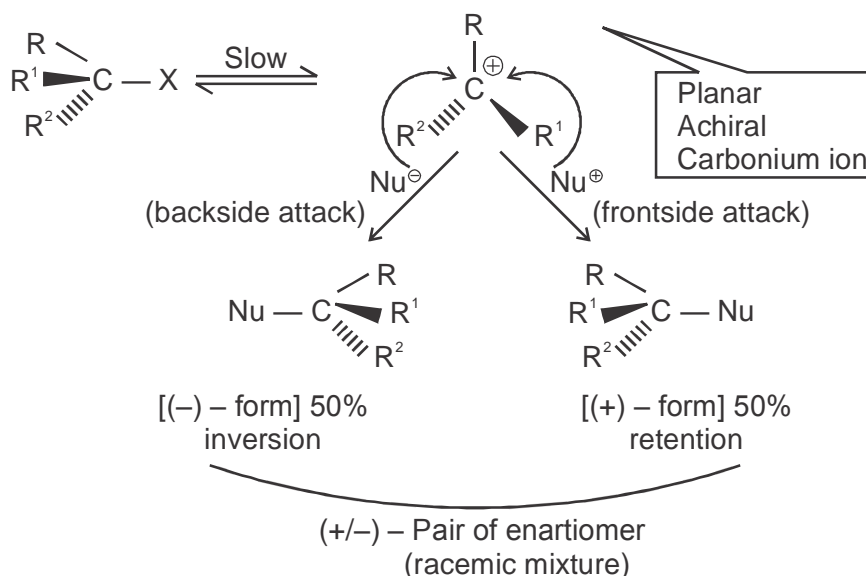
The S<sub>N</sub>1 reaction shows first-order kinetics as rate of the reaction depends only on the concentration of the substrate (RX) and does not depend on the concentration of the nucleophile reacting with it. The rate expression is therefore :

$$\text{Rate} = k[\text{RX}]$$

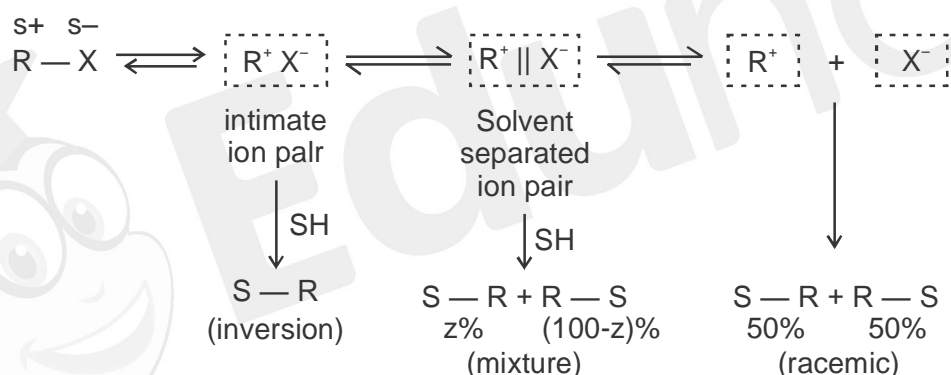
Where k is the rate constant.

**Stereochemistry of the S<sub>N</sub>1 Reaction :** The S<sub>N</sub>1 reaction proceed with partial racemisation and some inversion.

An S<sub>N</sub>1 reaction involve the formation of a carbocation in the slow and rate-determining step if there is a free carbocation, it would be planar and achiral : the incoming nucleophile (Nu<sup>-</sup>) subsequently should attack the species with equal ease from either of the plane leading to 50 : 50 mixture of two enantiomers.



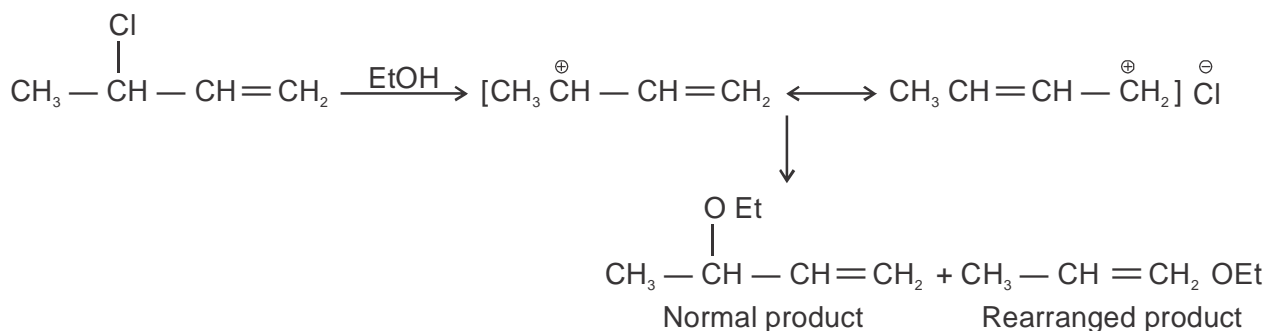
In most of the cases there is always the inverted product in excess over the other isomer, so it is believed that carbocation and leaving group exist for a while as an intimate ion pair and the attack of nucleophile during this time takes place only on the back side of carbocation, but not on the front side, giving rise to inversion. Now attack of nucleophile on free symmetrical carbocation occurs from the backside or from the side with equal probability.



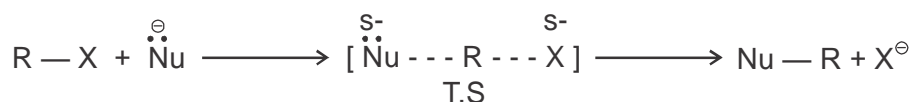
**Solvent Effect :** Nature of solvent has a profound influence on reaction rate. Polar protic solvent greatly enhance the reaction rate because of the fact that the amount of energy required to apply externally to carry out an reaction is minimized due to evolution of solvation energy caused by the solvation of intermediate carbocation and nucleophile, thereby facilitating ionization of the substrate.

For example, the ionization of t-butyl chloride to t-Bu<sup>+</sup> and Cl<sup>-</sup> in the gas phase require 630 KJ/mole, while in water this ionization require only 84 KJ/mole. The difference is the solvation energy.

**Rearrangement in SN<sup>1</sup> Reaction :** Since mechanism involves carbocation intermediate therefore, unexpected products are also formed. for example, hydrolysis of 2-bromo-3-methyl butane yields 2-methyl-2-butanol



**(2) S<sub>N</sub>2 (Substitution Nucleophilic Bimolecular) :** The concerted (one step) mechanism with no intermediate for the displacement of a leaving group by a nucleophile in aliphatic and alicyclic compounds involving both nucleophile and substrate in the transition state is termed as substitution nucleophilic bimolecular and symbolically designated as S<sub>N</sub>2.

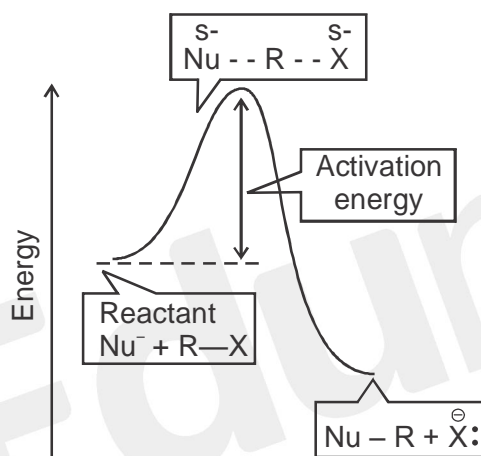


Kinetic evidence shows that the rate of this reaction is proportional to both the concentration of substrate and nucleophile. Thus the reactions follow second-order kinetics and is described by the rate expression:

$$\text{Rate} = k [\text{RX}] [\overset{\ominus}{\text{Nu}}]$$

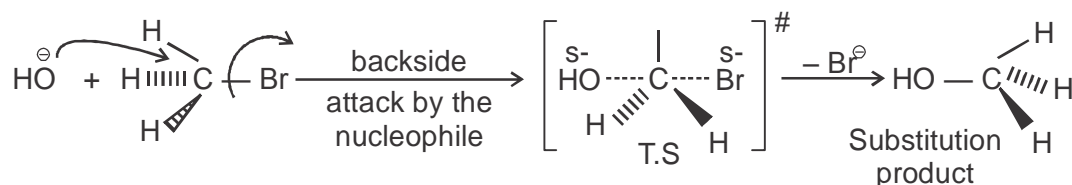
Where k is rate constant.

The energy profile diagram for an S<sub>N</sub>2 reaction is shown as -



**Stereochemistry of S<sub>N</sub>2 Reaction :** S<sub>N</sub>2 mechanism takes place with stereoelectronic controls involving a backside attack by the nucleophile on the bond between the C-atom and the leaving group in a concerted process without intermediate.

Let us take the example of alkaline hydrolysis of methyl bromide to give methanol



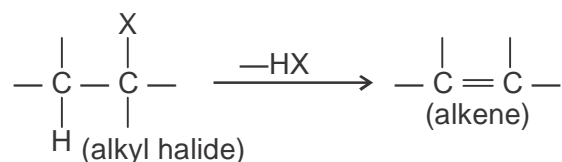
Thus, the mechanism leads to inversion of configuration at the chiral centre under attack.

This inversion of configuration is called the Walden inversion, as observed by P. Walden.

The reaction is a second-order reaction following the rate-law given below:

$$\text{Rate} = k[\text{substrate}][\text{nucleophile}]$$

**Elimination Reaction :** The elimination reactions are reverse of addition reactions. In elimination reaction two groups are removed from a molecule, neither being replaced by another group. In these reactions an atom or group from α-carbon atom and a proton from the β-carbon are eliminated.



### Types of Elimination Reactions :

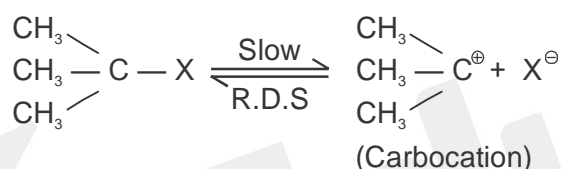
In general, elimination reactions are divided into two types, i.e.

- (1)  $\alpha$ -elimination
- (2)  $\beta$ -elimination
- (3)  $\gamma$ -elimination

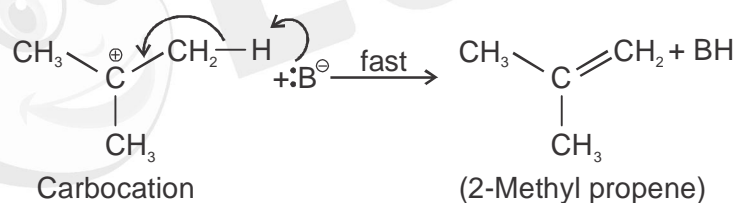
$\beta$ -elimination is the common elimination reactions to take place, and can occur via three distinct mechanism- E1 (elimination, unimolecular), E2 (elimination, bimolecular) and E1cB (elimination, unimolecular, conjugate base) pathways.

**E1 (Unimolecular Elimination Reactions) :** Like  $S_N1$  reaction the E1 (elimination, unimolecular) mechanism is a two step process-

**Step 1 :** The first step is the rate-determining step involving heterolysis of the substrate to form a carbenium ion intermediate that rapidly loses a  $\beta$ -proton in the second step.



**Step 2 :** The second step involves the fast abstraction of a proton from the adjacent  $\beta$ -carbon atom giving rise to the formation of the alkene.



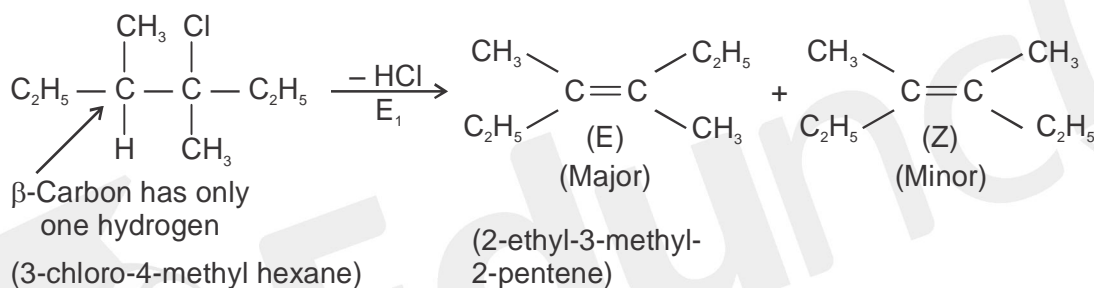
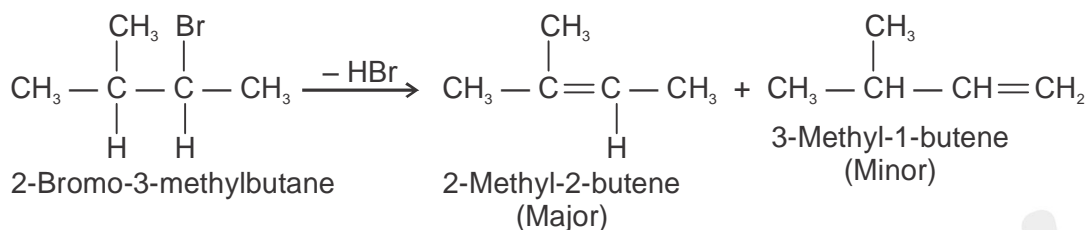
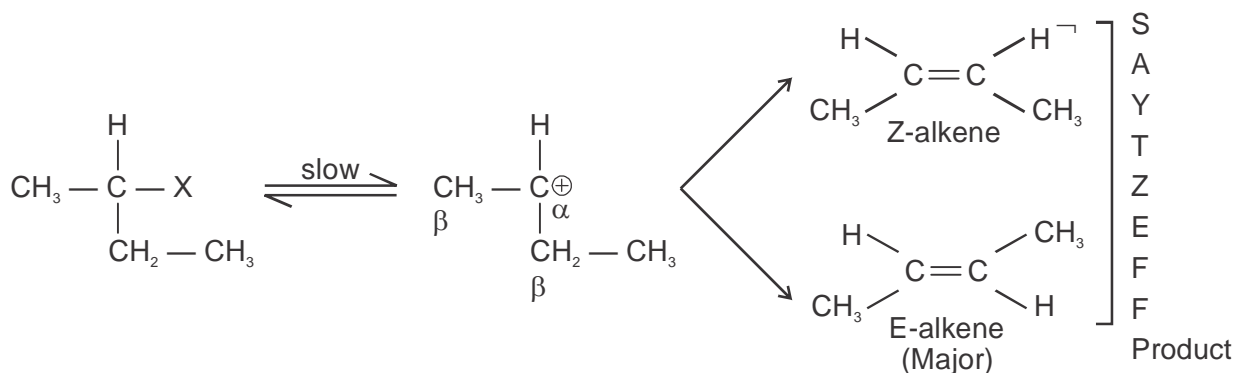
- Because the E1 reaction involves the formation of a carbocation intermediate, rearrangement of carbon skeleton can occur before the proton is lost.
- In these reactions the rate of elimination is dependent only on the concentration of the substrate and is independent of the concentration of the nucleophile and the reaction is of first-order.

$$\text{Rate} = k[\text{substrate}]$$

E1 reactions maintain regio- and stereo selectivity.

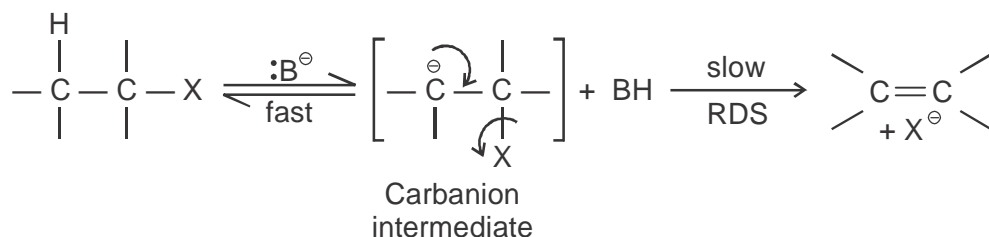
**(1) Regioselectivity :** E1 elimination afford predominantly the thermodynamically more stable alkenes (i.e. more substituted alkenes; Saytzeff elimination).

**(2) Stereoselectivity :** E1 elimination give predominantly the E-alkene rather than the z-isomer because of steric reason.

**Example :**


**E1cB Reaction :** The E1cB mechanism (elimination, unimolecular, conjugate base) involves two steps like the E1 mechanism, but in this case the C(β)-H bond initially ruptures to form a carbanion intermediate (i.e. conjugate base of the substrate) followed by the subsequent loss of the leaving group.

The carbanion is then converted to an alkene. Conversion of carbanion to an alkene is the rate determining step.



The E1cB reaction is first order in base and first order in substrate.

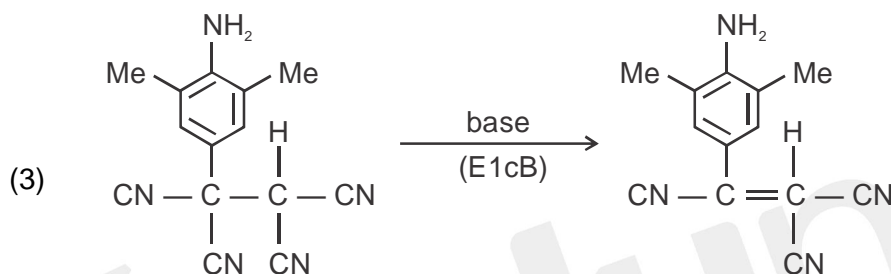
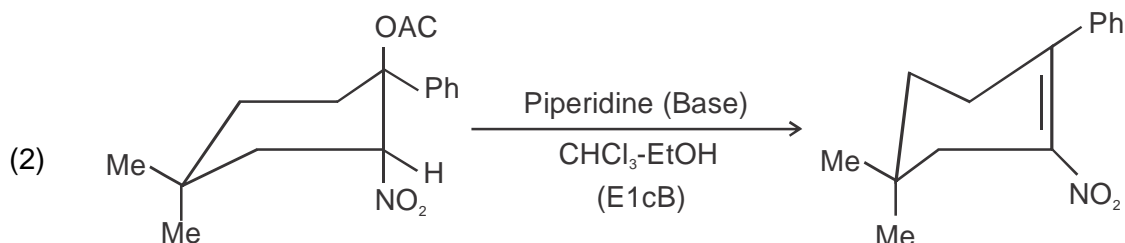
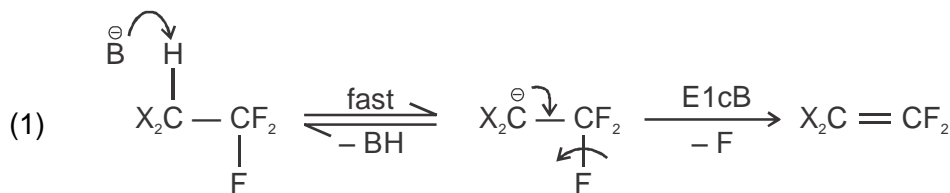
$$\text{Rate} = k[\text{Alkyl halide}][\text{Base}]$$

Thus, the reaction is second order, first order with respect to alkyl halide and first order with the base.

**Conditions for E1cB Reaction :**

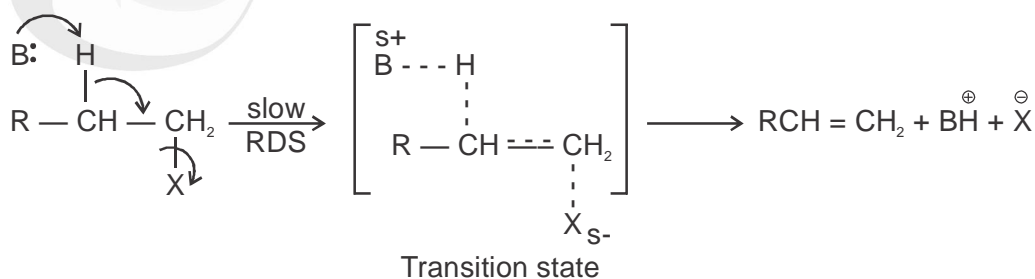
- Reaction should take place in the presence of strong base.
- The leaving group should be poor.
- The substrate should bear strong electron-withdrawing atoms/groups on the α-carbon to make the β-H more acidic.
- Product formation generally takes place by Hofmann rule.



**Examples :**


**E2 (Elimination, Bimolecular) Reaction :** The E<sub>2</sub> (elimination, bimolecular) mechanism is a concerted (one-step) process involving the simultaneous removal of two groups, one of which is usually a proton that is pulled off by an added base. Thus in case of an alkyl halide undergoing E<sub>2</sub> reaction, a new C = C (π) bond begins to form at the same time as the C-H and C-X (two σ) bonds being to break.

The mechanism of this reaction is represented as follows:



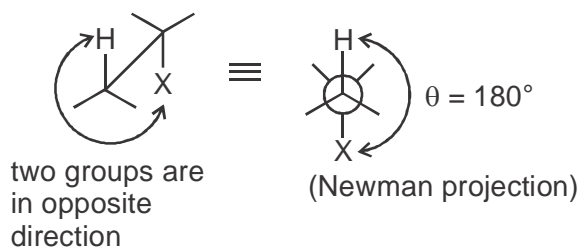
This reaction also known as 1,2-elimination or simply β-elimination.

- Since the transition state of the single concerted rate determining step of an E2 reaction involve both the substrate and the base. It is bimolecular and kinetically second order.

$$\text{Rate} = k[\text{Substrate}][\text{Base}]$$

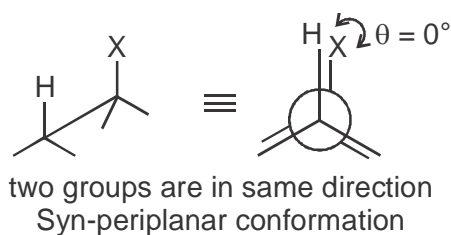
**Stereochemistry of E2 Path :** An E2 reaction involves the removal of two substituents (say H and X). The bonds to the eliminating (H and X) must be in same plane.

There are two ways in which the C-H and C-X bonds can be in the same plane. They can be parallel to one another either in the same side of the molecular (syn-periplanar) or on the opposite sides of the molecule (anti-periplanar).



(Sawhorse formula)

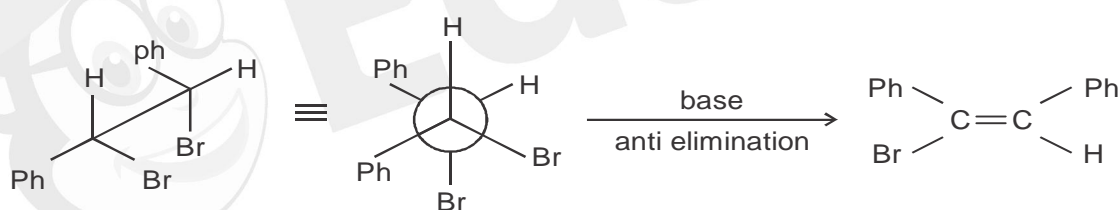
Anti periplanar conformation



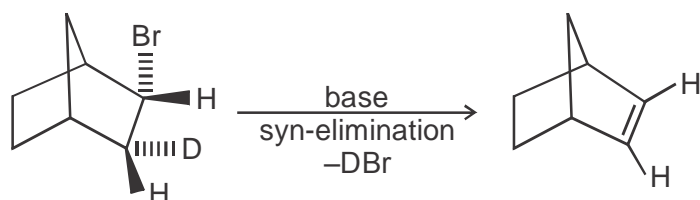
The anti-periplanar arrangement is lower in energy than syn-periplanar arrangement having an eclipsed conformation. In most cases, anti-elimination usually becomes more favoured over syn-elimination, because of the fact that the substrate molecule require less energy to reach the staggered transition state in comparison to the high energy eclipsed transition state involve in the latter case.

However, syn-elimination have also been observed to occur particularly when special structural features of the substrate molecules retard anti-elimination.

**Anti-elimination :**

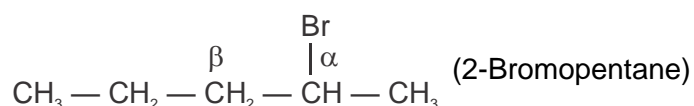


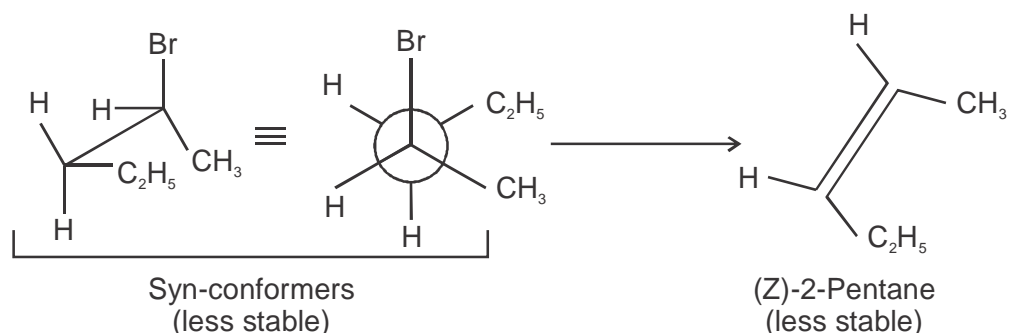
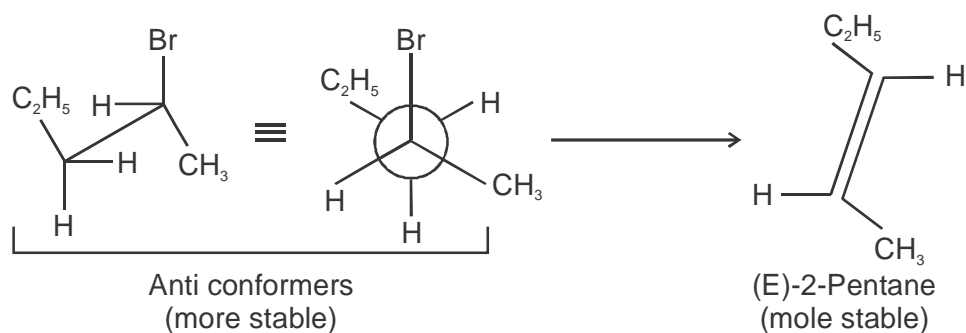
**Syn elimination -**



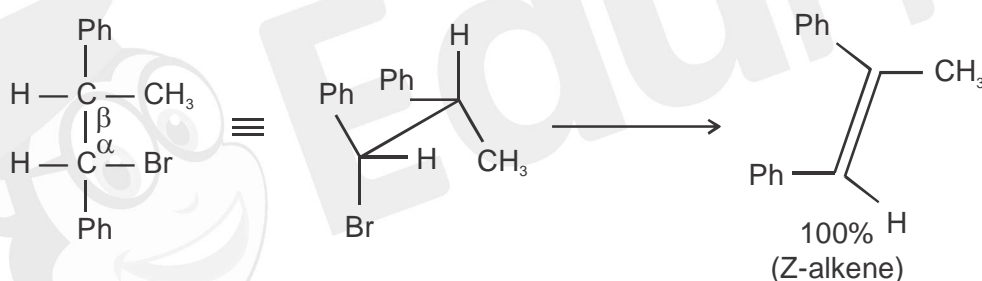
- The E2 reaction is also stereoselective. Stereoselective reaction gives on predominant product because the reaction pathway has a choice either the pathway of lower activation energy is preferred or the more stable product.

**Example :**



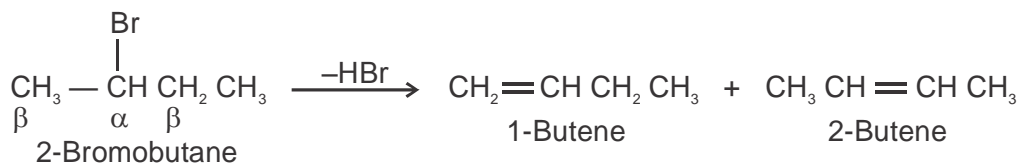


- If  $\beta$ -Carbon is bonded to only one hydrogen, only one alkene product can be obtained as a result of anti-elimination.

**Example :**


**Regioselectivity : Saytzeff vs. Hofmann :** Unsymmetrical substrate which has hydrogen attached to two different  $\beta$ -Carbons can afford two alkenes.

For example,

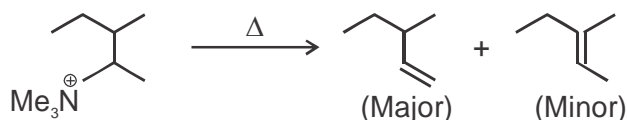
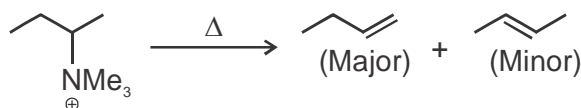
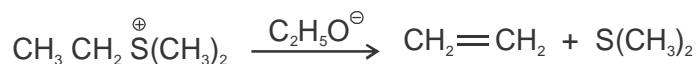


The question arises as to which alkene will be obtained in major amount in the above dehydrohalogenation. The orientation of the reaction is determined by Hofmann and Saytzeff rule.

**Hofmann Rule :** This rule is applicable for those substrates in which carbon atom is attached to a positively charged atom (e.g.  $\text{SMe}_2^{\oplus}, \text{NMe}_3^{\oplus}$ ).

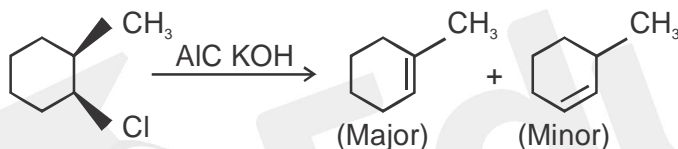
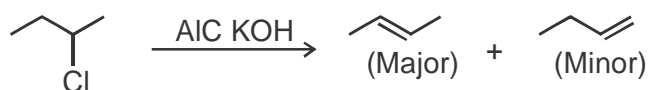
The Hofmann rule is also normally expected when using bulky bases.

According to this rule, in the elimination reaction of positively charged species, the major product will be the alkene which is least substituted.

**Example :**


**Saytzeff Rule :** According to this rule, hydrogen is eliminated preferentially from the carbon atom which has less number of hydrogen atoms and so the highly substituted alkene is the major product.

When weak base is used and X is a good leaving group than the Saytzeff product is formed as the major product.

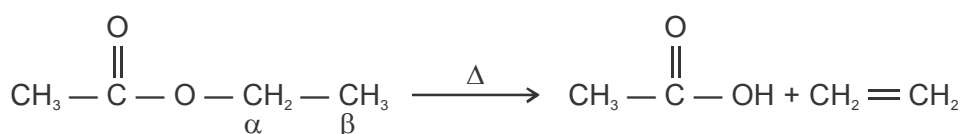
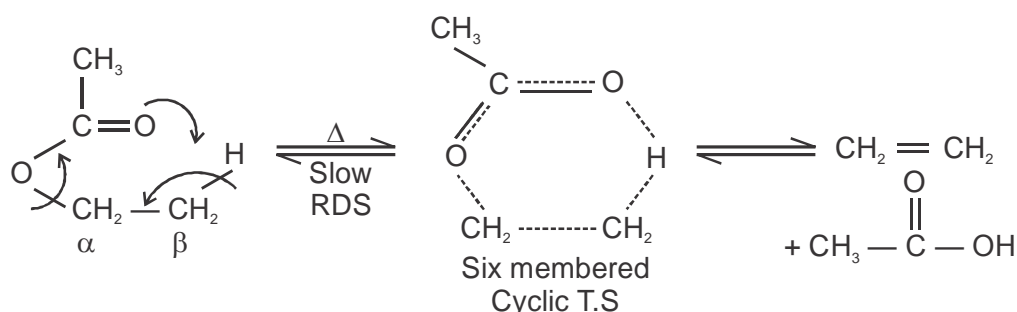
**Example :**


**Ei (Elimination Internal) or Pyrolytic-syn-elimination Reaction :** There is another type of elimination which are supposed to occur through cyclic transition state.

Ei-reactions are therefore Pericyclic elimination reactions, thus, these eliminations do not involve acidic or basic catalyst, however, there is wide variation in temperatures at which these elimination proceed.

Here syn-elimination product formation always takes place Hofmann rule.

These elimination occurs in esters, Xanthates, esters and amine-oxides.

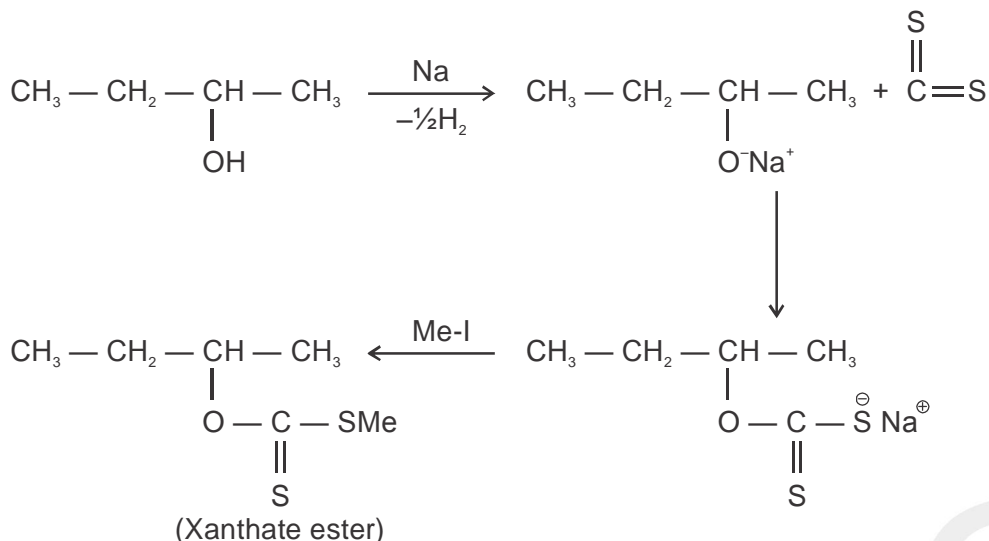
**(1) Pyrolysis of Esters :**

**Mechanism :**


This reaction follows the first order kinetics.

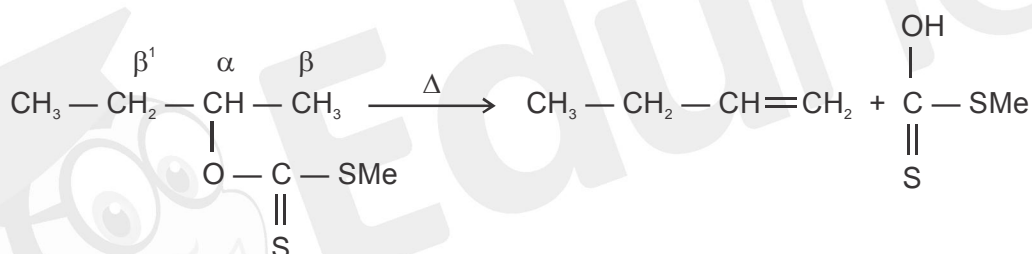
$$\text{Rate} = k[\text{esters}]$$

**(2) Pyrolysis of Xanthate Ester :** Pyrolysis of Xanthate is known as Chugaev reaction.

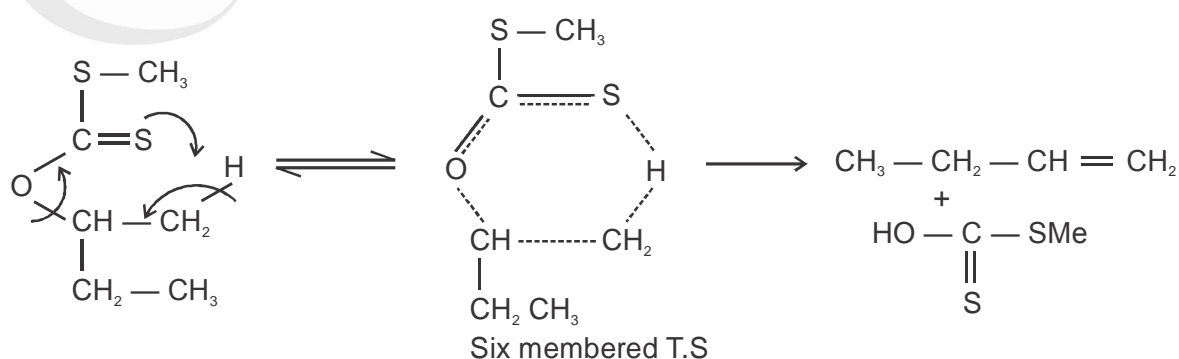
**Preparation of Xanthate Ester :**



**Pyrolysis :**



**Mechanism :**

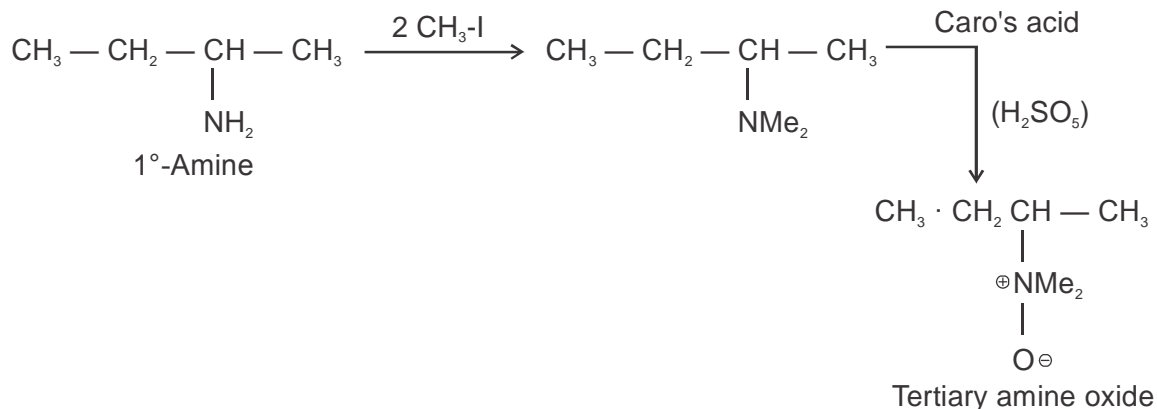
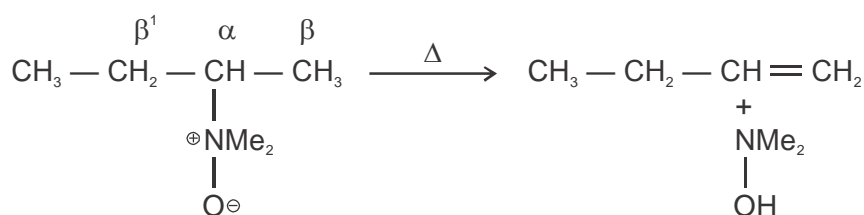
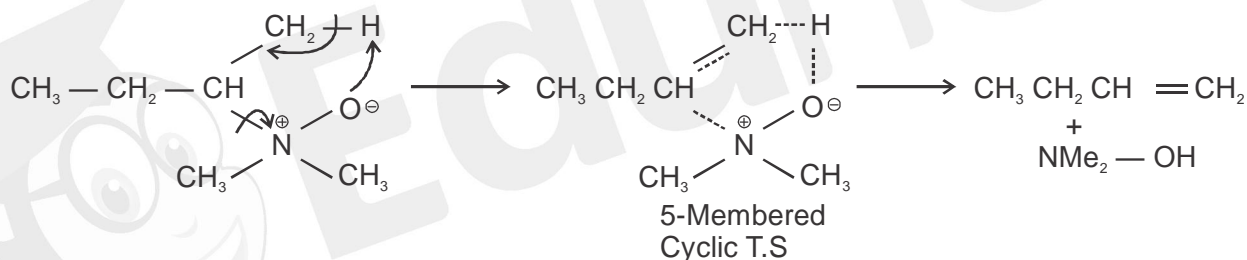


This reaction follows the first order kinetics.

$$\text{Rate} = k[\text{Xanthate esters}]$$

**(3) Pyrolysis of Tertiary Amine Oxides :** Tertiary amine oxide having at least one  $\beta$ -hydrogen undergoes thermal elimination. This thermal elimination is known as Cope elimination.

Product of the reaction is an alkene and N, N-disubstituted hydroxylamine.

**Preparation of Tertiary Amine :**

**Pyrolysis :**

**Mechanism :**


This reaction follows the first order kinetics.

$$\text{Rate} = k [\text{3}^\circ\text{-amine oxide}]$$

## 2. CHEMISTRY REACTIVE INTERMEDIATES (CARBINE, NITRENE, BENZYNE)

### Intermediates

A chemical reaction that occurs in several steps involve the formation of one or more intermediates the species which are short-lived and are never present in high concentration because they react as quickly as they are formed. These species are termed as intermediate.

The most common reaction intermediate which are usually come across are-

- Carbocations
- Carbanions
- Free radicals
- Carbenes
- Nitrenes
- Benzyne

These reactive intermediates are not isolated but are detected by spectroscopic method.

### Carbocations (Carb, Carbon + Onium, Positive charge)

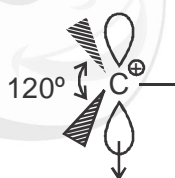
Organic species which has a carbon atom bearing six electrons in its outermost shell and have positive charge is called Carbocation.

Hence Carbocation may be represented as :

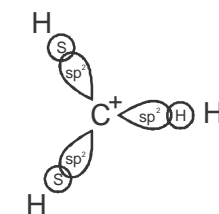


Examples are :  $\text{CH}_3^+$ ,  $\text{CH}_2\text{CH}_2^+$ ,  $(\text{CH}_3)_3\text{C}^+$

**Geometry** : Carbocations are electron-deficient species, the positive charge carbon atom is bonded to three other atoms and has no nonbonding electrons. It is  $\text{sp}^2$  hybridized with a planar structure and bond angle of about  $120^\circ$ . There is a vacant unhybridized p-orbital and lie perpendicular to plane.



Vacant P-orbital  
Planar  
(side view)



Methyl Cation  
(top view)

### Generation

(1) From Alkyl Halide



(2) From Alkene



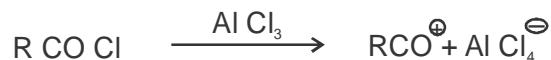
(3) From Alcohol



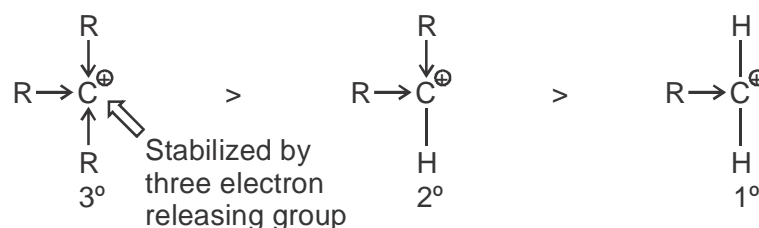
(4) From diazonium Salt



(5) From Acyl Halide



**Stability of Carbocation** : If an electron releasing group such as alkyl group is present adjacent to the carbon atom bearing positive charge, then the stability of the carbocation increases.



Two factors are deemed to play a role in this case

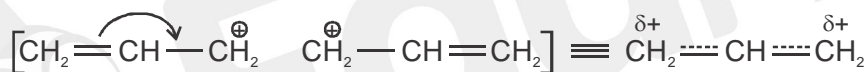
(A) Inductive Effect

(B) Hyperconjugation

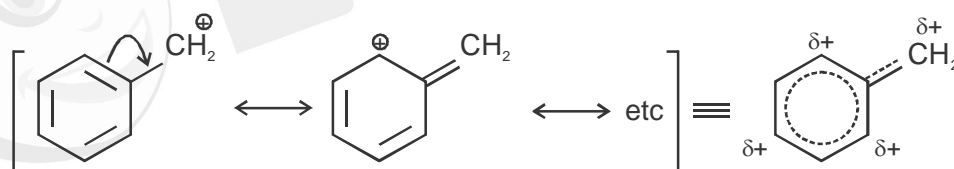
The stability of Carbocation can also be explained by 'resonance'

If a  $\pi$ -bond is adjacent to the positive charged carbon of carbocation. The filled p-orbitals of the  $\pi$ -bond will overlap with the empty p-orbital of the central carbon atom. This is said to be resonance stabilization.

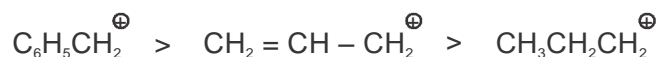
**Ex. :** Allyl Carbocation



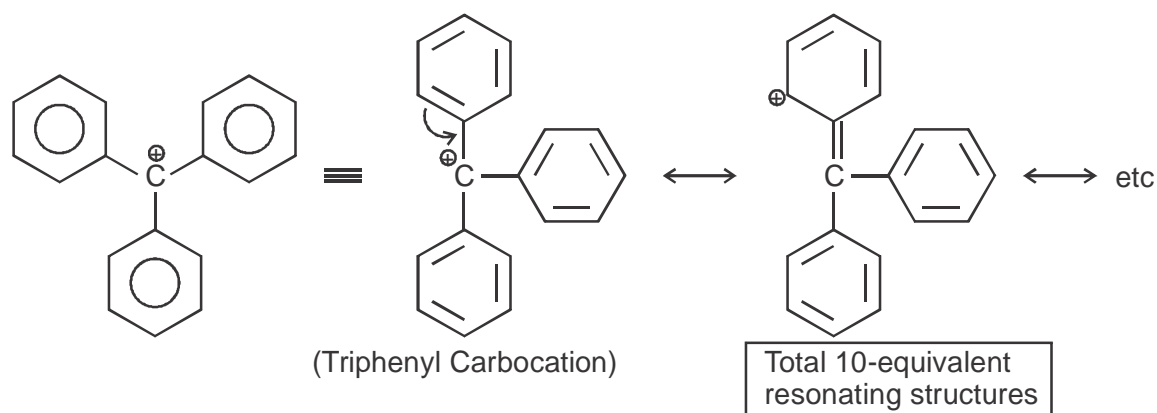
Benzyl Carbocation



So order of stability of the three carbocations are :

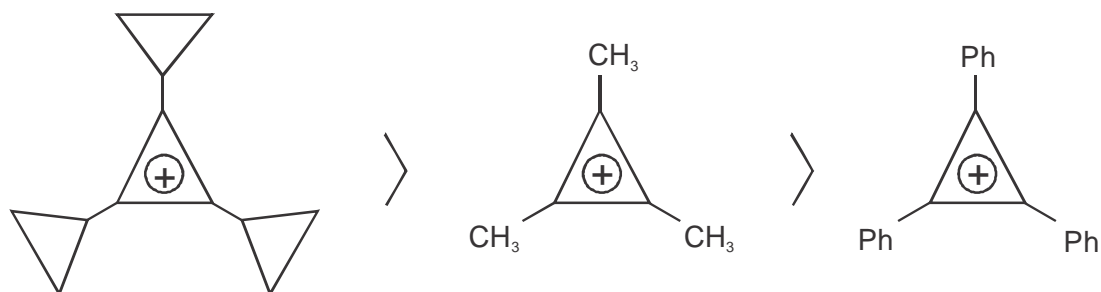


Some carbocations are very stable and so can be isolated. The stability of these carbocations is explained in term of resonance.





Aromatic cations are so stable that even their solid state known. Stability of some aromatic cations in decreasing order is given below:

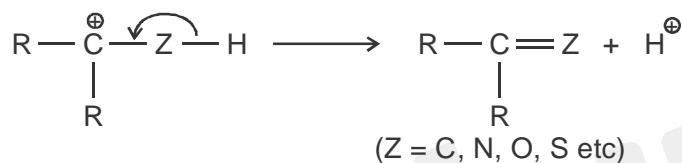


### Reactions undergone by Carbocations :

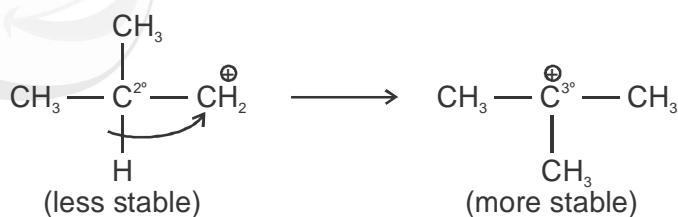
- (i) Carbocations behaves as powerful electrophiles (Lewis acid) and react with any nucleophile.



- (ii) **Loss of a Proton :**



- (iii) **Rearrangement Reaction :**

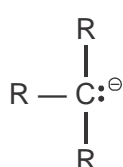


- (iv) **Addition Reaction :**



### Carbanions

Carbanions are negative charge species in which carbon atom carries three bonds and a lone pair of electrons.



examples are -

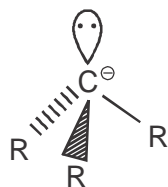
$\text{H}_3\text{C}^{\ominus}$ ,  
methyl  
anion

$\text{PhCH}_2^{\ominus}$ ,  
benzyl  
anion



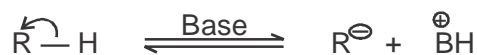
Cyclopentadienyl  
anion

The carbon atom is  $sp^3$ - hybridized. Hence tetrahedral may be represented as-



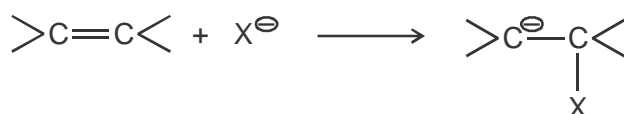
### Generation

(i) By heterolytic fission

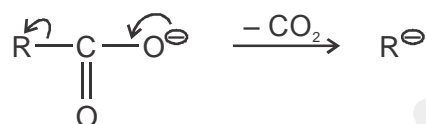


Commonly used base are : NaH/ether; NaOEt/EtOH;  $K^+ tBuO^{\ominus}/tBuOH$ ;  $NaNH_2/liq NH_3$  etc.

(ii) By addition of an anion to an alkene



(iii) Decomposition reaction



### Stability of Carbanion

A carbanion possesses an unshared pair of electrons and is therefore a base. Thus the carbanion may accept a proton to give its conjugate acid.

Let us take the  $p^{ka}$  values of some alkanes :

Acid	Conjugate base	$P^{ka}$
$CH_3CH_2CH_3$	$CH_3 - CH^{\ominus} - CH_3$	44
$CH_3 - CH_3$	$CH_3 - CH_2^{\ominus}$	42
$CH_4$	$CH_3^{\ominus}$	40

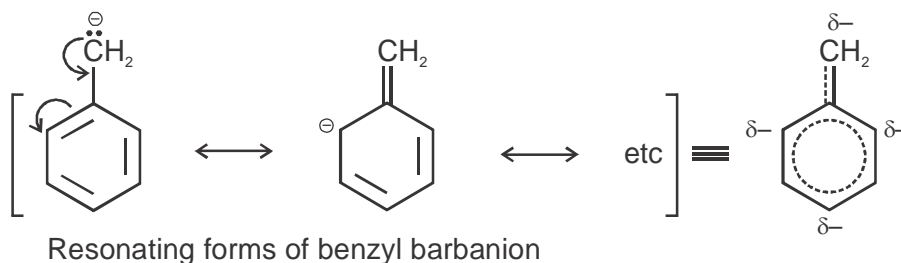
The above  $p^{ka}$  values indicate that the stability of carbanions in the following orders :

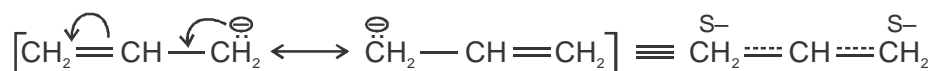
Methyl > Primary > Secondary

This order of stability of carbanions can be explained on the basis of +IE of alkyl group. It is clear that greater the negative charge on carbon atom of the carbanion due to +IE of alkyl group lesser is the stability of carbanions.

Like Carbocations, the carbanions are also stabilized by resonance.

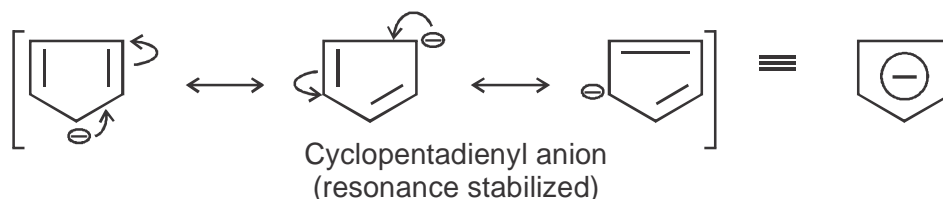
**Ex. : benzyl carbanion**



**allylic carbanion -**


- Thus allylic and benzylic carbanions and carbanions having the substituents like  $-\text{NO}_2$ ,  $-\text{COR}$ ,  $-\text{COOR}$ ,  $-\text{CN}$ ,  $-\text{SO}_2$  etc. (electron withdrawing group) at the  $\alpha$ -position with respect to carbanion carbon are greatly stabilized.
- If the unshared electron pair of Cl carbanion is involve in constituting an aromatic system then the carbanion becomes greatly stabilized.

For example,


**Reactions Undergone by Carbanion**

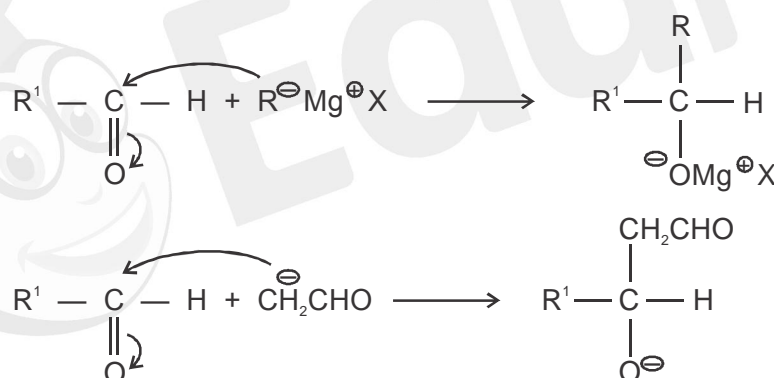
- (i) Combination with a positive species (lewise acid-base reaction)



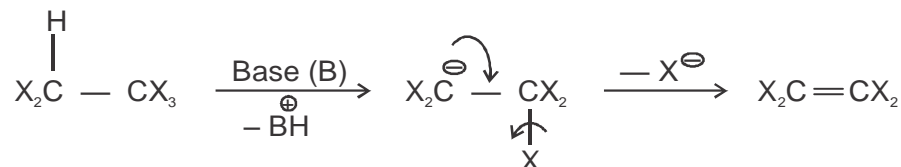
- (ii) Displacement Reactions :



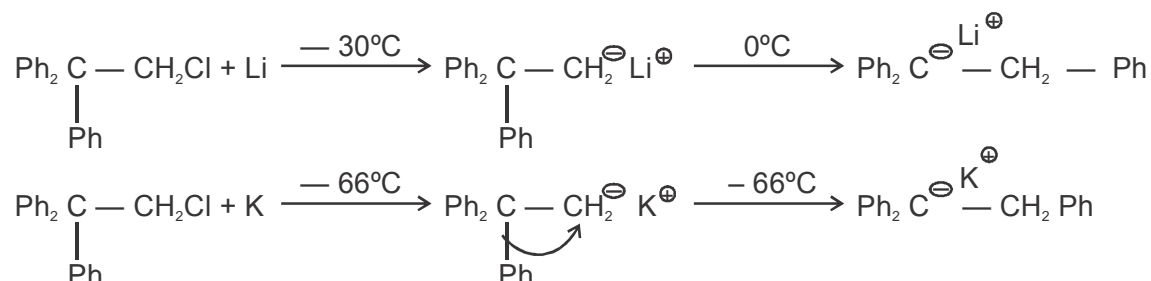
- (iii) Addition to a multiple bond :



- (iv) Elimination Reaction :

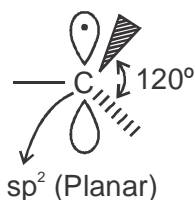


- (v) Rearrangement Reaction :

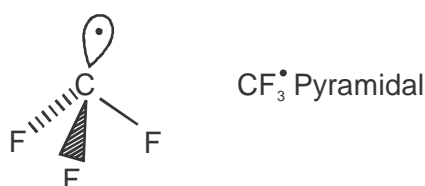


## Free Radicals

Free radicals is a reaction intermediate which may be defined as an atom or a group of atoms carrying unpaired electrons. The carbon atom of a free radicals is  $sp^2$  hybridized i.e.

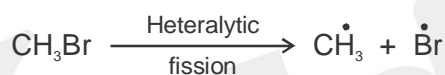


- It is a neutral intermediate and is electron deficient because it lacks an octet around the central carbon atom (has only seven valence electrons)
- Free radicals in which carbon is attached with strong electronegative atoms/group (e.g.  $CF_3$ ) prefer to attain a pyramidal shape- increase in the electronegativity increases the deviation from planarity.



## Generation

- (1) By homolytic fission of covalent bond



- (2) By thermal decomposition of peroxides and azo compounds

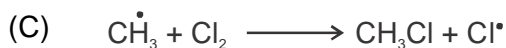
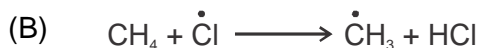
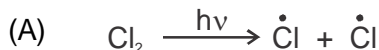


- (3) By photodecomposition of molecules :

This involves decomposition of molecules using sunlight.



## Mechanism



## Characteristics of Free radicals :

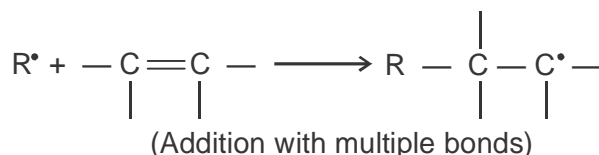
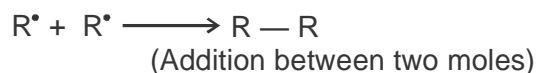
- (1) Free radicals are Paramagnetic
- (2) Free radicals can be detected by radical scavenger like hydro-quinone, and ESR spectroscopy.

## Reaction Undergone by Free radicals :

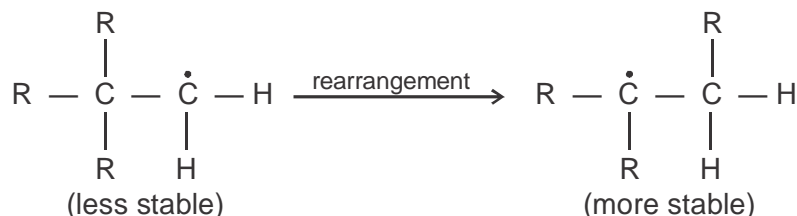
- (1) Abstraction of hydrogen



(2) Addition Reaction :

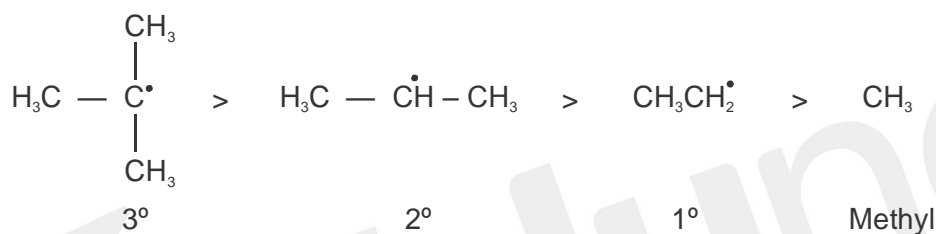


(3) Rearrangements :



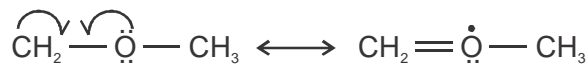
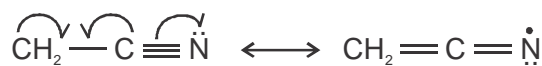
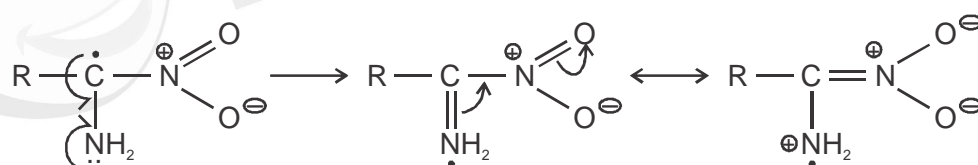
### Stability of Free Radicals :

The stability of alkyl free radicals is :

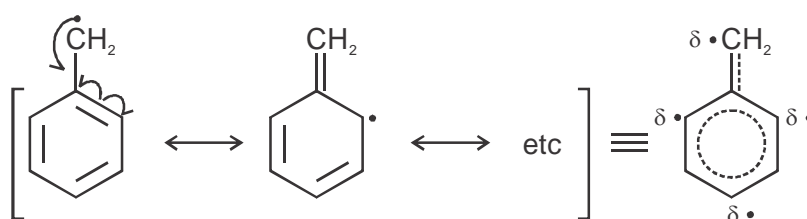
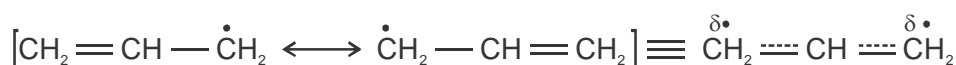


This stability order can be explained by hyper conjugation

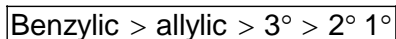
- Both electron-attracting groups such as Carbonyl, cyano, and nitro and electron donating groups such as methyl, methoxy and dimethylamine have a stabilization effect on a radical intermediate. This is called the captodative effect (or push-pull effect resulting from enhanced resonance).



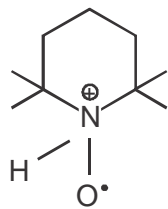
- Allyl and benzyl free radicals are more stable than alkyl free radicals and can be satisfactorily explained by resonance.



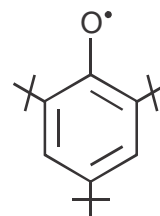
Stability order :



- Simple alkyl radicals are extremely short lived but some radicals survive almost indefinitely. Such radicals are known as persistent radicals.



TEMPO  
(Tetra Methyl Piperidine-N-Oxide)



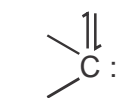
(Tritertiary butyl Phenoxy radical)

## Carbene

Carbene are reaction intermediate in which carbon atom carries two unpaired electrons, thus a carbene carbon has only six valence electrons and is electron deficient.

If the two nonbonded electrons of carbene species are paired. It is called singlet while the species is called triplet when the nonbonded electrons remain unpaired.

A singlet carbene is diamagnetic, while the triplet is paramagnetic.

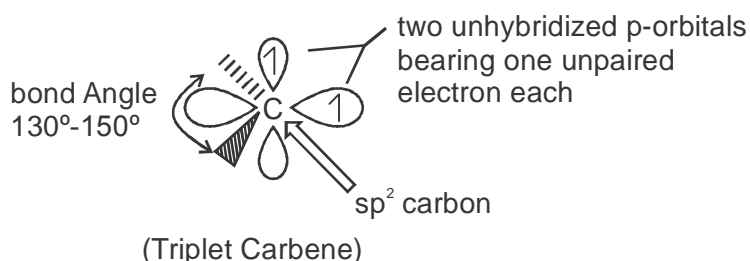
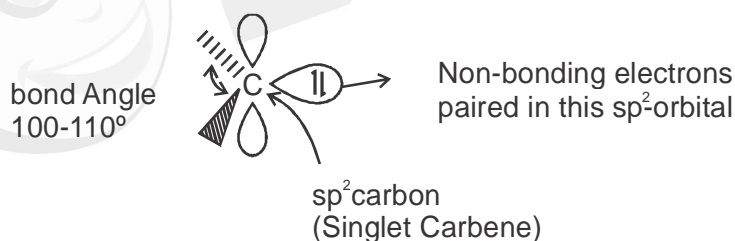


Singlet  
(Diamagnetic)



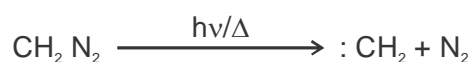
Triplet  
(Paramagnetic)

**Geometry :** Carbene are usually to be  $sp^2$  hybridized there are two bonding electrons (both in  $sp^2$ -orbital) and two non-bonding electron associated with the carbon.

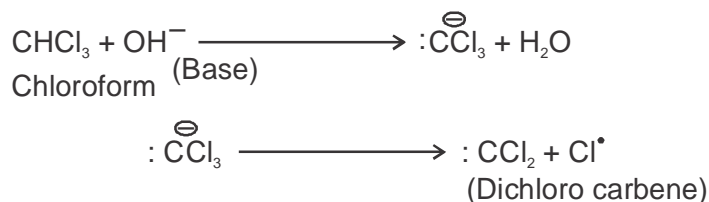


## Generation :

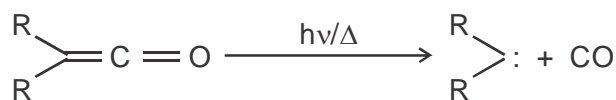
- From diazo Compounds -



- (2) By the action of base on suitable polyhalogen compound

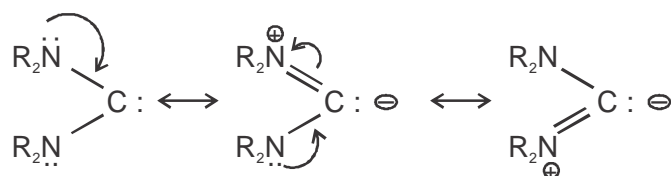


- (3) From Ketene



### Stability of Carbene

Carbene in which the carbon atom is attached to two atoms, each bearing a lone pair of electrons are most stable due to resonance.

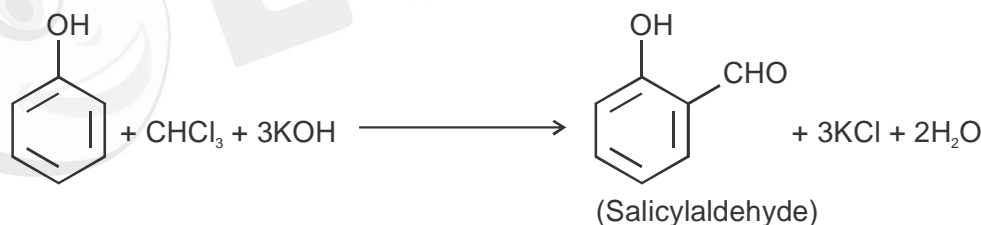


### Reactions involving Carbene :

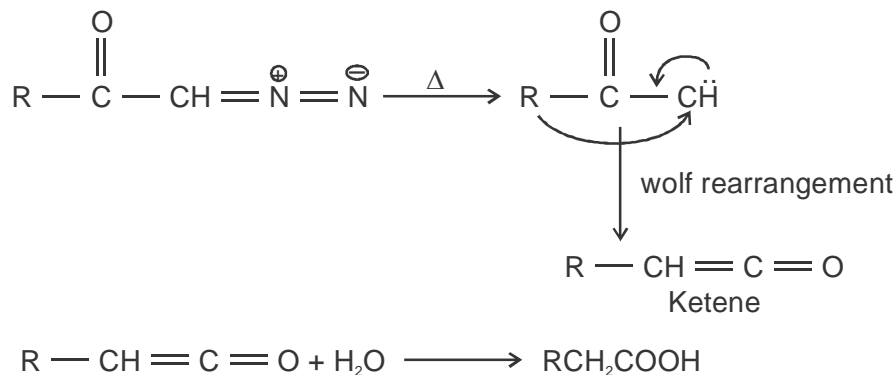
- (1) **Carbylamine Reaction :**



- (2) **Reimer Tiemaan Reaction :**



- (3) **Wolf Rearrangement :**



### Nitrenes

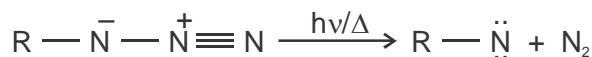
Nitrenes are the nitrogen analogous of carbene. These are electron deficient nitrogen species. The nitrogen atom in nitrogen has a sextet of electrons.

As in the case of carbene, the nitrenes exist in singlet and triplet state

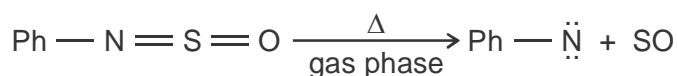


### Generation

(1) From Azide :



(2) From Sulfinylamines :



(3) From Nitro and Nitroso Compounds :



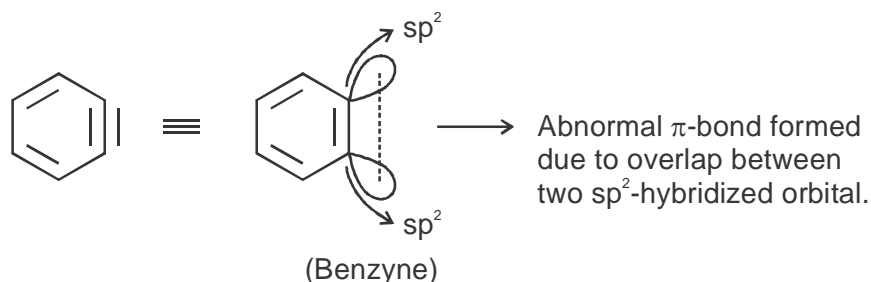
### Reactions involving nitrene intermediate :

- (1) Hofmann rearrangement
- (2) Curtius rearrangement
- (3) Lossen rearrangement

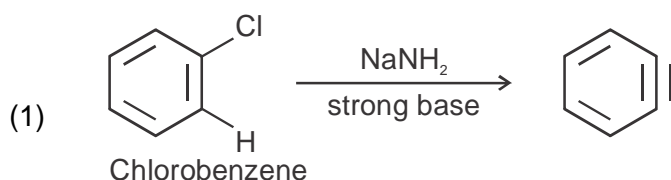
### Benzynes :

1, 2- dihydrobenzene,  $C_6H_4$  and its derivatives are called Benzynes.

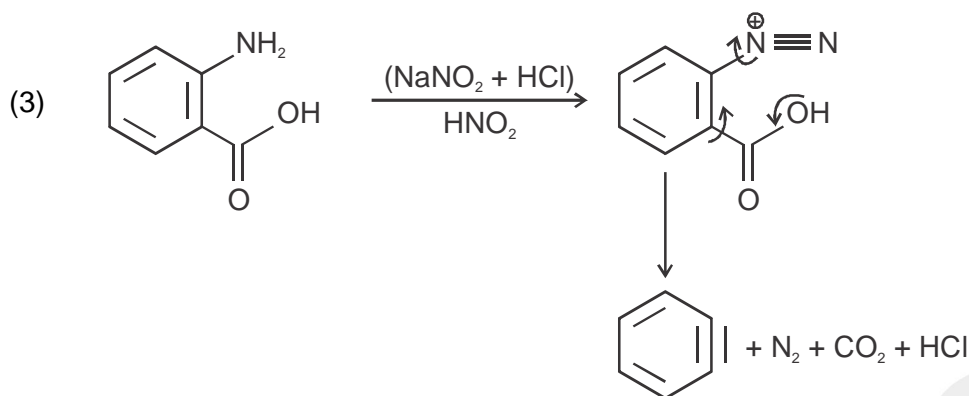
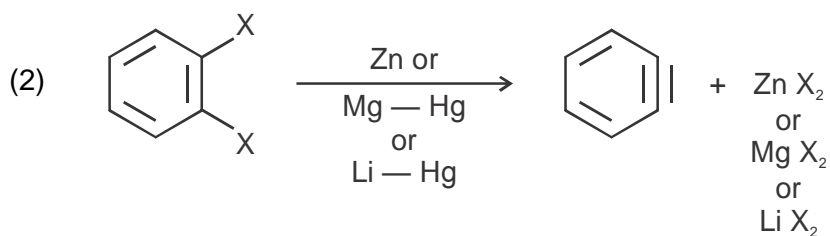
Benzynes are neutral, highly reactive reaction intermediate. Benzynes (or Arynes) contain a carbon carbon triple bond and may be regarded as aromatic counterpart of acetylene.



### Generation





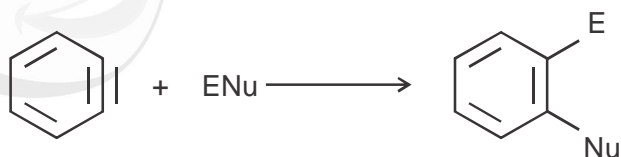


### Chemical Properties of Benzyne :

(1) Dimerisation :

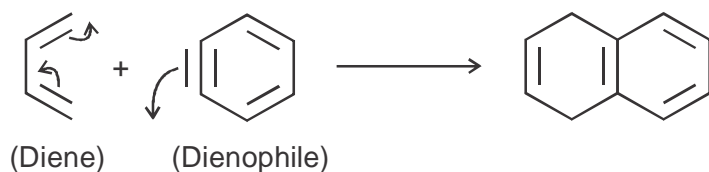


(2) Nucleophilic Addition Reaction :



(3) Diels Elder Reaction

(4 + 2 Cycloaddition reaction)



This process is called trapping of Benzyne.

### 3. NAME REACTIONS AND REAGENTS

#### Name Reactions :

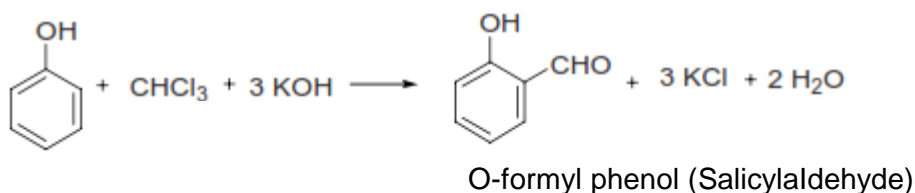
1. Reimer –Tiemann reaction
2. Darzens reaction
3. Wittig reaction
4. Mc-Murry reaction
5. Baeyer villiger oxidation
6. Simmons-smith reaction
7. Diels-Alder reaction
8. Sigmatropic reaction
9. Hofmann rearrangement
10. Schmidt rearrangement
11. Curtius rearrangement
12. Lossen rearrangement
13. Dienone-phenol rearrangement
14. Pinacol-Pinacolone rearrangement
15. Benzilic acid rearrangement
16. Favorskii Rearrangement

#### Reagents :

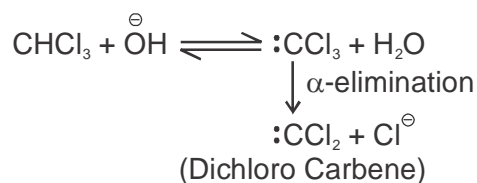
1. Organometallic reagents
  - (A) Grignard reagent
  - (B) Organolithium compounds
2. Oxidizing Agents
  - (A) Selenium Dioxide ( $\text{SeO}_2$ )
  - (B) Chromium Oxidants
    - (i) Chromium Trioxide
    - (ii) Jones Reagent
    - (iii) Pyridinium Chlorochromate (PCC)
    - (iv) Sarett oxidation ( $\text{CrO}_3 + \text{Py}$ )
    - (v) Etard reaction
3. Oppenauer Oxidation
4. Oxidation with Peracids
5. Osmium tetroxide ( $\text{OsO}_4$ )
6. Ruthenium Tetroxide ( $\text{RuO}_4$ )
7. Potassium Permanganate
8. Potassium Persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ )
9. Nitric acid ( $\text{HNO}_3$ )
10. Periodic acid ( $\text{HIO}_4$ )

**1. Reimer –Tiemann reaction :**

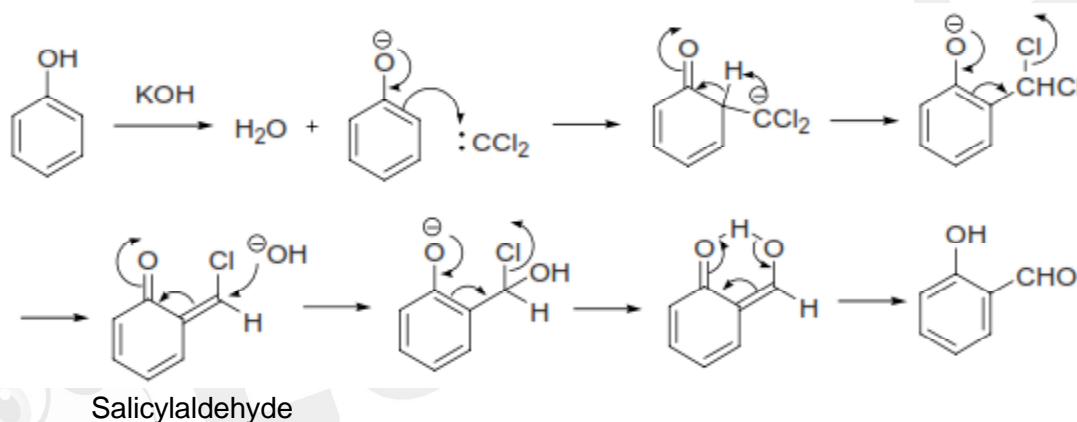
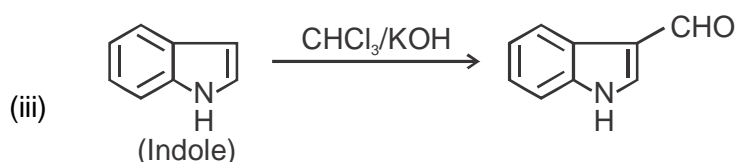
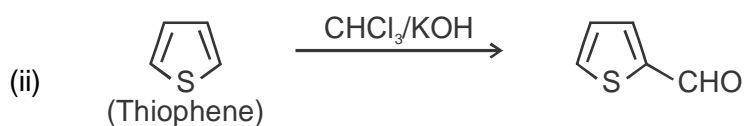
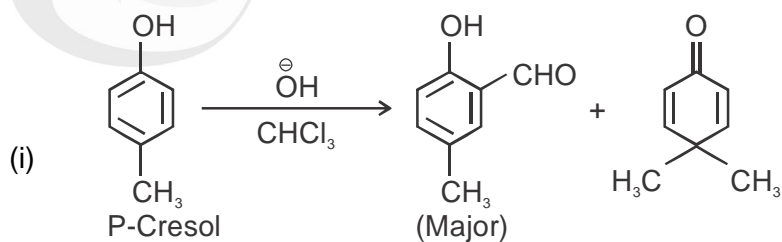
Synthesis of o-formyl Phenol from Phenol and Chloroform in alkaline medium.


**Mechanism:**

(i) Carbene generation :

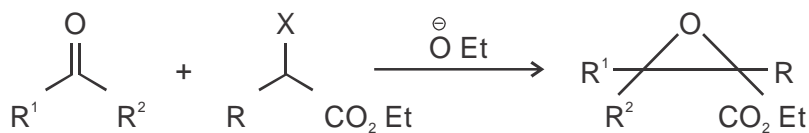


(ii) Addition of dichloro carbene and hydrolysis :

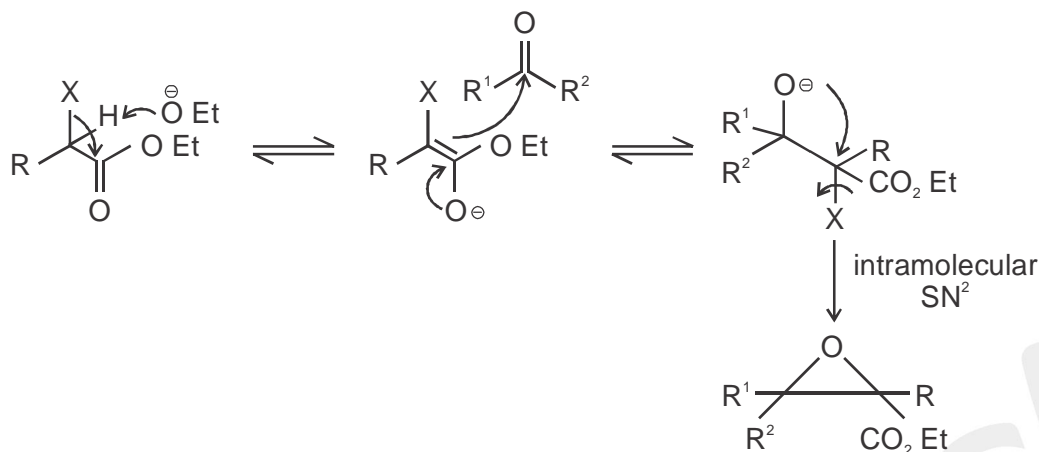

**Application:**


## 2. Darzens reaction :

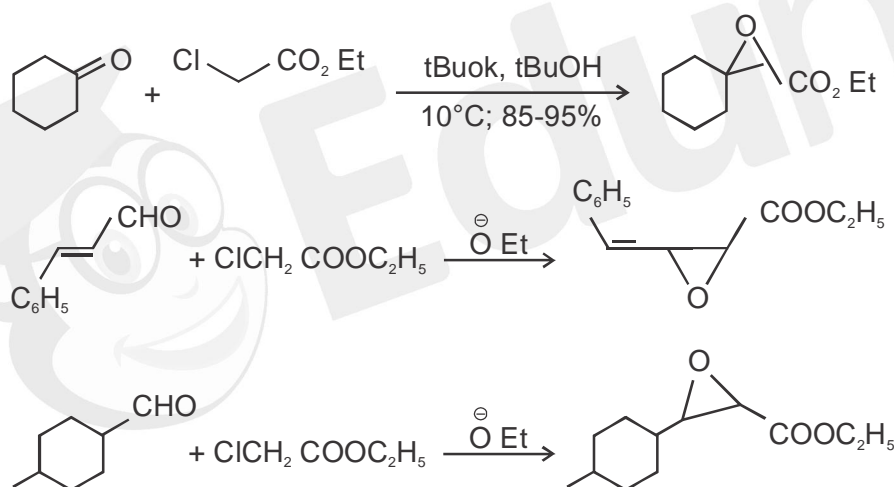
Condensation of aldehydes or ketones with  $\alpha$ -haloesters in the presence of a base,  $\alpha$ ,  $\beta$ -epoxy ester will be formed.



**Mechanism :**

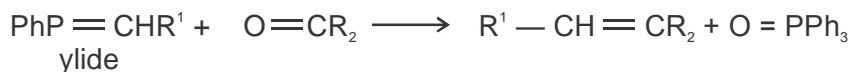


**Applications :**



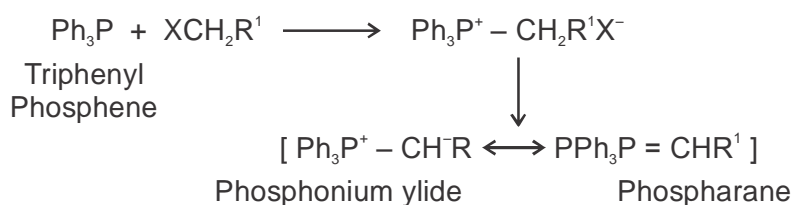
## 3. Wittig reaction :

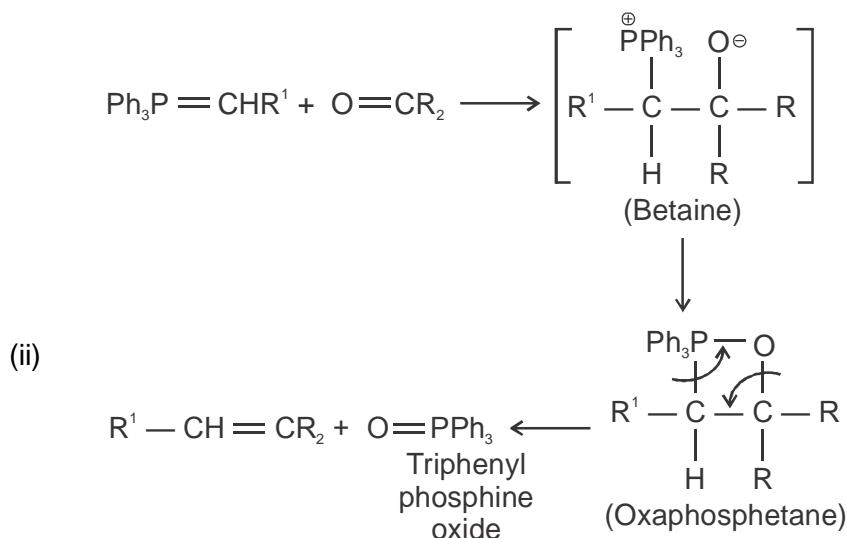
The reaction of aldehydes and ketones with Phosphorane or phosphonium ylide to produce an alkene is known as Wittig reaction.



**Mechanism:**

(i) Preparation of Phosphonium ylide :

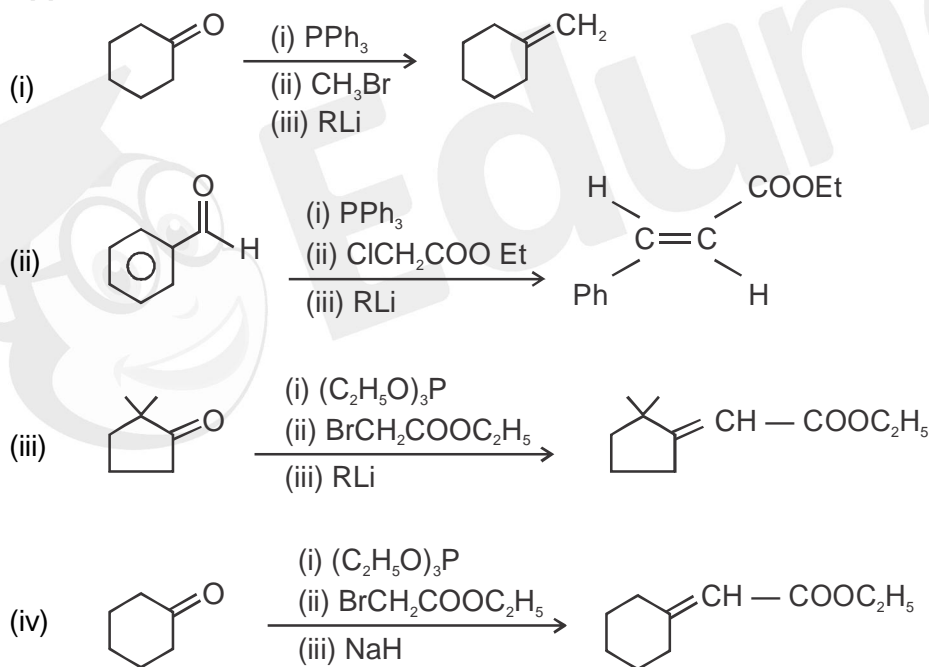




The ylides used in Wittig reaction may contain a wide variety of substituents which will not interfere in the reaction of ylides with other compounds. If R<sup>i</sup> or R<sup>ii</sup> is an electron-withdrawing group (COR, CN, CHO, COOR).

The ylide becomes stable because of resonance and their reactivity towards carbonyl group is decreased. Such ylides called stable ylides, react with aldehydes but not with ketones.

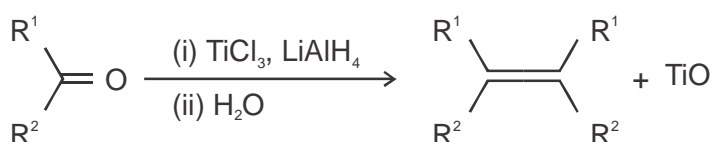
#### Applications :

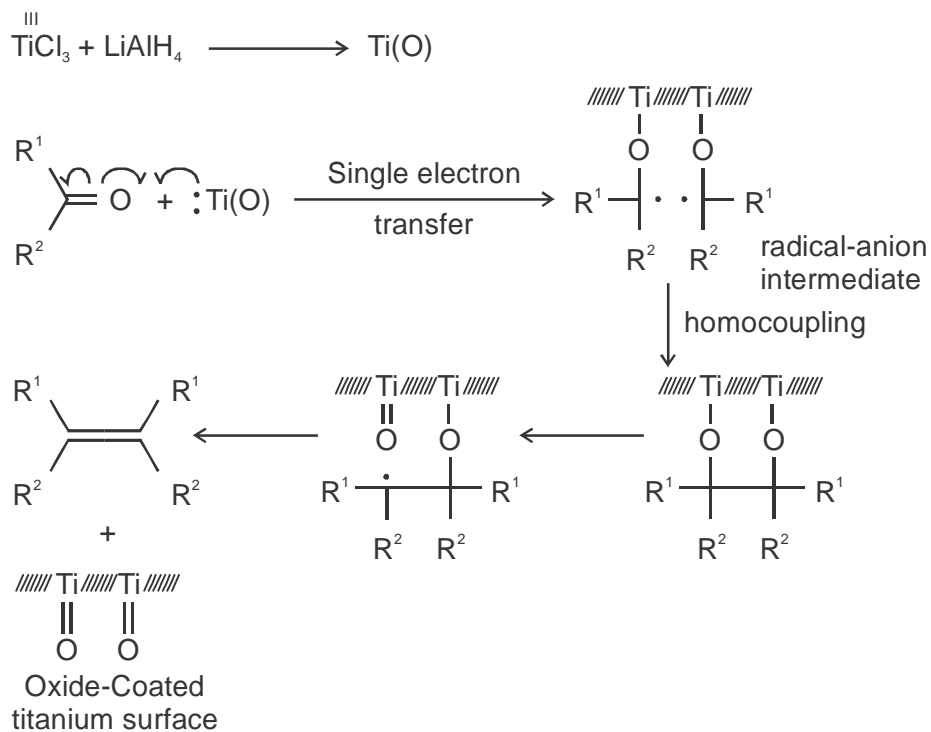
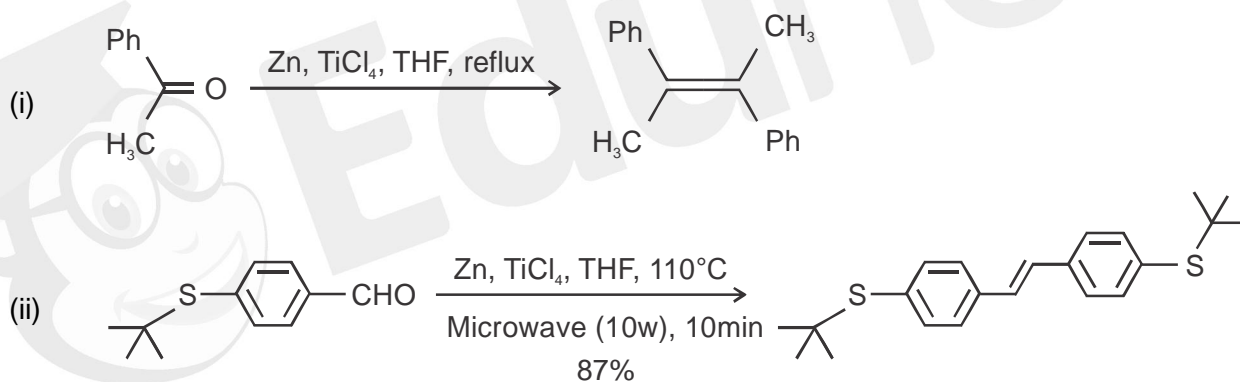


#### 4. Mc Murry Reaction :

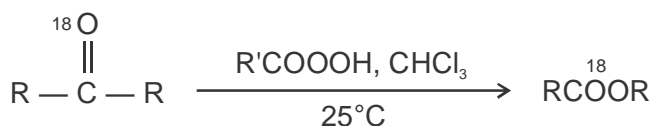
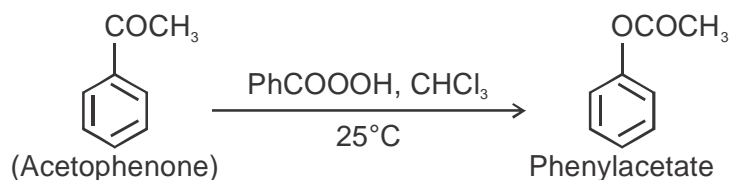
It involves the olefination of carbonyls with low valent titanium such as Ti(O) derived from TiCl<sub>3</sub>/LiAlH<sub>4</sub>.

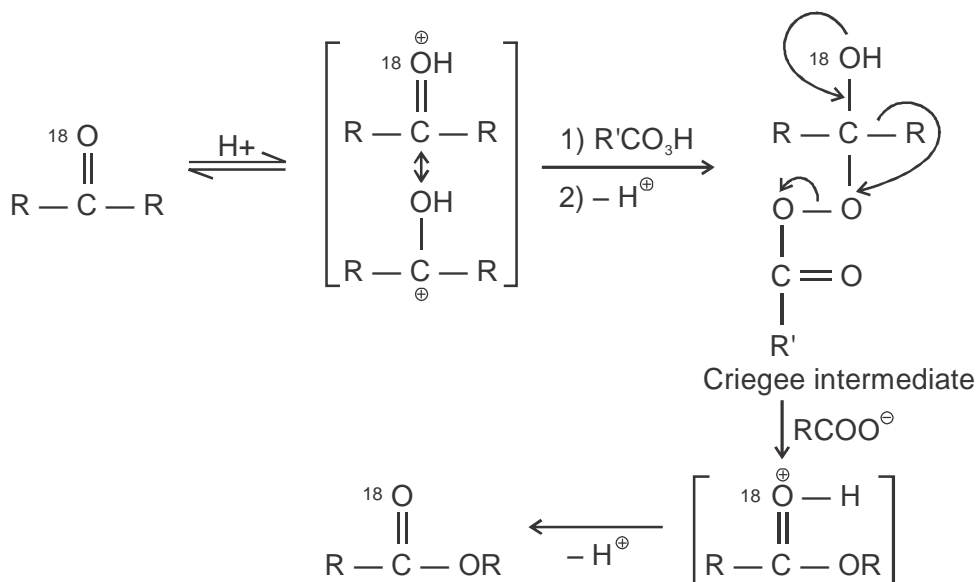
A single electron process :



**Mechanism :**

**Application :**

**5. Baeyer-Villiger Oxidation :**

Oxidation of ketones to esters with hydrogen Peroxide or with Peracids ( $\text{RCO}_3\text{H}$ ) is known as Baeyer-Villiger oxidation.



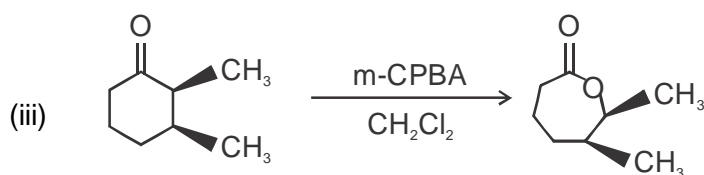
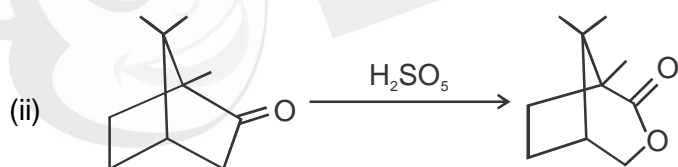
**Mechanism :**

**Migrating Aptitude :**

The most electron-rich alkyl group (more substituted carbon) migrates first, the general migration order :

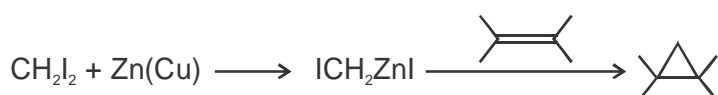
Tertiary Alkyl > Cyclohexyl > Secondary alkyl > benzyl > Phenyl > Primary alkyl > Methyl > H

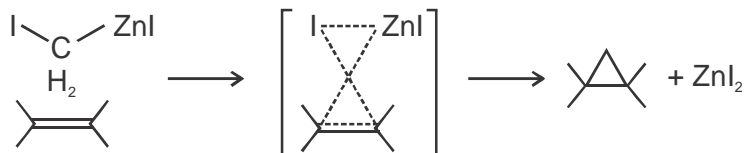
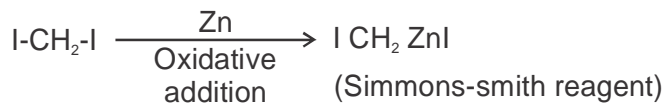
For substituted aryls:

p-MeOAr > p-MeAr > p-Cl-Ar > p-O<sub>2</sub>N-Ar

**Application :**

**6. Simmons-Smith Reaction :**

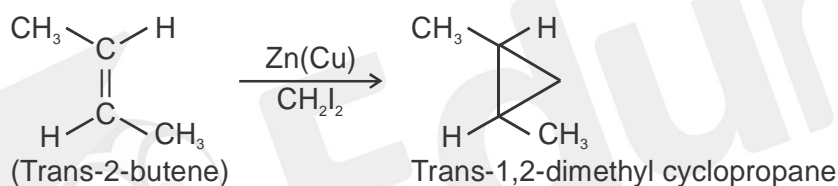
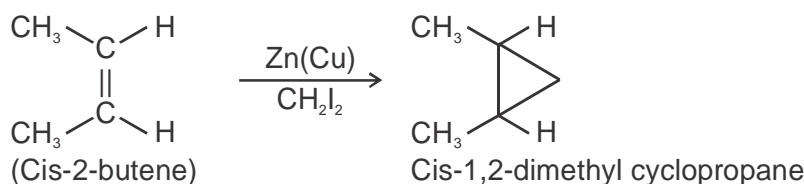
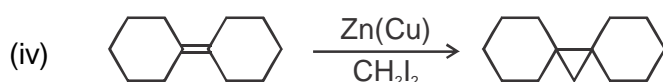
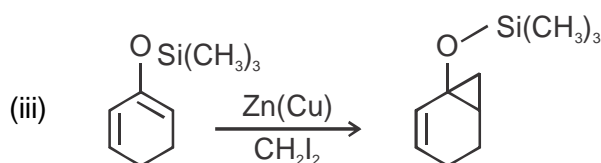
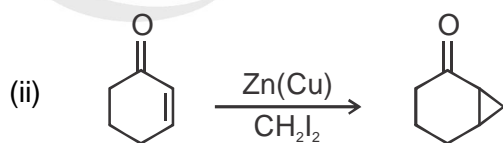
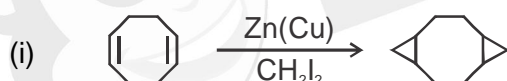
Cyclopropanation of olefins using CH<sub>2</sub>I<sub>2</sub> and Zn(Cu)



**Mechanism :**


Generally substituted alkenes react faster than unsubstituted alkenes.

The reaction is stereo specific Cis and trans give Cis and trans product respectively.

**For example -**

**Application :**

**7. Diels-Alder Reaction :**

Diels-Alder reaction is the [4+2] cycloaddition reaction between a conjugated diene (4- $\pi$  electron system) and a compound containing a double or triple bond.



In this reaction, a 1,3-diene (conjugate diene) reacts with a dienophile to form a six-membered ring with a double bond.

For ex-



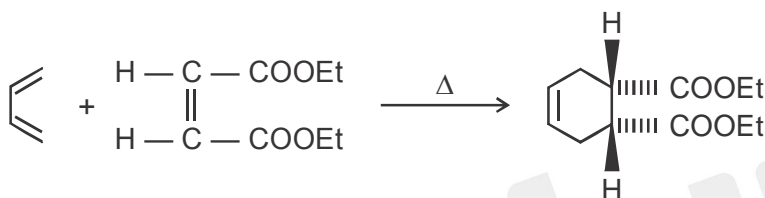
Diene    Dienophiles

In Diels-Alder reaction two new  $\sigma$  bonds are formed at the expense of  $\pi$ -bonds in the starting materials.

**Stereochemistry** : The reaction is stereospecific.

For ex-

Diethyl maleate reacts with butadiene to give Cis diethyl cyclohexene-4, 5-dicarboxylate.

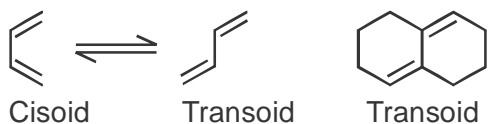


Similarly diethyl fumarate gives trans Product.

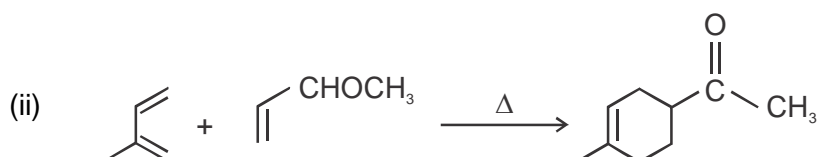
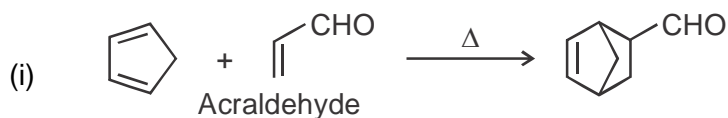


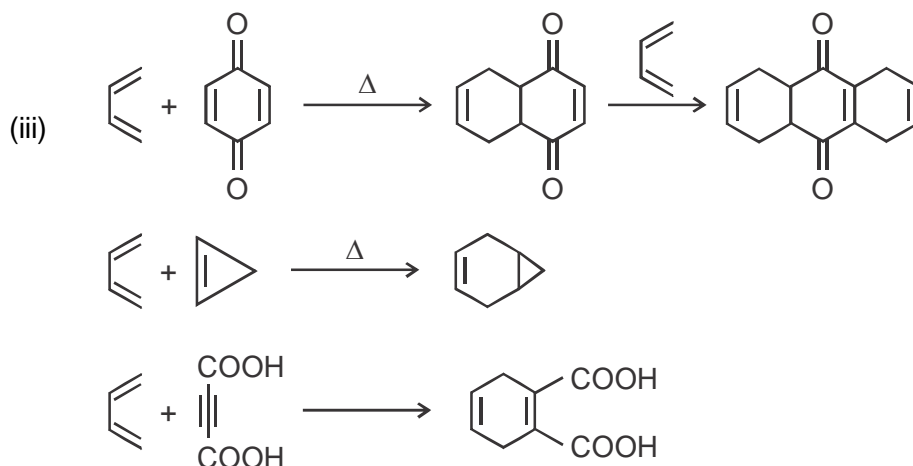
Thus stereochemistry is maintained throughout the chemical reaction.

Diene can exist in a cisoid and a transoid conformation and only the cisoid form undergoes this reaction.



**Application :**



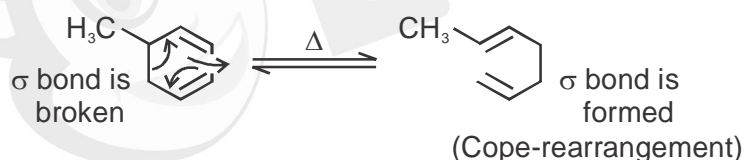
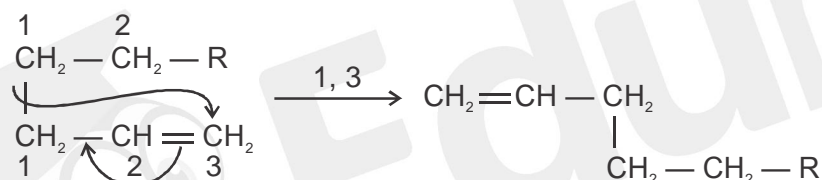


### 8. Sigmatropic Reaction :

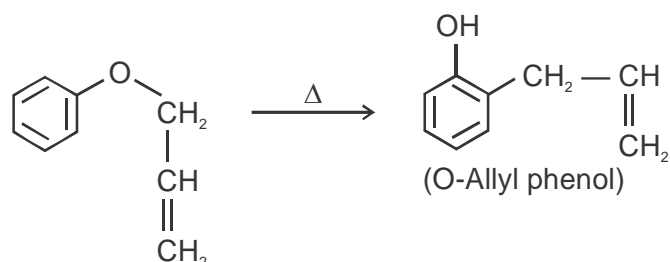
These are concerted intramolecular rearrangements involves a concerted reorganization of electrons during which a group attached by a sigma bond migrates to the terminus of an adjacent pi-electron system. The reactions are called Sigmatropic rearrangement because a sigma bond appears to move from one place to another during the reaction.

There is a simultaneous shift of the pi-electrons.

For ex-



Another common example of sigmatropic rearrangement is claisen rearrangement.

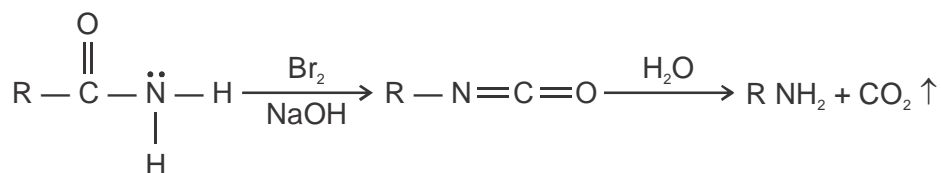


### 9. Hofmann Rearrangement :

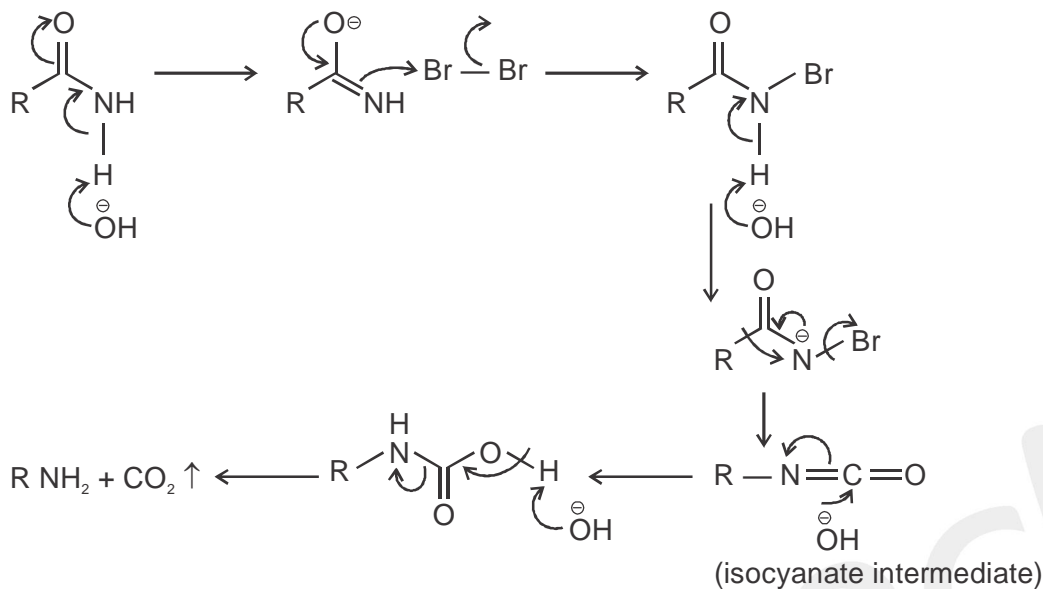
Upon treatment of primary amides with hypohalites, primary amines with one less carbon are obtained via the intermediacy isocyanate.

Also known as hofmann degradation reaction.

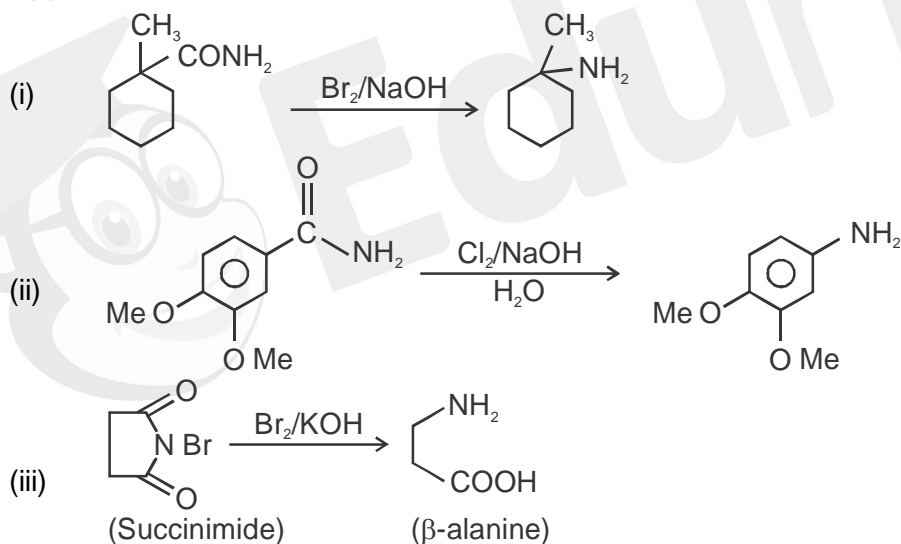
These reactions involve a migration of alkyl or aryl group from adjacent carbon to electron deficient nitrogen.



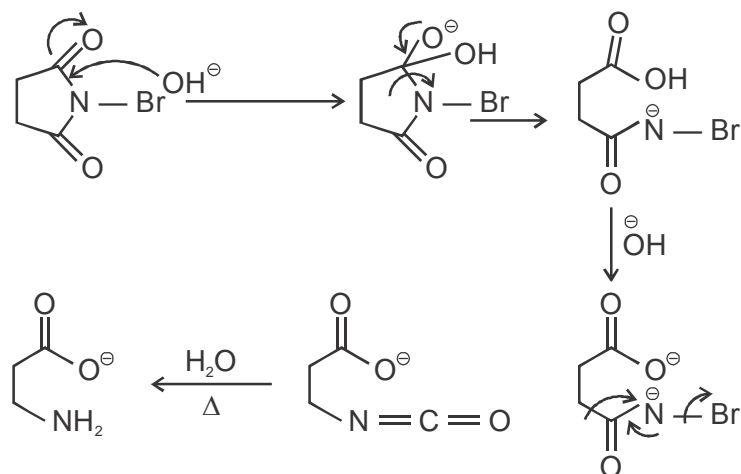
**Mechanism :**



**Application :**

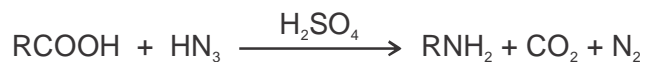
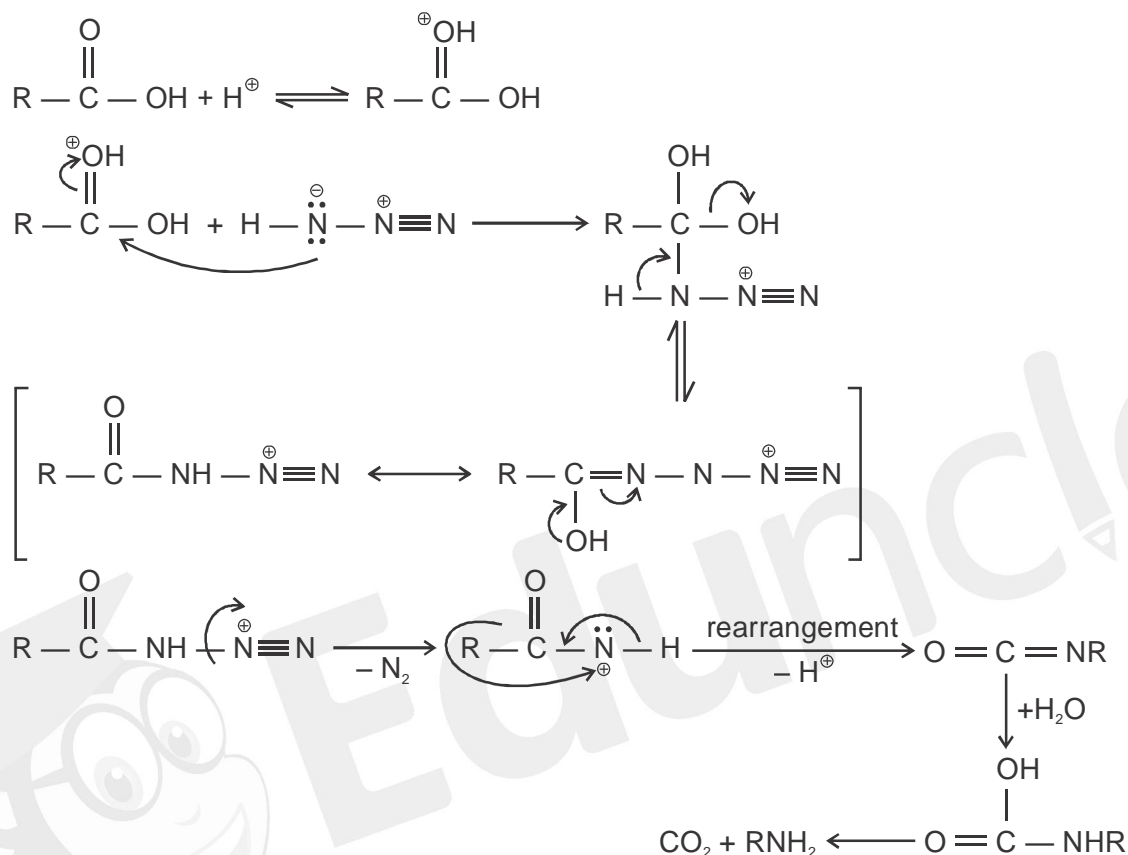


**Mechanism :**

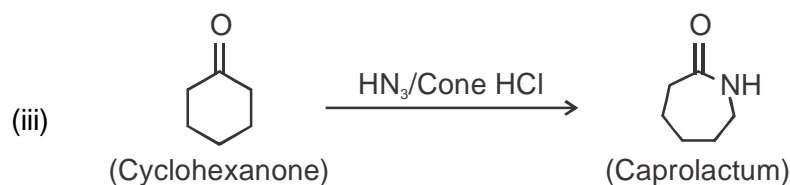
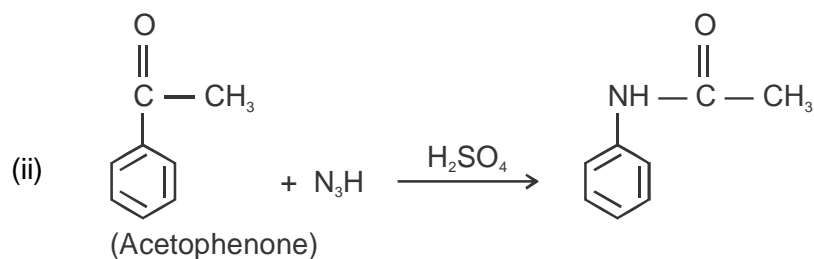
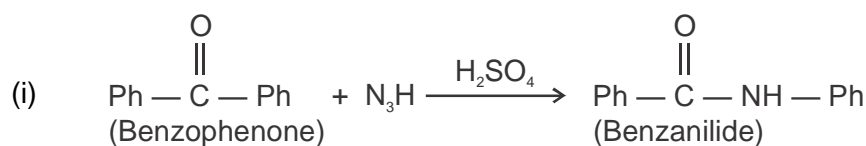


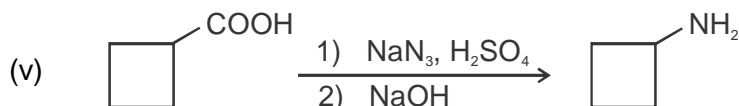
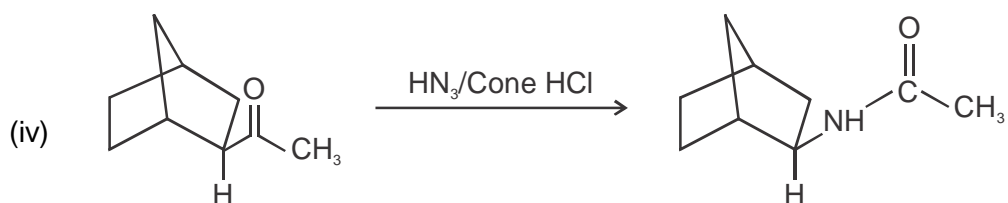
**10. Schmidt Rearrangement :**

The Schmidt reactions refer to the acid-catalyzed reactions of hydrazoic acid with electrophiles, such as Carbonyl compounds, tertiary alcohols and alkenes. These substrates undergo rearrangement and extrusion of nitrogen to furnish amines, nitrites, amides, or imines.


**Mechanism :**

**Application :**

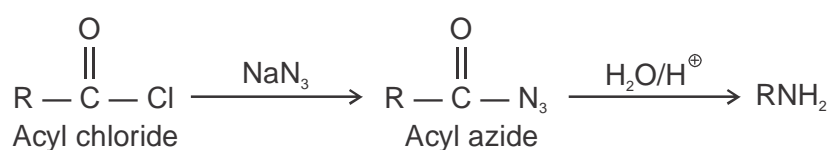
Schmidt reaction also given by aldehydes and ketones



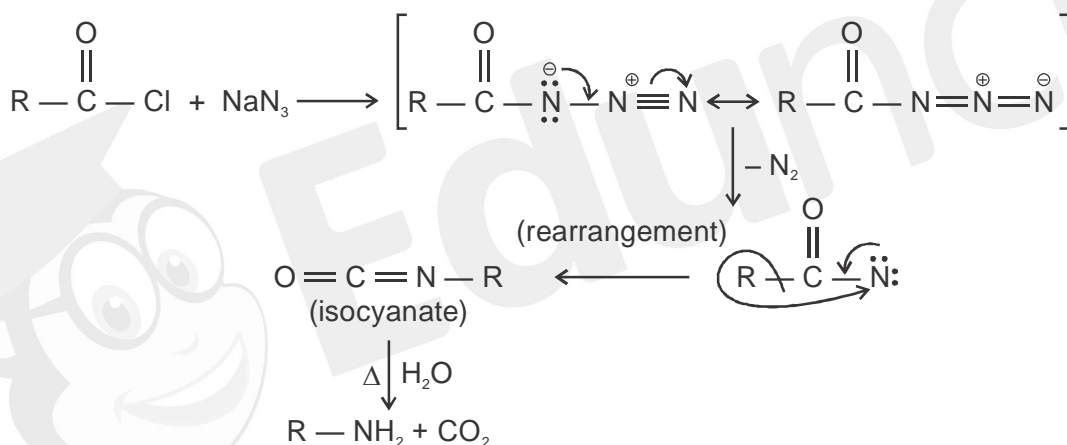


### 11. Curtius Rearrangement :

When acid halide react with  $\text{NaN}_3$  (Sodium azide) then Curtius rearrangement would be takes place and isocyanate would be formed.

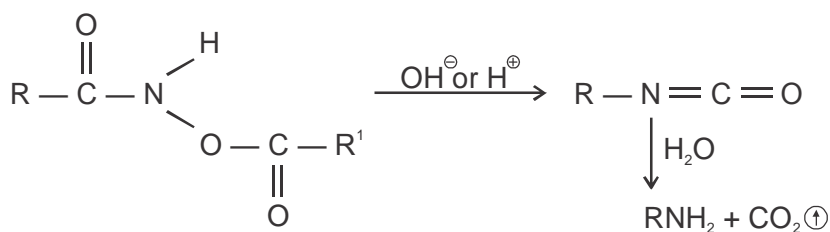
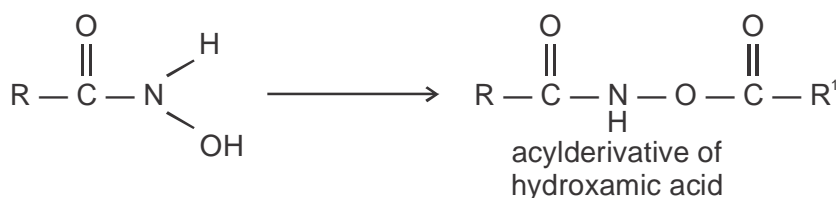


#### Mechanism :



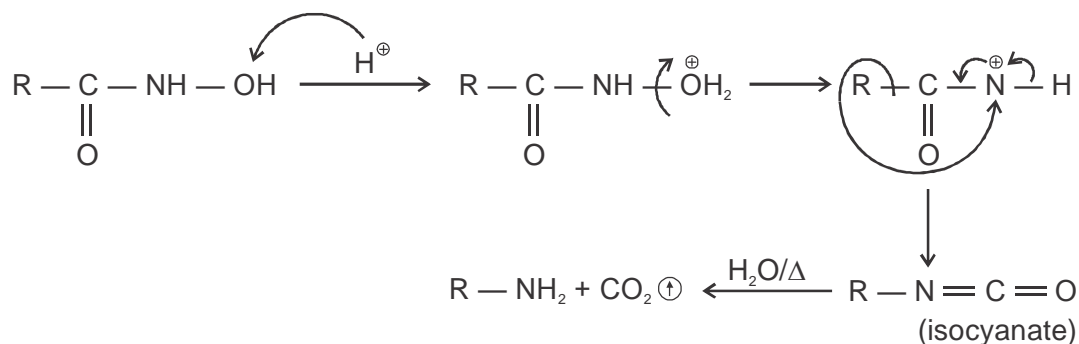
### 12. Lossen Rearrangement :

The rearrangement of acyl derivative of hydroxamic acid to isocyanate, followed by hydrolysis to corresponding amine is known as lossen rearrangement.

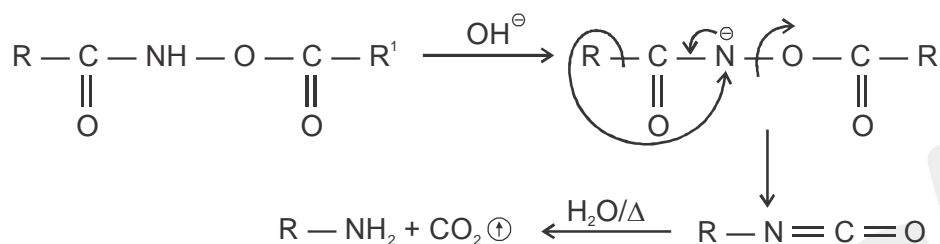


**Mechanism :**

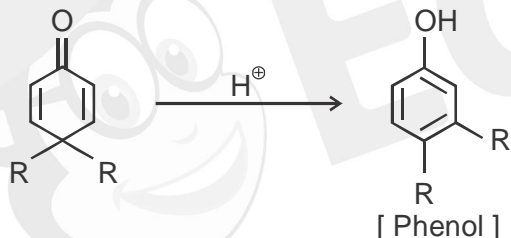
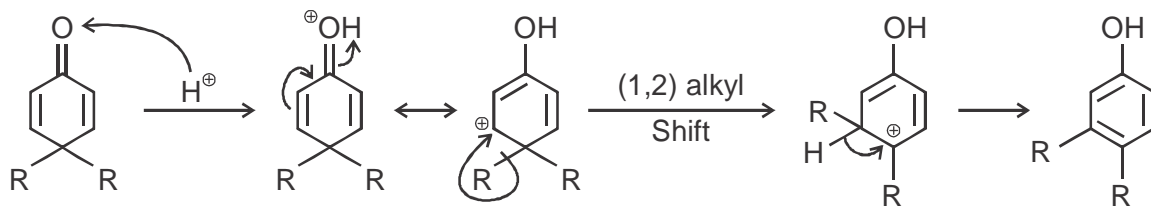
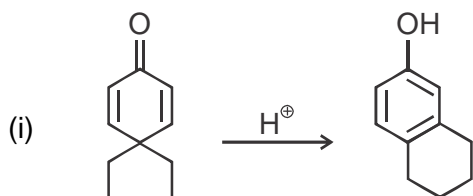
(A) Acid catalyzed-

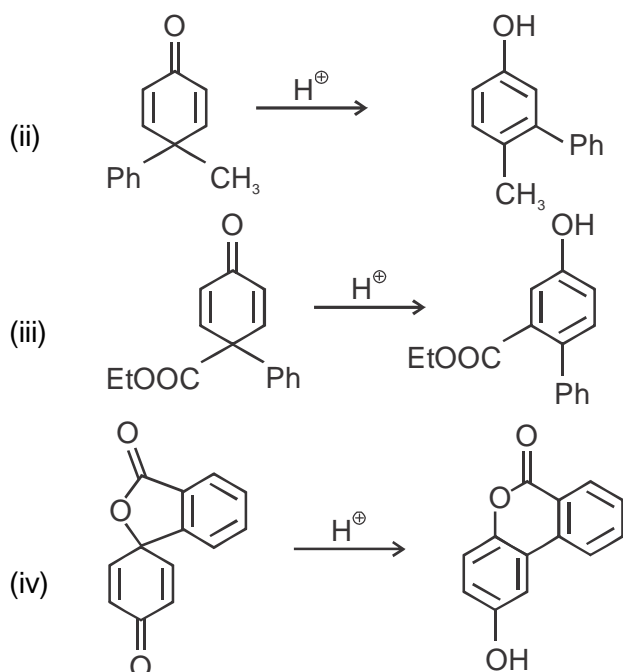


(B) Base catalyzed-


**13. Dienone-Phenol Rearrangement :**

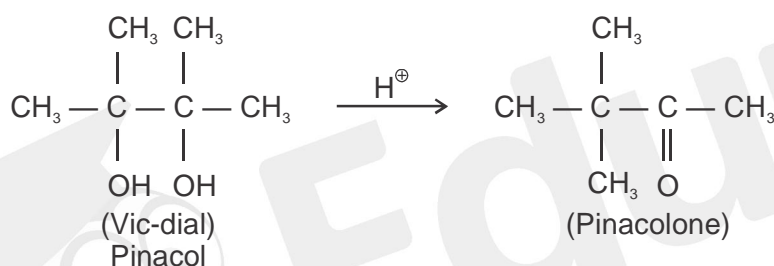
It involves the conversion of 4,4-dialkyl Cyclohexadienone into Phenol with rearranged Carbon-Skeleton in the presence of acidic media.


**Mechanism :**

**Application :**


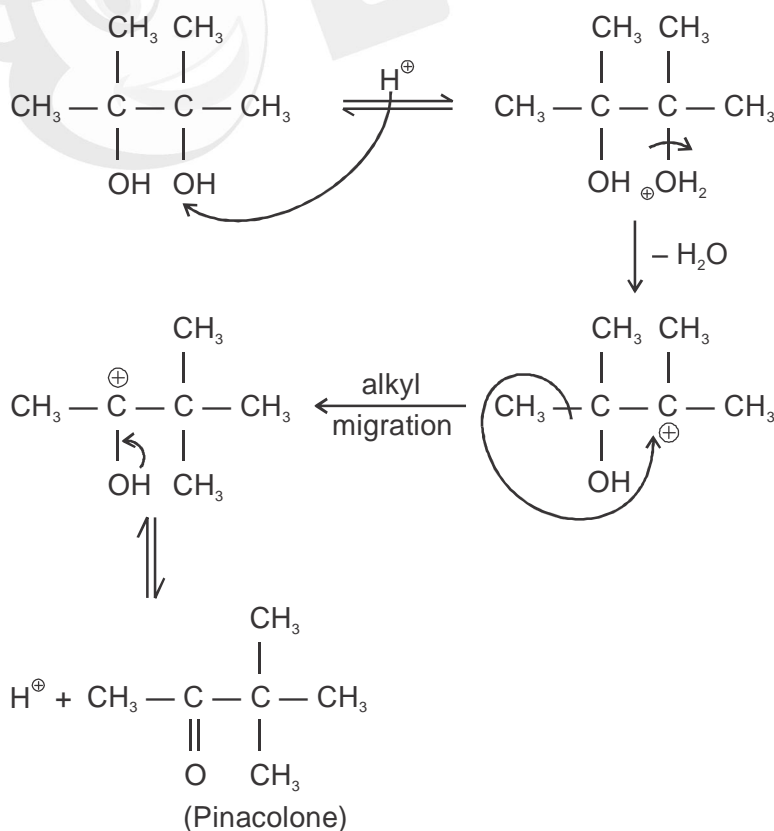


#### 14. Pinacol-Pinacolone Rearrangement :

Acid-catalyzed rearrangement of vicinal diols (Pinacols) to Carbonyl compounds.



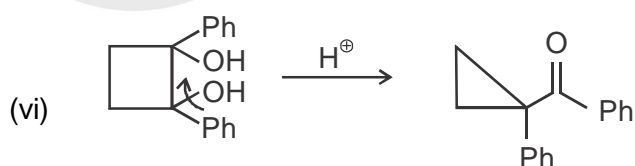
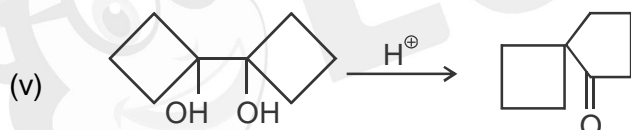
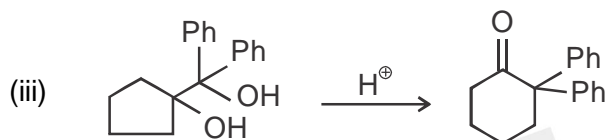
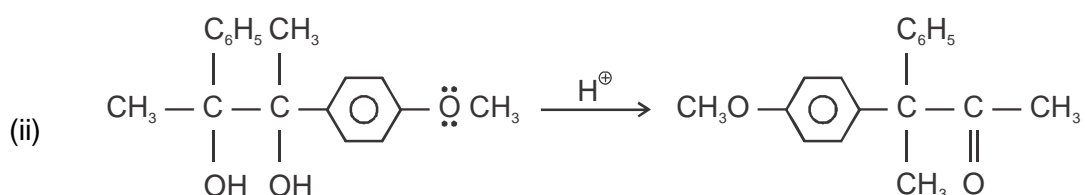
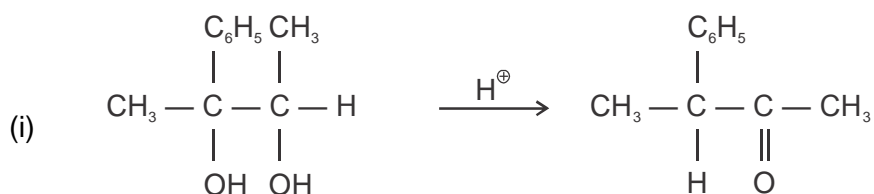
##### Mechanism :



The most electron-rich alkyl group (more substituted carbon) migrates first. The general migration order :

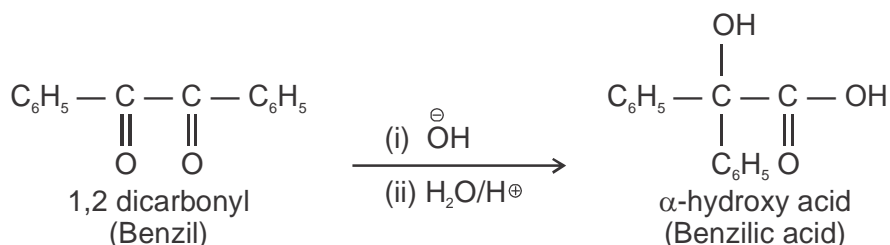
Tertiary alkyl > Cyclohexyl > Secondary alkyl > Benzyl > Phenyl > Primary alkyl > Methyl >> H

**Application :**



### 15. Benzilic acid Rearrangement :

Rearrangement of benzyl to benzilic acid via aryl migration

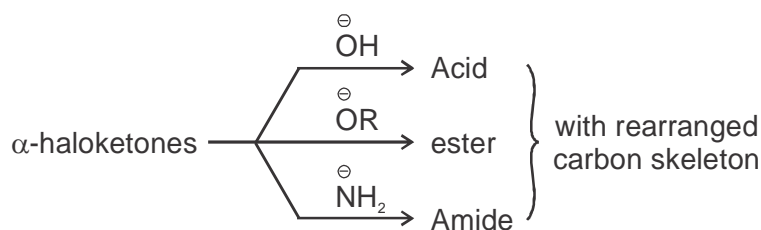




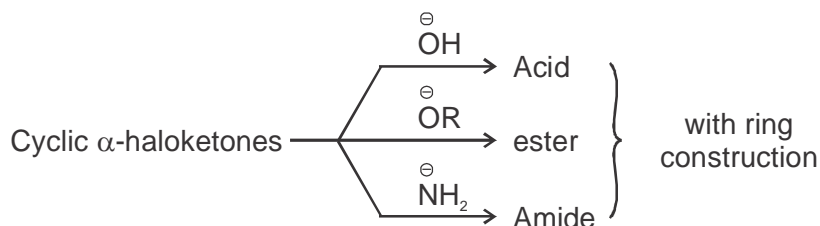


**16. Favorskii Rearrangement :**

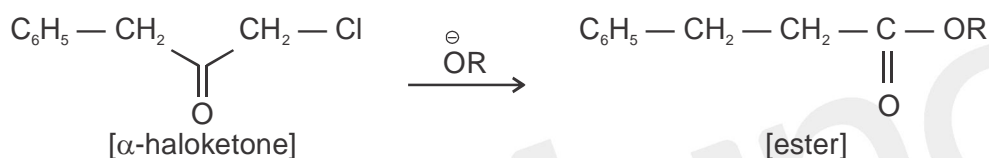
The base-catalysed rearrangement of  $\alpha$ -haloketones to carboxylic acids, esters or amides:



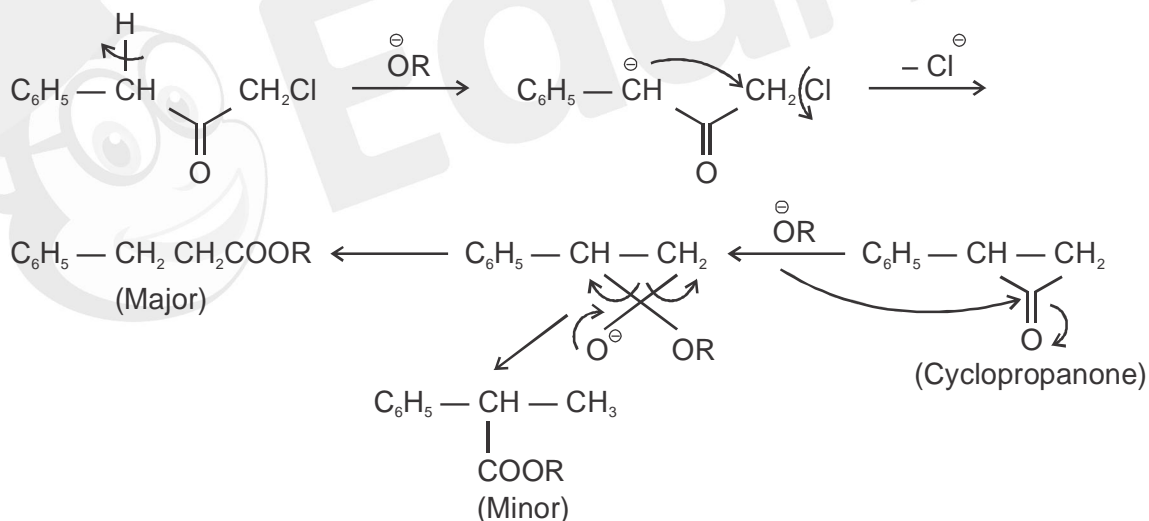
The rearrangement of cyclic ketones involves ring construction:



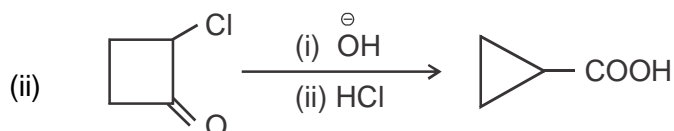
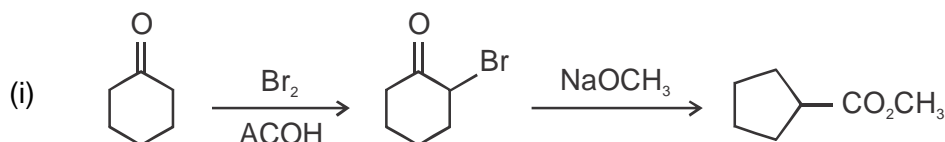
**For example :**

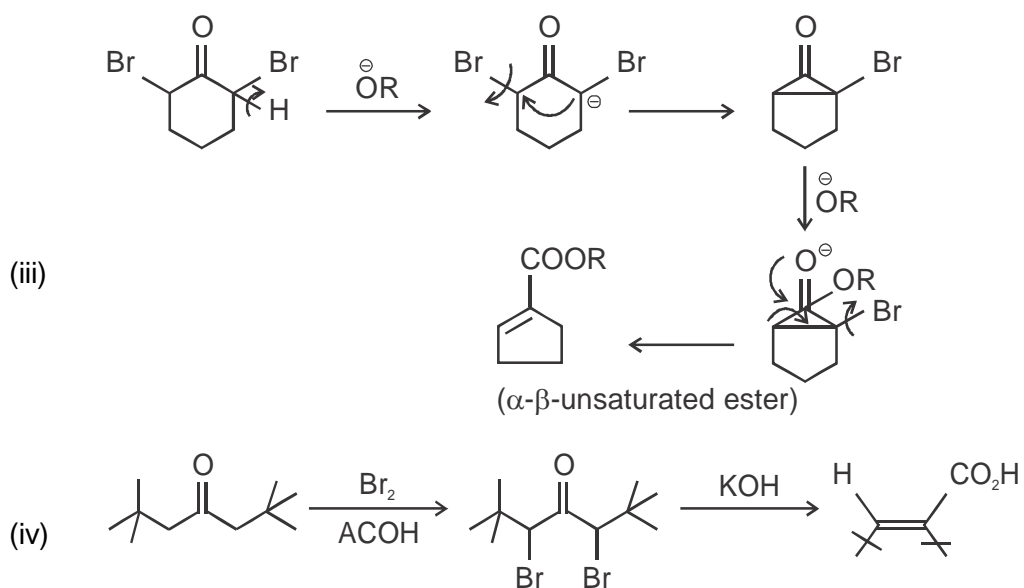


**Mechanism :**



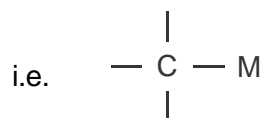
**Applications :**





## 4. ORGANOMETALLIC REAGENTS

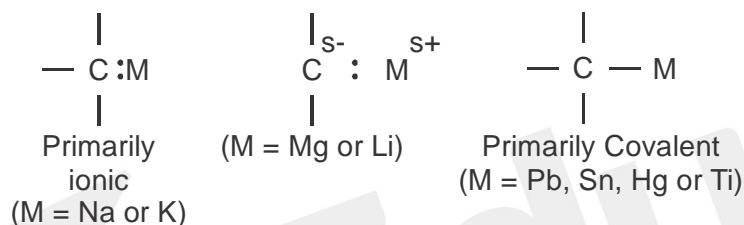
The compounds in which a metal is directly attached to carbon are known as Organometallic compounds.



Some examples of these compounds are :

- i) Grignard reagent (RMgX)
- ii) Super Grignard reagent (R-Li)
- iii) Gilman reagent (R<sub>2</sub>CuLi)
- iv) Dialkyl Cadmium (R<sub>2</sub>Cd)
- v) Dialkyl zinc (R<sub>2</sub>Zn)

The nature of the carbon-metal bonds varies widely, ranging from bonds that are essentially ionic to those that are primarily covalent. e.g,



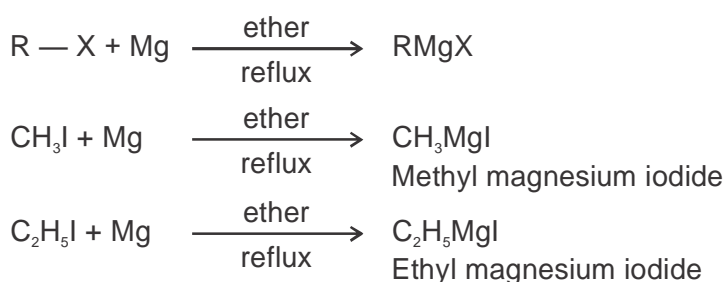
The reactivity of Organometallic compounds increase with the percent ionic character of the Carbon-Metal bond.

### Grignard Reagent :

The organomagnesium halides are known as Grignard reagents. They have the general formula RMgX, where R is univalent radical like alkyl or aryl radical and X is generally bromine or iodine.

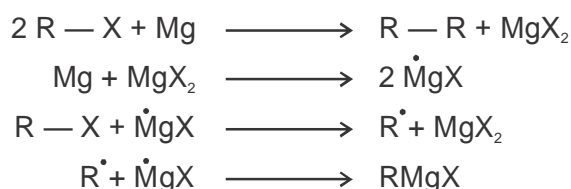
### Preparation :

Grignard reagents are prepared by the action of magnesium on alkyl halide in anhydrous ether



### Mechanism :

The reaction most likely occurs via free radical mechanism.



**Reactions of Grignard reagent :**

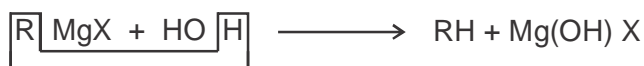
Grignard reagent acts as a nucleophile (strong base) and has been used to prepare almost all classes of organic compounds.

Some applications are as follows:

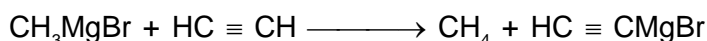
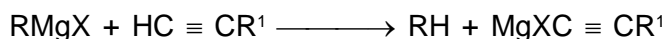
**1) Reaction with compounds containing active hydrogen:**

Grignard reagent form hydrocarbons with a compound containing active hydrogen atom.

**For ex:**

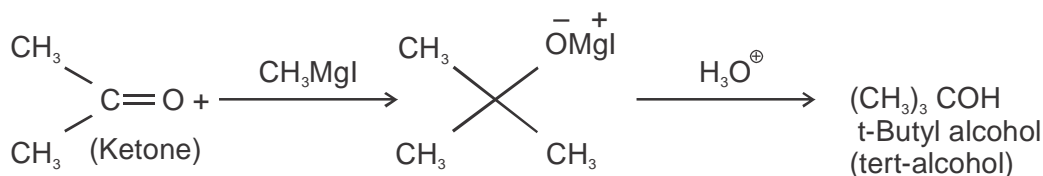
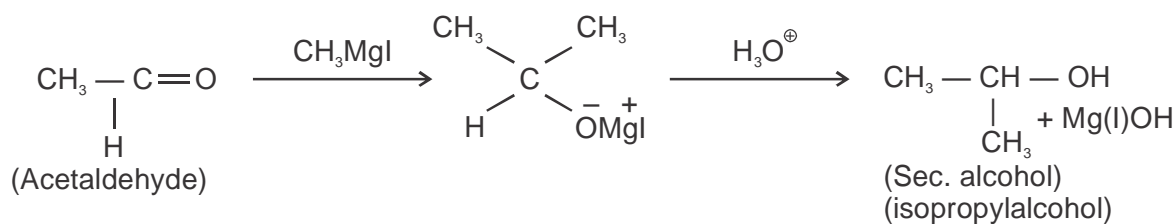
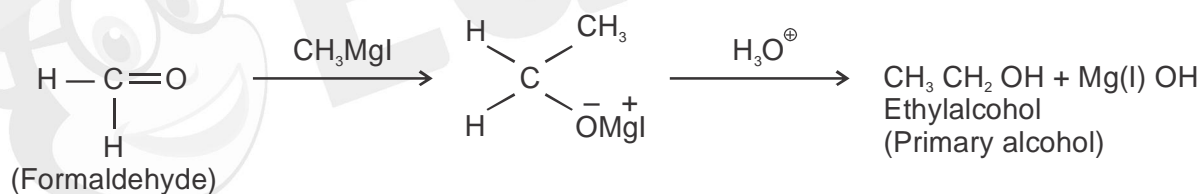


Alkanes can also be prepared by the reaction of Grignard reagent with terminal hydrogen atom of alkynes.


**2) Reaction with Carbonyl compounds:**

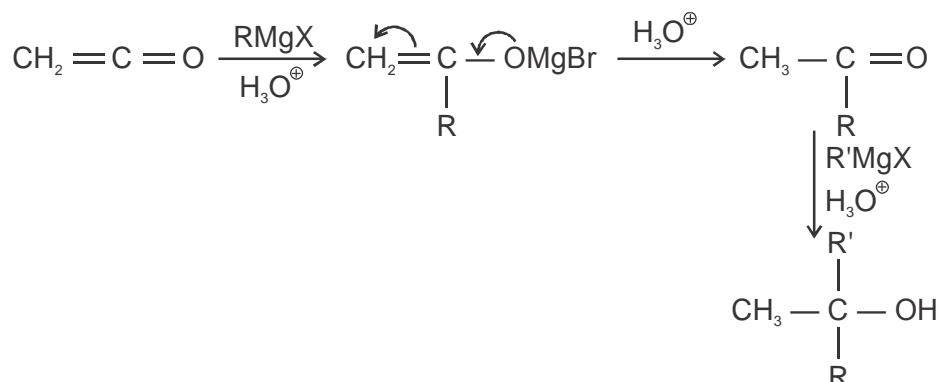
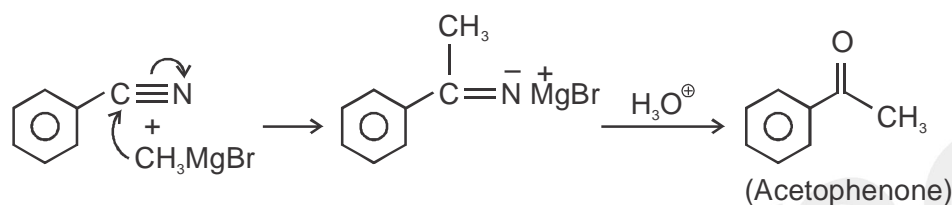
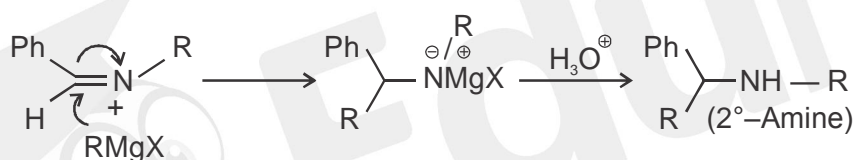
Being nucleophilic in nature, the Grignard reagent attack the carbonyl group of aldehydes, ketones, esters, anhydrides, acid halides and amides to give a complex (addition product).

These addition products on decomposition with water give the hydroxyl compounds (alcohol).

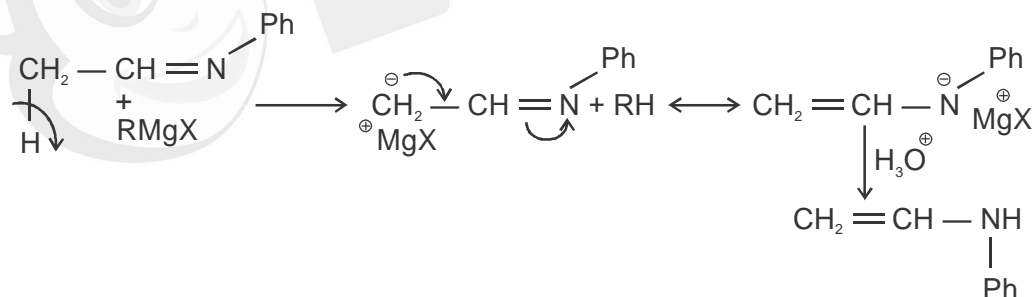




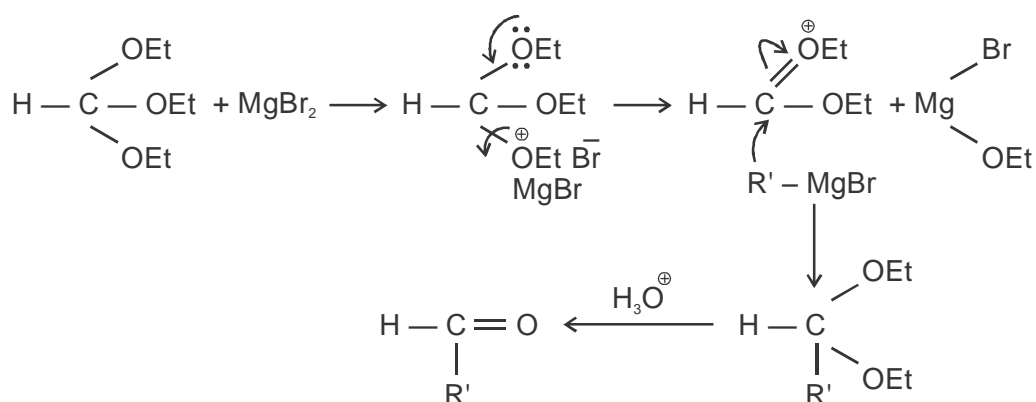
**6) Reaction with oxygen:**

**7) Reaction with ketene:**

**8) Reaction with Cyanide:**

**9) Reaction with imines:**


If imines have -H atom then following major side reaction will be takes place:

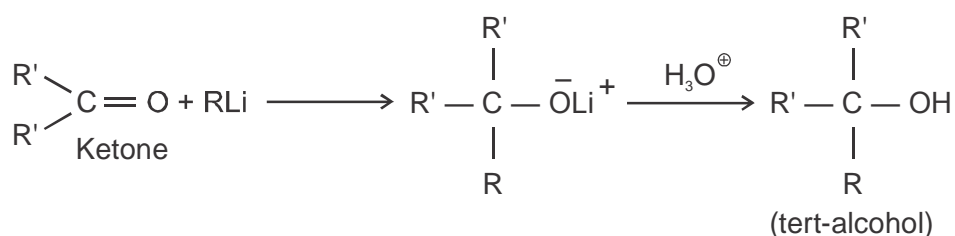
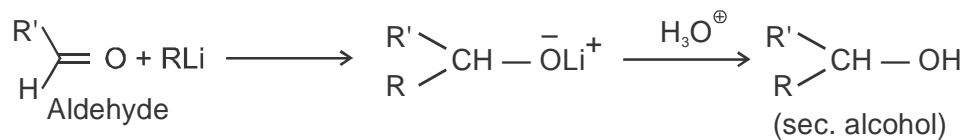
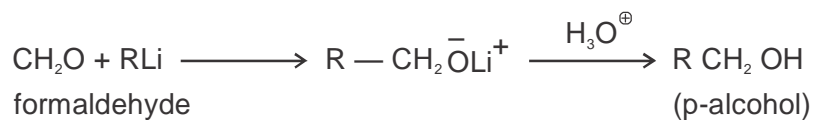
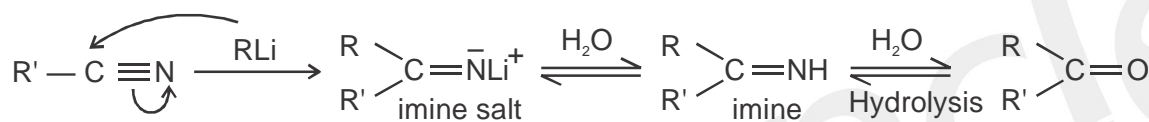

**10) Reaction with ortho ester:**

Here reaction takes place in presence of lewis acid ( $\text{MgBr}_2$ )







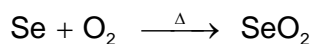
**(2) Reaction with carbonyl compounds :**

**(3) Reaction with alkyl cyanide :**

**(4) Reaction with epoxide :**


## 5. OXIDIZING AGENTS

### A) Selenium dioxide (SeO<sub>2</sub>) :

- It is a white crystalline solid
- It is soluble in solvents like dioxane, ethanol, acetic acid, acetic anhydride etc.

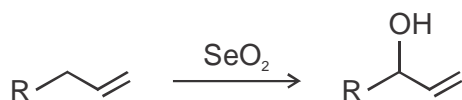
**Preparation :**



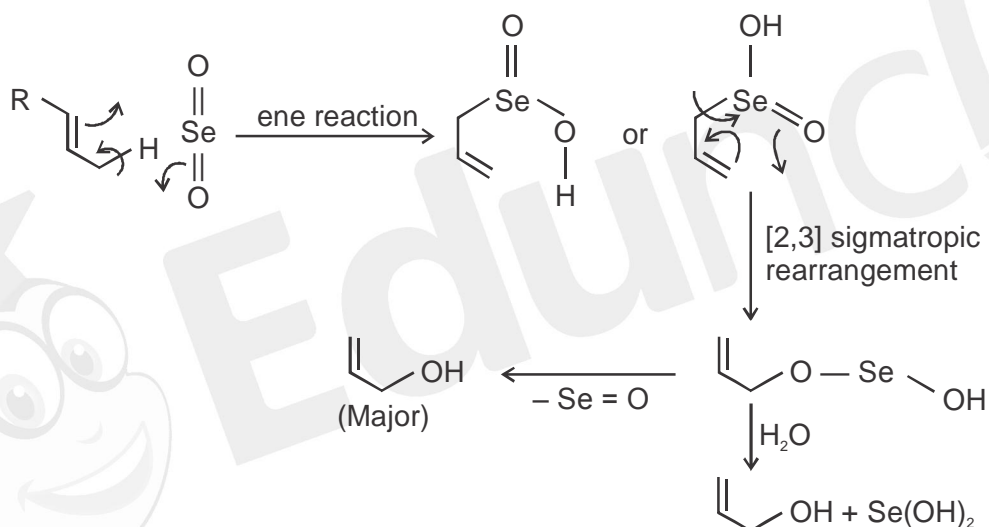
**Application :**

#### i) Oxidation of allylic or benzylic compounds :

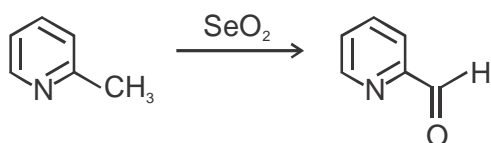
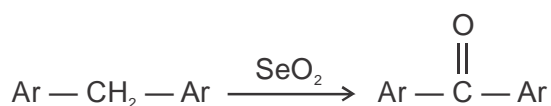
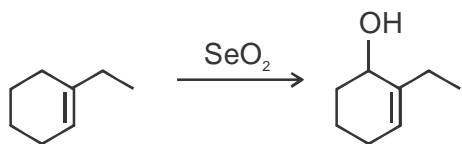
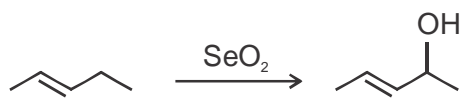
It is used for the oxidation of Allylic or benzylic C-H fragments to the corresponding Allylic or benzylic alcohol.

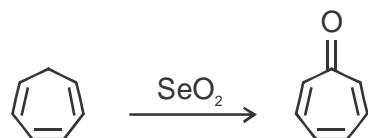
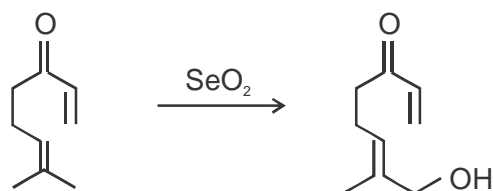
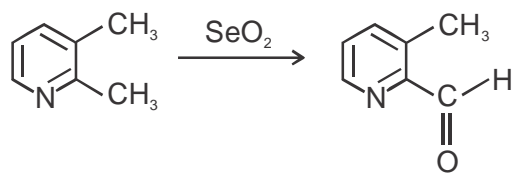


**Mechanism :**



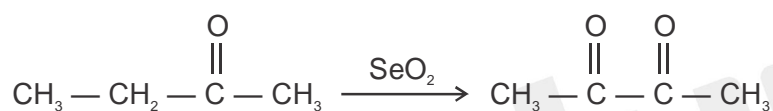
**Examples :**



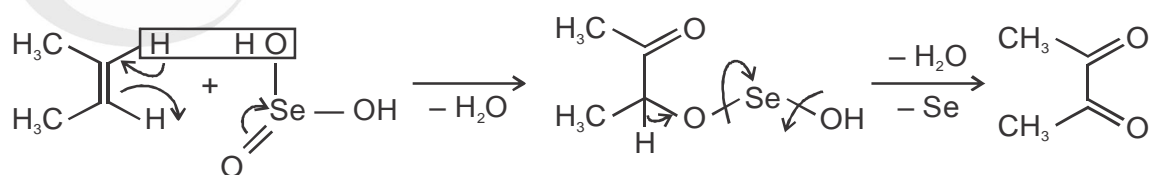
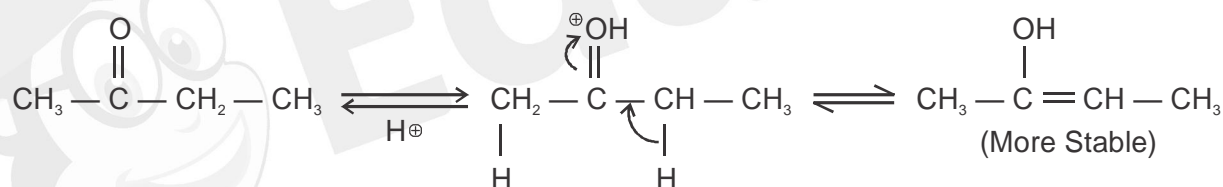


## ii) Oxidation of Carbonyl Compounds :

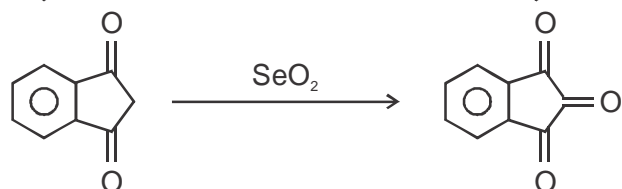
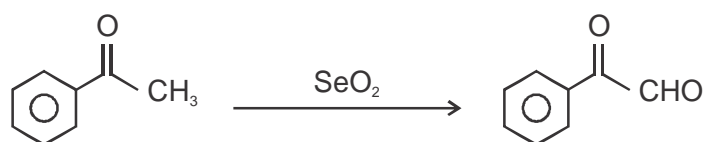
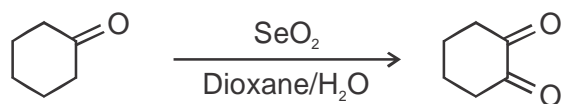
The aldehyde or ketones with a Methyl or Methylene group  $\alpha$ - to the carbonyl group are oxidized to the 1,2-dicarboxyl compounds.

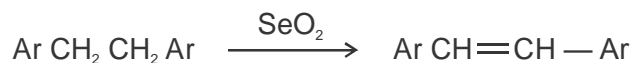
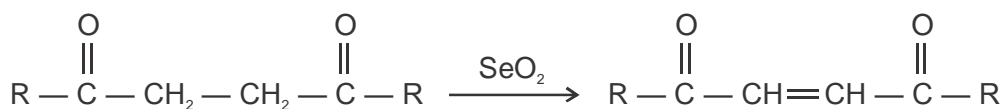
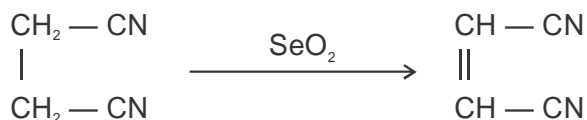


### Mechanism :



### Examples :

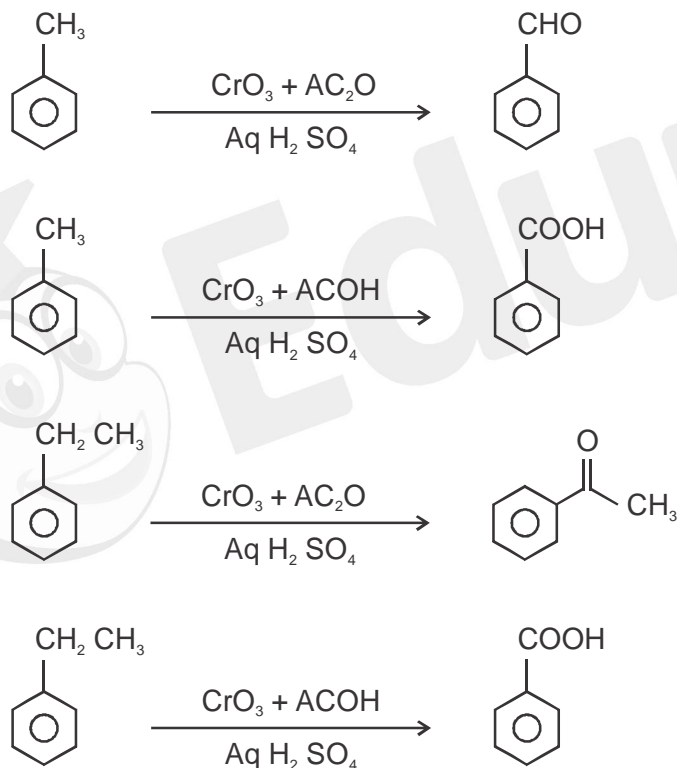


**iii) Dehydrogenation :**

**B) Chromium (VI) oxidants :**
**i) Chromium trioxide :**

Used for the oxidation of active position mostly benzylic position.

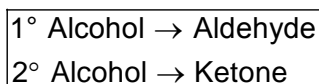
- Here product formation depends upon reaction condition

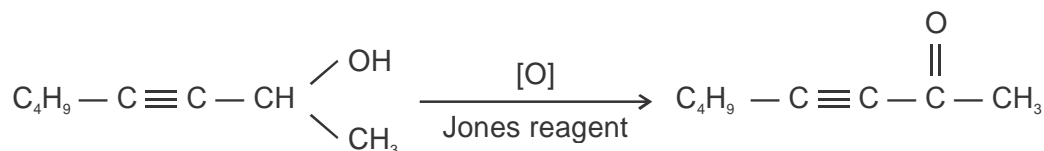
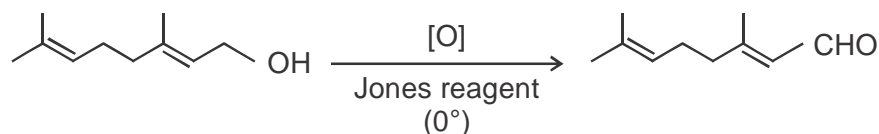
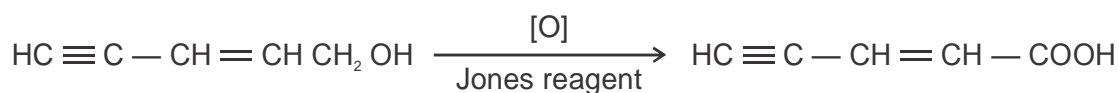
For example :


**ii) Jones reagent :**

The oxidation of alcohols with chromium trioxide-acetate sulfuric acid reagent is known as Jones oxidation.

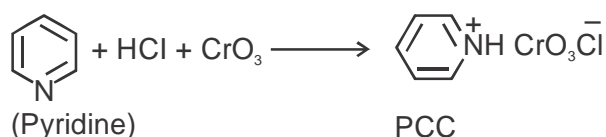
- This reagent is very selective as it is useful for oxidation of alcohols which contain C-C double or triple bond, Allylic or benzylic C-H bonds.
- The reaction is carried out at 0 to 20°C.





### iii) Pyridinium Chlorochromate (PCC) :

This reagent is obtained by adding pyridine to a solution of chromium (VI) oxide in hydrochloric acid.



It is used for the oxidation of primary and secondary alcohols to the corresponding carbonyl compounds.

$1^\circ$ Alcohol $\rightarrow$ Aldehyde $2^\circ$ Alcohol $\rightarrow$ Ketone
------------------------------------------------------------------------------------



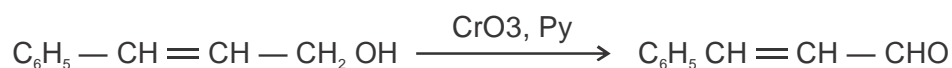
$\text{R}^1 = \text{H}$  (Primary alcohol)

$\text{R}^1 = \text{alkyl}$  (Sec. alcohol)

### iv) Sarett Oxidation ( $\text{CrO}_3 + \text{Py}$ ) :

It is also used for the oxidation of primary and secondary alcohol to the corresponding carbonyl compounds. If oxidation is carried out in dichloromethane solution then it is known as Collins oxidation.

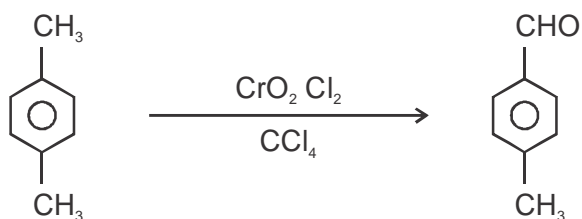
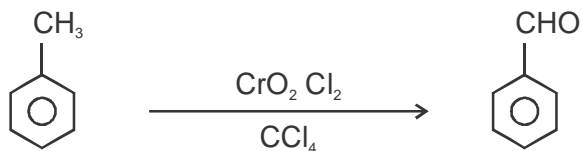
$1^\circ$ Alcohol $\rightarrow$ Aldehyde $2^\circ$ Alcohol $\rightarrow$ Ketone
------------------------------------------------------------------------------------



### v) Etard Reaction :

Another useful chromium reagent is chromyl chloride ( $\text{CrO}_2\text{Cl}_2$ ), it oxidizes a methyl group to a formyl group.

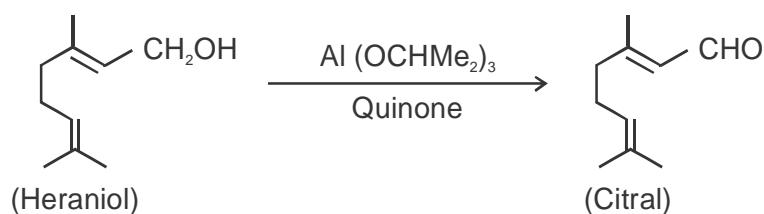
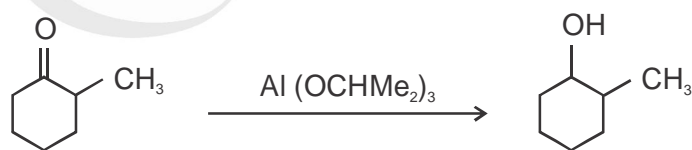
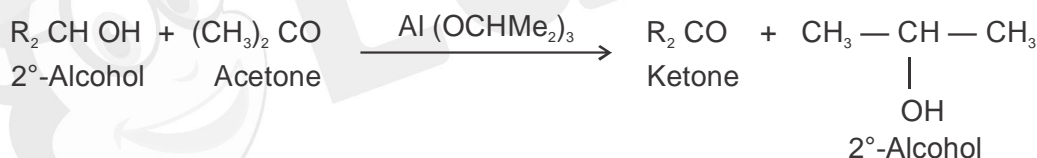
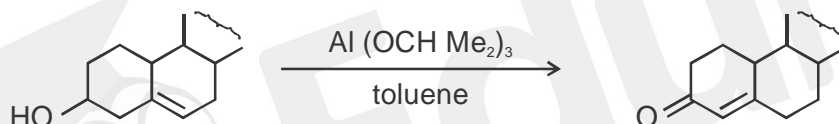
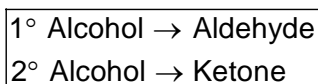
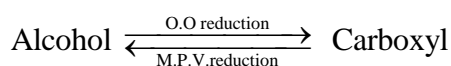
For ex-



### C) Oppenauer Oxidation :

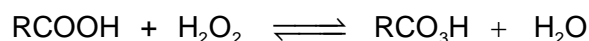
This reaction is reversible in nature, so 100% yield is not obtained.

The reversible reaction is known as Meerwein-Ponndorf-Verley reduction.



### D) Oxidation with Peracids :

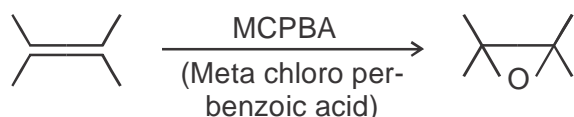
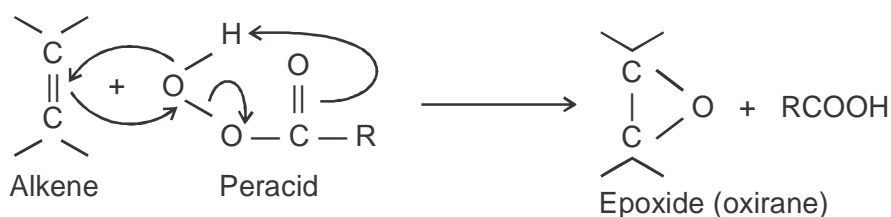
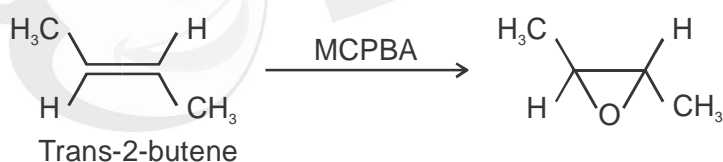
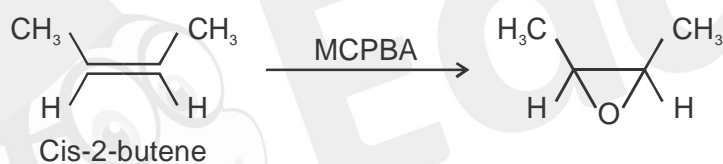
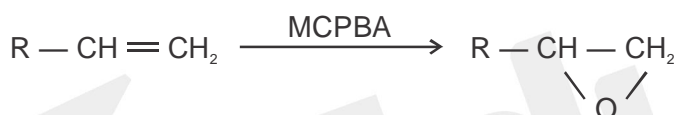
A number of peracids having the general formula,  $\text{RCO}_3\text{H}$  has been used to effect oxidation. Peracids are generally prepared in situ by the action of hydrogen peroxide on the corresponding carboxylic acids.



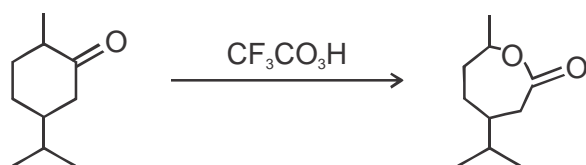
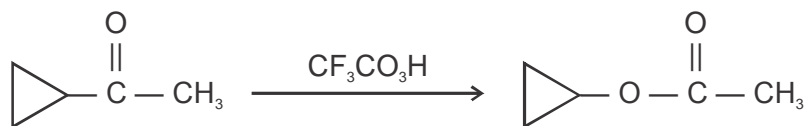
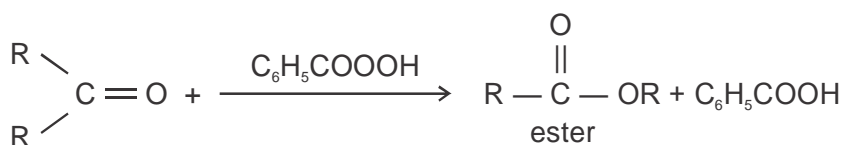
**Application:**
**i) Oxidation of alkenes :**

Peracids reacts with alkenes to give stable three-membered ring containing one oxygen atom (epoxides).

- Here concerted mechanism will be taken place, so stereochemistry of alkene should be maintained in the product.
- That means Cis gives Cis product and trans gives trans product.

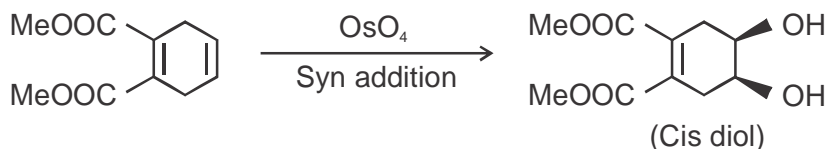

**Mechanism :**

**Examples :**

**ii) Oxidation of ketones (Baeyer-Villiger Oxidation)**

Ketones react with Peracids to give esters by insertion of oxygen.

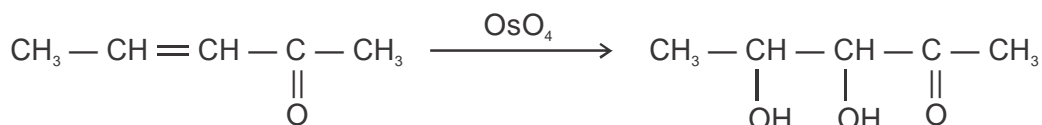
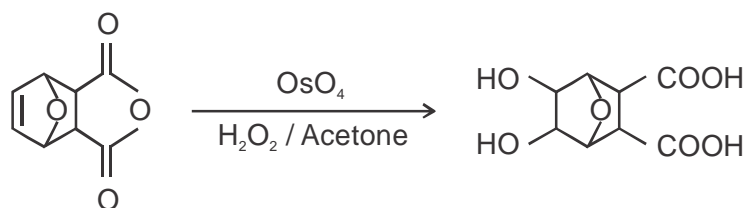
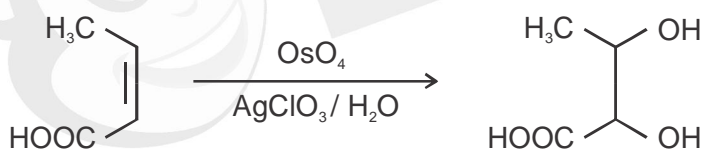
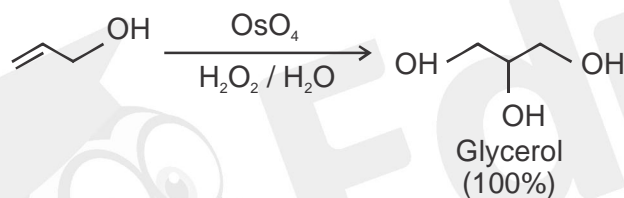
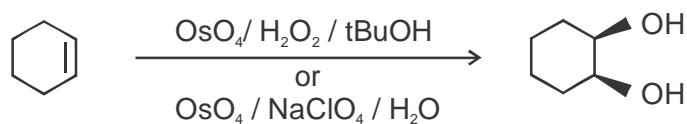
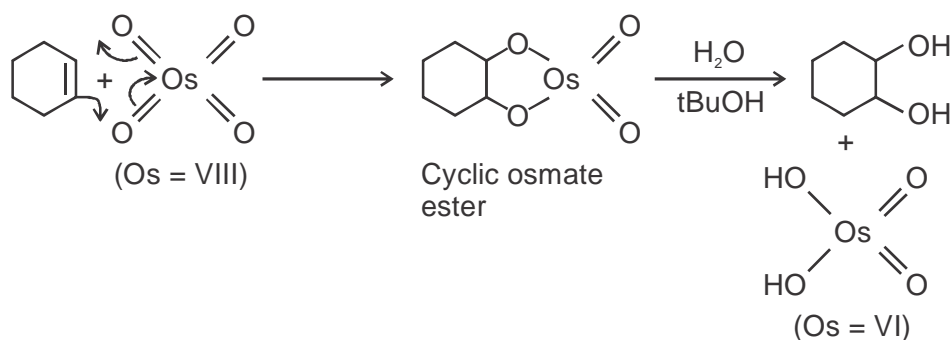


**E) Osmium tetroxide (OsO<sub>4</sub>) :**

- It is regioselective.
- Diol formation will be takes place at more nucleophilic C = C.
- Syn addition will be takes place.
- More stable Cis diol will be obtained.



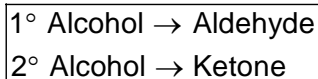
In the case of  $\alpha, \beta$  unsaturated carbonyl also diol formation takes place.


**Examples :**

**Mechanism :**


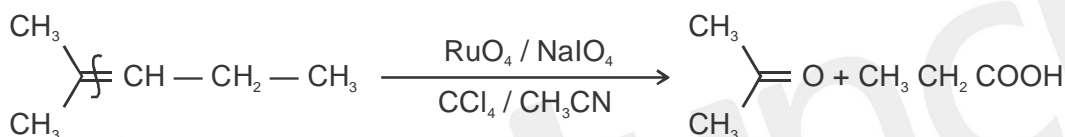
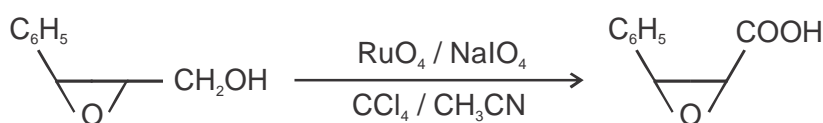
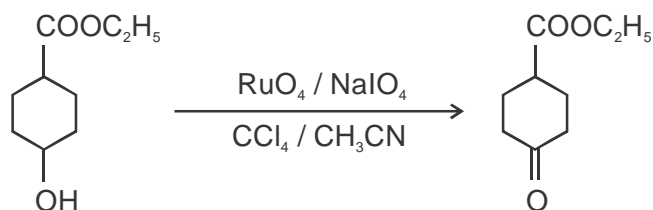


**F) Ruthenium Tetroxide :**

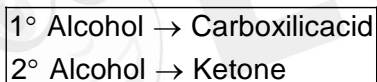
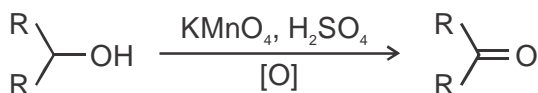
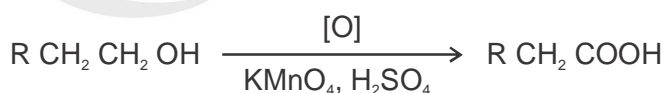
$\text{RuO}_4$  is the powerful oxidizing agent and oxidized various function group in presence of  $\text{CCl}_4$  and  $\text{CH}_3\text{CN}$  solution.



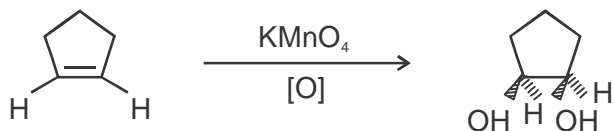
$\text{RuO}_4$  also cleavage the  $\text{C} = \text{C}$  and converted into the acid or ketone.

**Example :**

**G) Potassium Permanganate :**

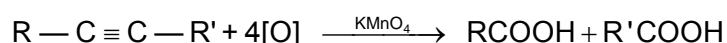
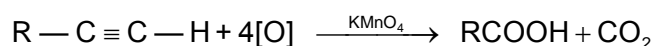
i) **Oxidation of alcohol :** Primary and secondary alcohol are oxidized to carboxylic acid and ketones respectively.

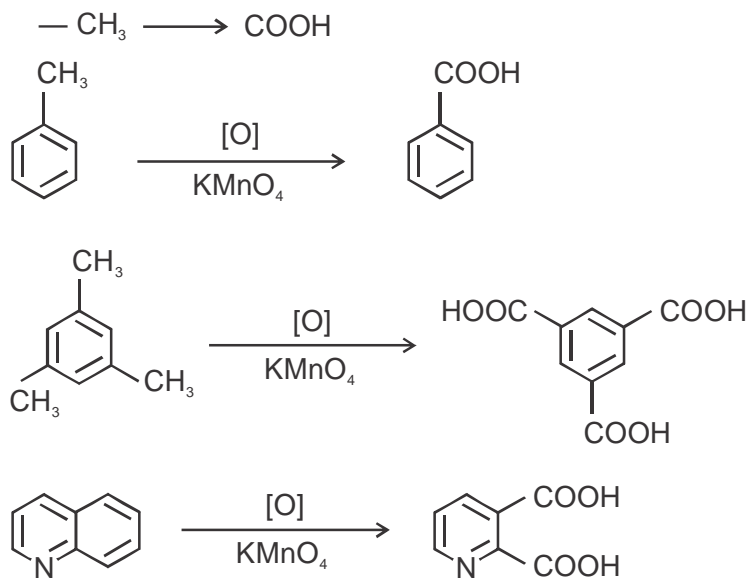

**Example :**


ii) **Conversion of an olefin to glycol :**

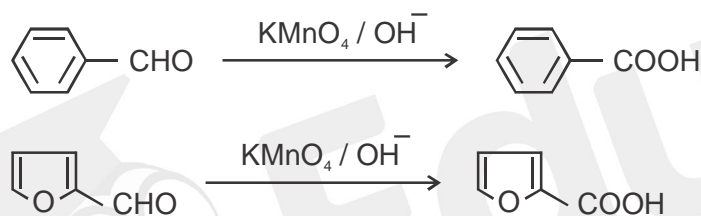


iii) **Oxidation of alkynes :**

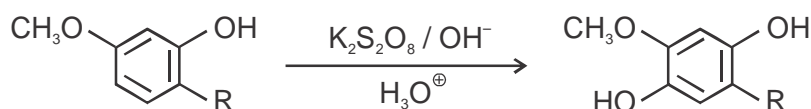
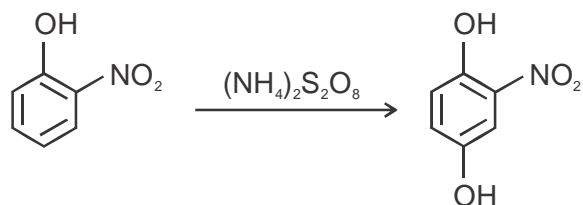
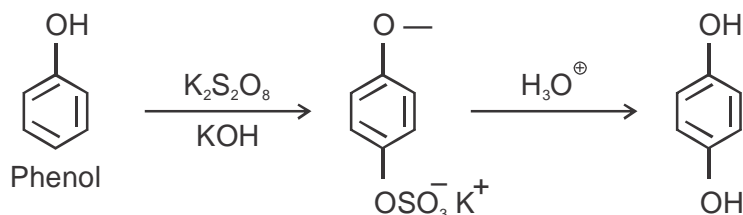


**iv) Oxidation of Aromatic side chains :**

**v) Oxidation of aldehydes and ketones :**

Here carboxylic acid will be formed

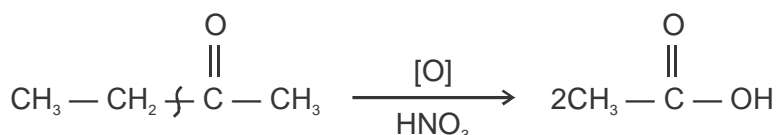
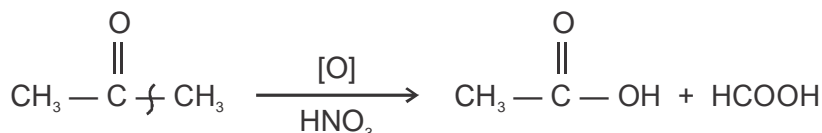
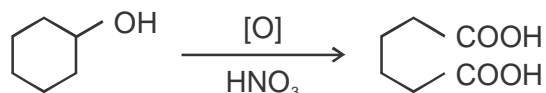

**H) Potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ) :**

- Potassium persulfate is used for the introduction of hydroxyl group in phenols.
- Hydroxylation occurs in Para position to the hydroxyl group. If Para position is already occupied then hydroxylation takes place at ortho position.



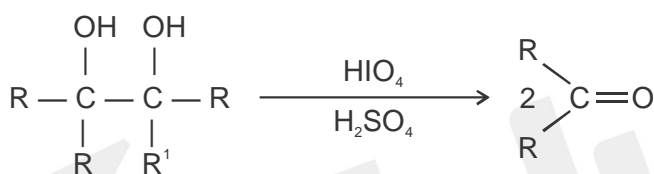
I) **Nitric acid (HNO<sub>3</sub>)** : It is used for the selective oxidation of alcohols.

It is used for the commercial preparation of adipic acid (used in manufacture of nylon).

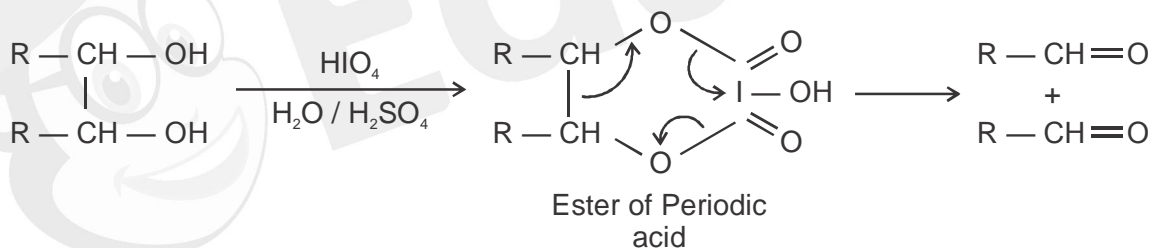


J) **Periodic Acid (HIO<sub>4</sub>)** :

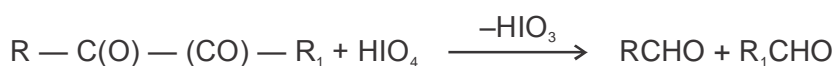
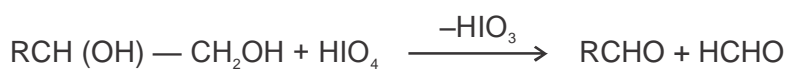
Periodic acid is used for the oxidative cleavage of bonds with adjacent oxidization groups, E.g. 1,2-diols,  $\alpha$ -hydroxyl Carbonyl compounds, 1,2-diketons and  $\alpha$ -amino acids.



**Mechanism :**



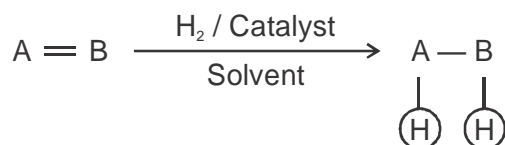
Some representative examples are given below :



## 6. REDUCING AGENTS

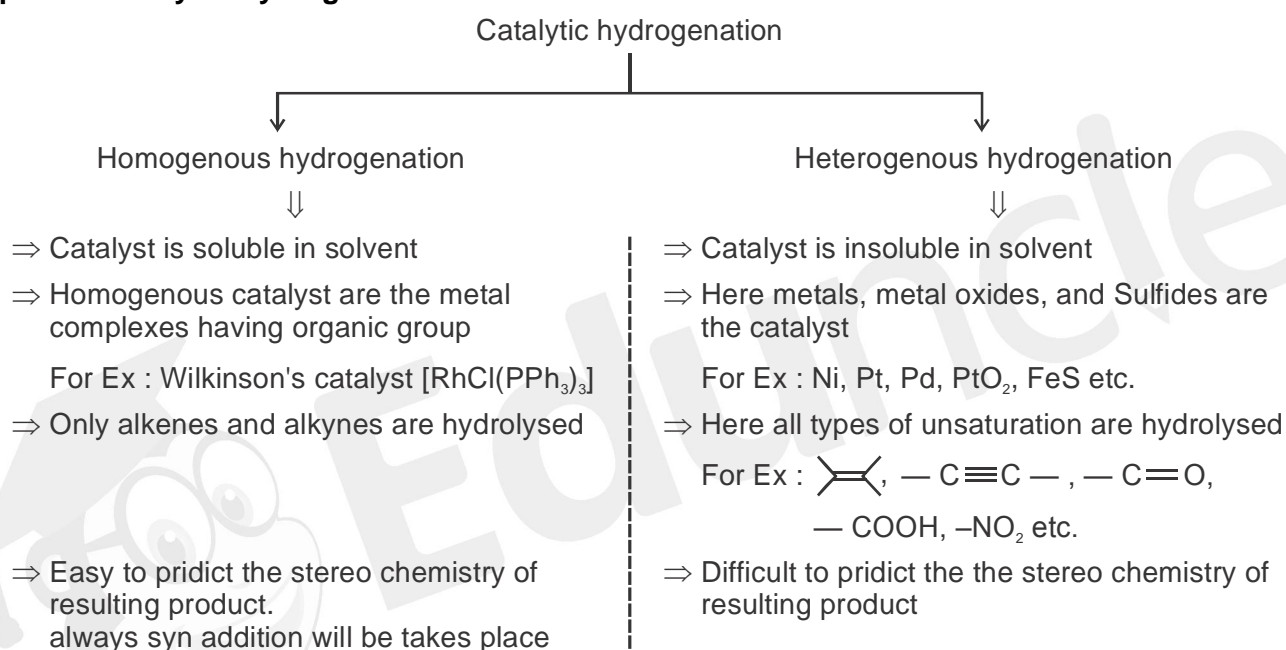
### 1. Catalytic Hydrogenation :

Addition of  $H_2$  to unsaturation in presence of catalyst is called Catalytic Hydrogenation.



Here, not only alkene but also almost all kind of unsaturation are reduced i.e., aldehyde, ketone, acid, ester, Nitro, Cyanide etc.

### Types of Catalytic Hydrogenation



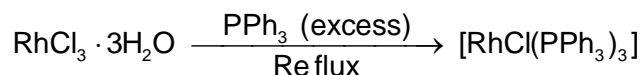
### Homogenous Hydrogenation :

#### Wilkinson Catalyst :

(Chlorotris Triphenylphosphine rhodium (I)  $[RhCl(PPh_3)_3]$ )

Red colour complex with high Melting Point.

#### Preparation-



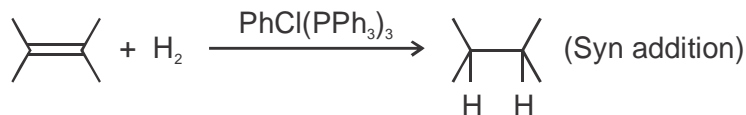
- Rh in + 1 oxidation state.
- $d^8$  electronic configuration
- Square-planar complex
- $dsp^2$  hybridization.
- 16 electronic species
- Not follow EAN

#### Applications

1. Syn hydrogenation of alkenes and alkynes

- Decarboxylation of acid halide and aldehyde
- Desulphonation

### 1. Hydrogenation of Olefins by Wilkinson's Catalyst

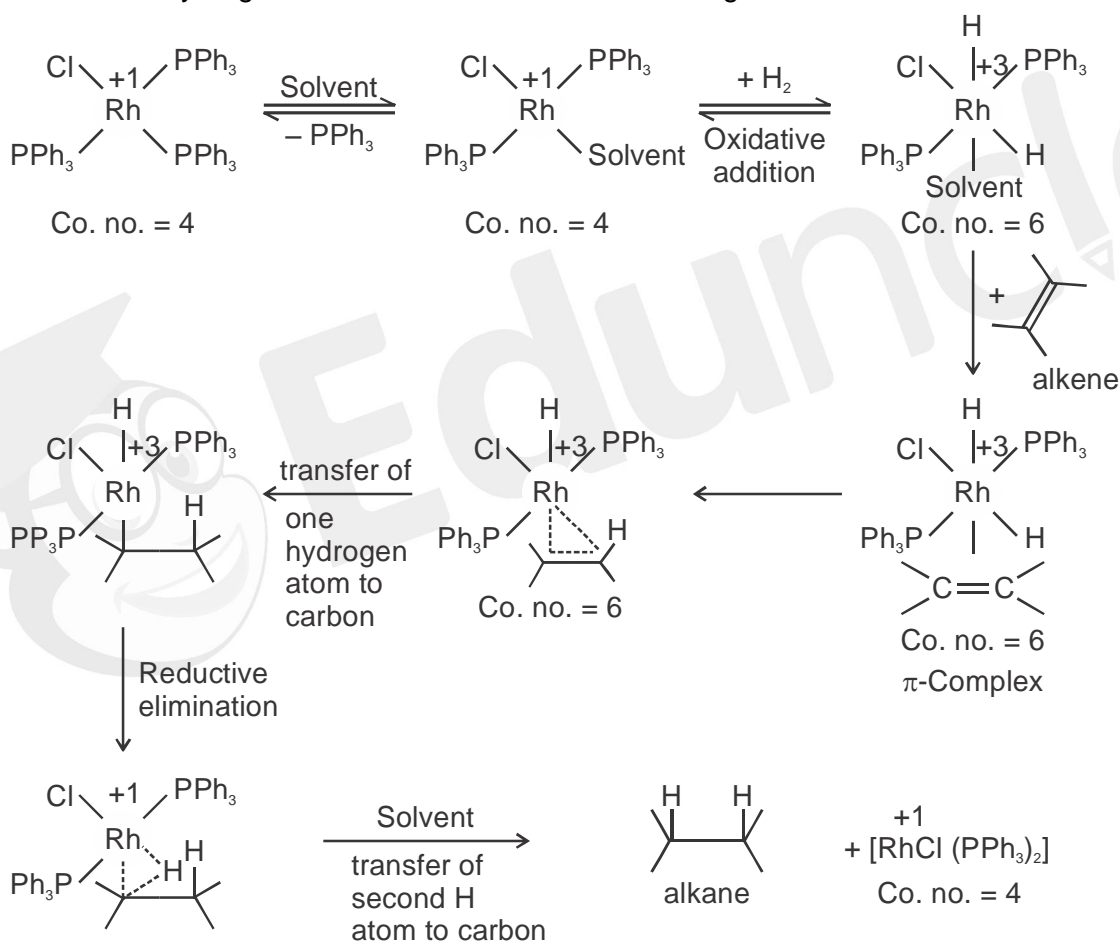


#### Mechanism :

Rhodium complex first exchange one ligand with a solvent molecule to form  $\text{RhCl}(\text{PPh}_3)_2$  (solvent) complex. Then react with one molecule of hydrogen to form the dihydride complex.

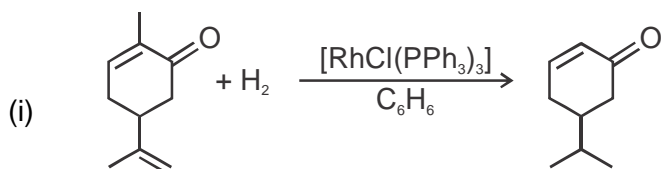
This complex adds on a alkene molecule by displacing one of the triphenylphosphene ligand to give  $\pi$  complex.

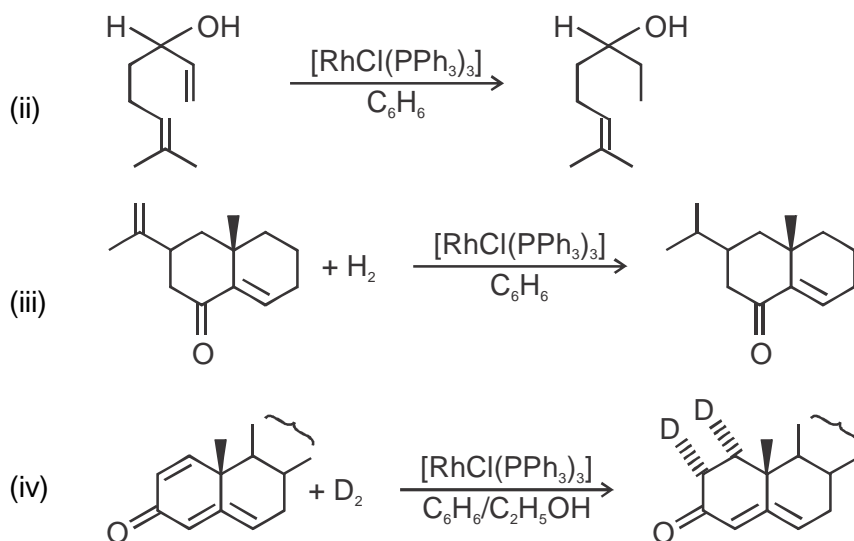
Transfer of hydrogens to carbon-carbon double bond gives alkane.



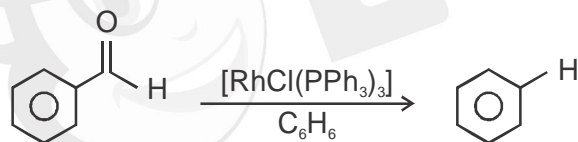
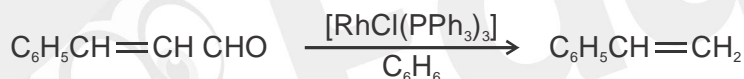
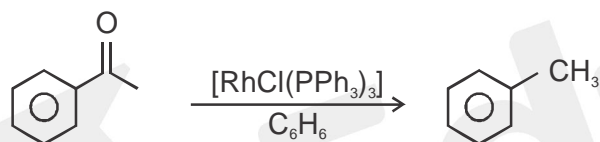
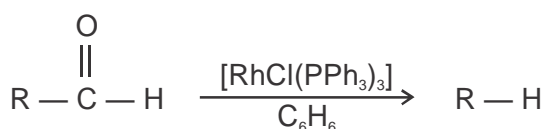
Since it is the example of catalytic hydrogenation. So, less sterically hindered  $\text{C} = \text{C}$  will be hydrolysed.

#### Examples :

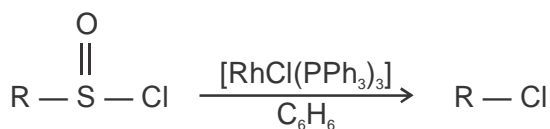




## 2. Decarboxylation - loss of CO



## 3. Desulphonylation - loss of SO



## Heterogeneous Catalytic Hydrogenation :

A number of catalyst have been used for catalytic hydrogenation they are used mainly as finely divided metals, metallic oxides or sulfides.

1. Metals – Ni, Pt, Pd
2. Metaloxide – PtO<sub>2</sub>
3. Metal sulphide – FeS
4. Pd- Charcoal /H<sub>2</sub> (it is generally causes antiaddition of H<sub>2</sub>)
5. Adam's catalyst – PtO<sub>2</sub> + ACOH
6. Raney – Nickel

7. Lindlar's catalyst
8. Rosenmund catalyst

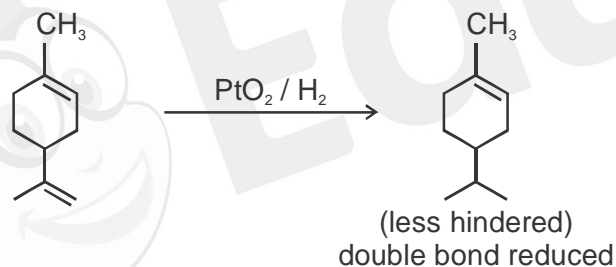
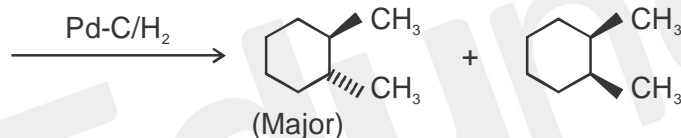
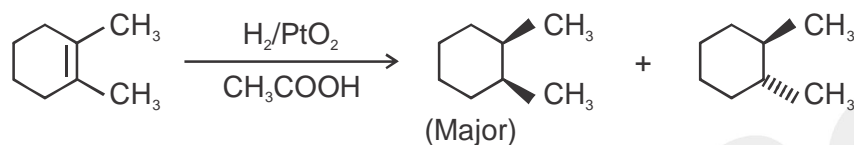
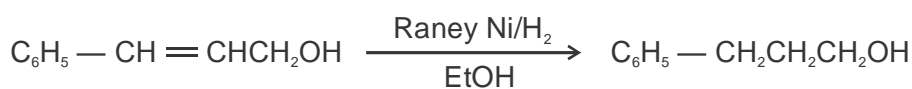
The general reactivity of C = C bond towards catalytic hydrogenation is -



### 1. Reduction of alkene :

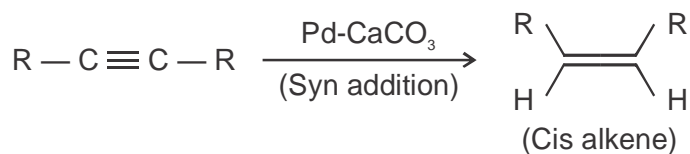
Reduction of carbon-carbon double bond is the easiest and takes place mostly under mild conditions.

The most frequently used catalyst for the reduction of alkenes are platinum and palladium catalyst. Raney-Ni also used in certain cases the choice of the reducing agent depends on the nature of functional group.



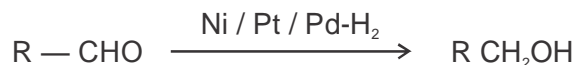
### 2. Reduction of Alkynes :

Alkynes can be reduced partially to give z- alkenes by palladium calcium carbonate (lindlar catalyst).



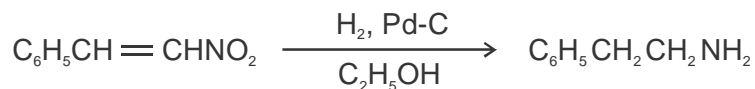
### 3. Reduction of aldehyde and ketones :

Carbonyl group can be easily reduced by platinum, Raney-nickel or Palladium-hydrogen.



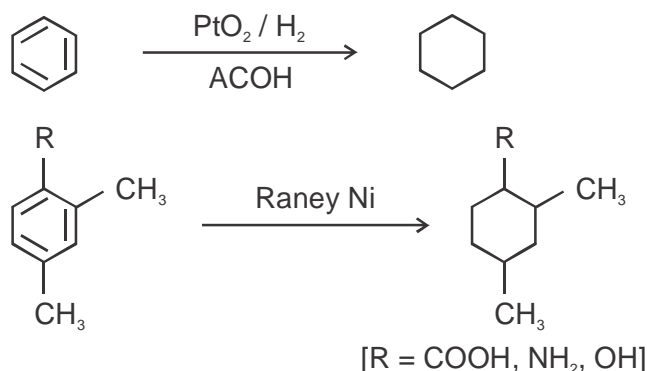
### 4. Reduction of Nitriles, oximes, and nitro compound :

Nitriles, oximes or nitro compound are reduced to Primary amines.

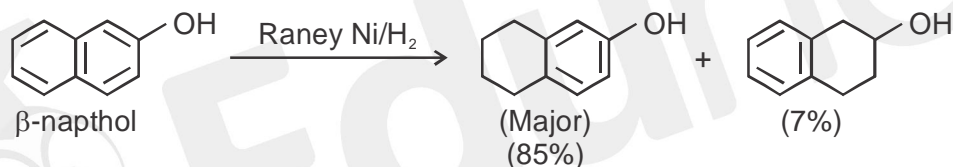


### 5. Reduction of Aromatic Compounds :

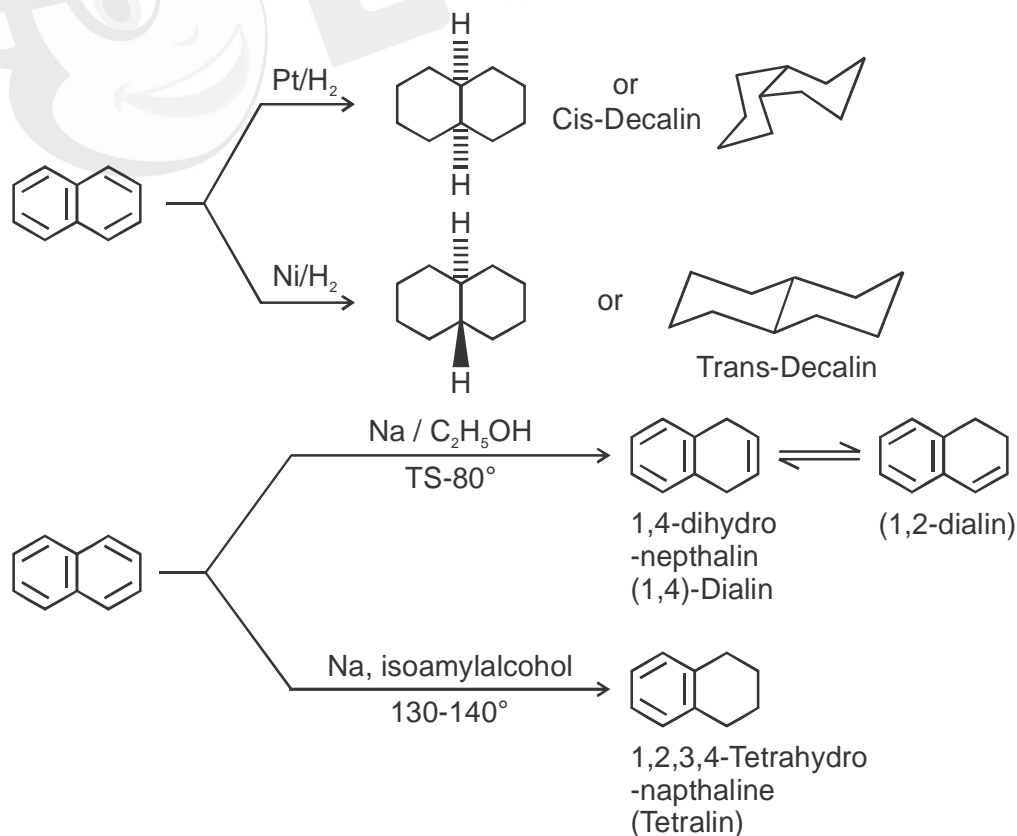
Aromatic compounds are stable so these are difficult to reduce by catalytic hydrogenation. Common catalyst for the reduction of aromatic compounds are platinum, rhodium, and Raney nickel.



Reduction of  $\beta$ -naphthol with Raney nickel /H<sub>2</sub>—produces the tetrahydro- $\beta$ -naphthol as the major product.

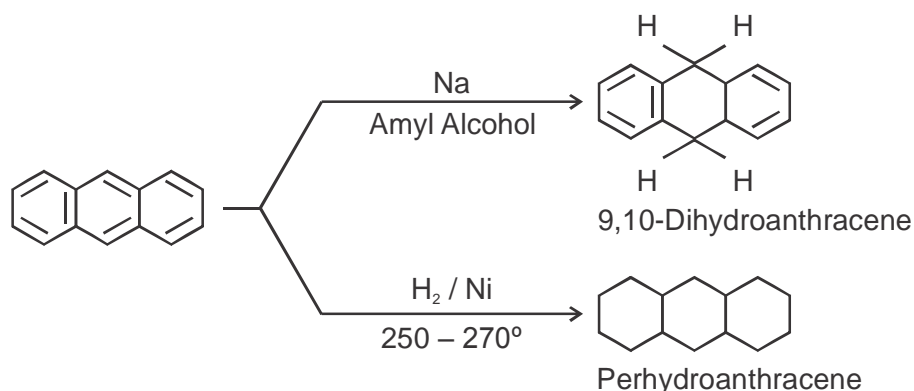


Napthalene can be reduced partially or completely depending on the reducing agents.





Anthracene on reduction with sodium and amyl alcohol gives 9,10-dihydroanthracene. However, on catalytic hydrogenation anthracene gives perhydroanthracene.



### Reduction by Metalhydrides –

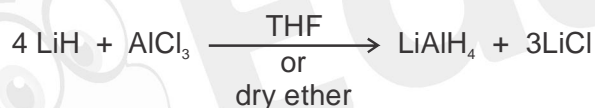
The reduction of metal hydrides proceeds by transfer of hydride ion to the substrate.

A number of complex hydrides have been used for reduction. The most common are

- (i)  $\text{LiAlH}_4$  - Lithium aluminium hydride.
- (ii)  $\text{NaBH}_4$  - Sodium borohydride
- (iii)  $\text{NaBH}_3\text{CN}$  - Sodium Cyanoborohydride
- (iv)  $\text{B}_2\text{H}_6$  - Diborane

#### 1. Lithium aluminium hydride ( $\text{LiAlH}_4$ ) :

##### Preparation -

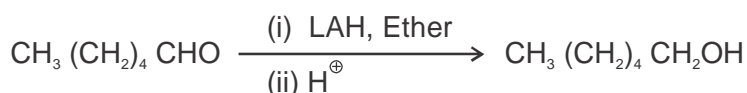


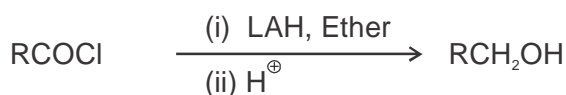
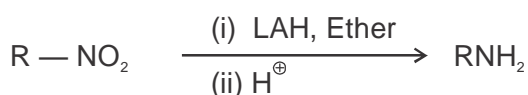
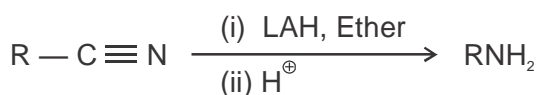
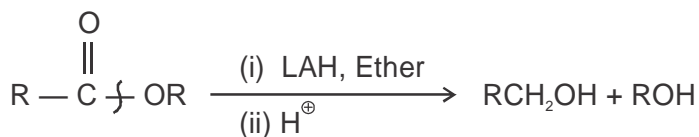
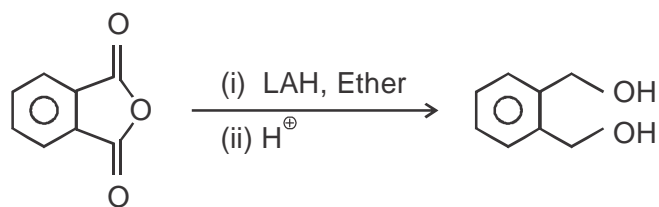
It is the one of the most important and useful reagent for the reduction of ketones, carboxylic acids, esters, acid halides, anhydrides, epoxides, nitriles and nitro compounds.

##### Applications -

Functional Group	New Functional Group
1. Aldehyde	Alcohol
2. Ketone	Alcohol
3. Carboxylic acid	Alcohol
4. Anhydride	Alcohol
5. Esters	Alcohol
6. Acid Halide	Alcohol
7. Nitro ( $\text{NO}_2$ )	Amines
8. Nitriles(CN)	Amine
9. Epoxide	Alcohol

Some typical examples are

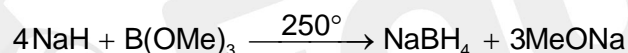




## 2. Sodium borohydride (NaBH<sub>4</sub>) :

Sodium borohydride is a very selective reducing agent and reduces aldehyde and ketones to alcohols. Group like halogen, cyano, amino, alkoxy carbonyl are unaffected.

### Preparation :

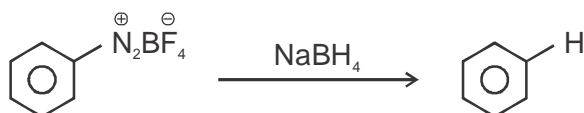
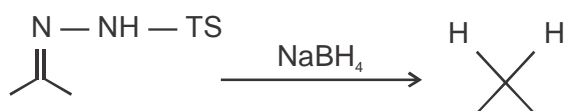


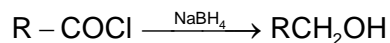
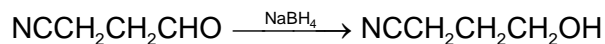
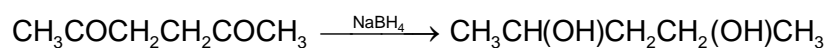
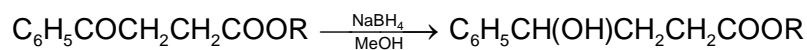
NaBH<sub>4</sub> can be used in the aqueous media, the solvent used are ether, alcohol, chloroform etc.

### Applications –

Functional Group	New Functional Group
1. Aldehyde	Alcohol
2. Ketone	Alcohol
3. Acid Halide	Alcohol
4. Ozonide	Alcohol
5. epoxide	Alcohol
6. Imine	Amine
7. Alkyl azide	Amines
8. Tosylhydrazone	Hydrocarbon
9. Benzene diazonium borofluorate	Hydrocarbon
10. R-X(1°,2°)	Hydrocarbon

### Some typical examples are -





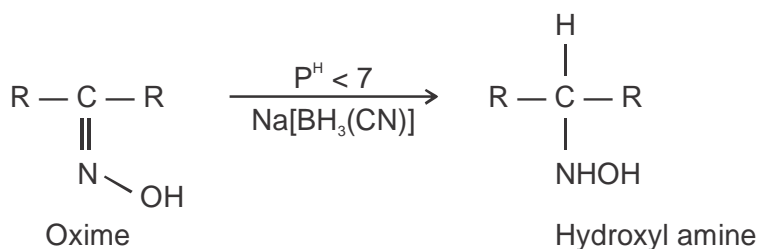
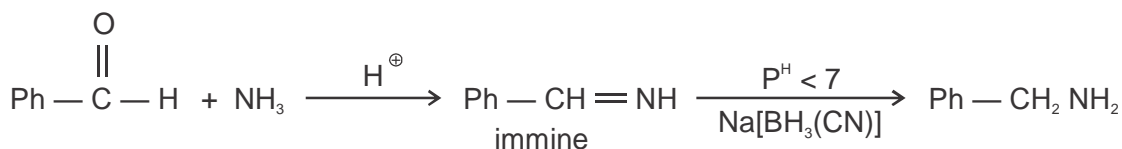
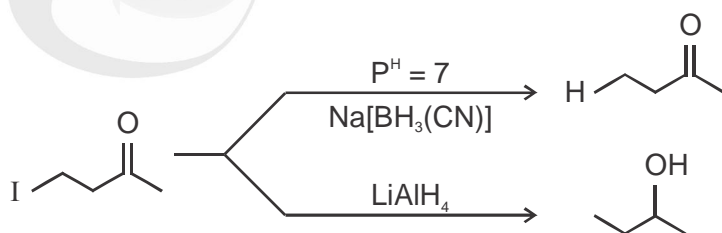
### 3. Sodium cyanoborohydride :

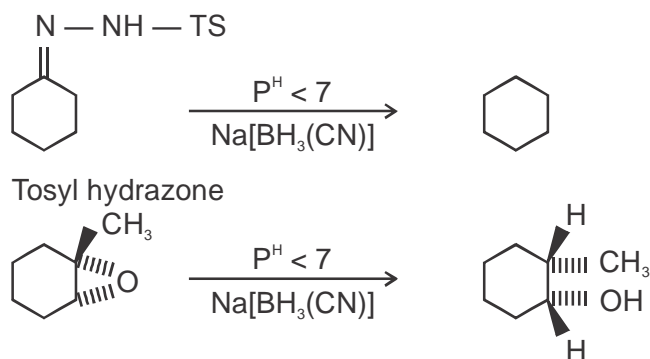
- It is less reactive and more selective than the sodium borohydride.
- It's reducing property depends upon the  $P^H$  of the reaction media.

#### Applications :

	Functional group	New Functional group
(A) At $P^H = 7$ :	C — (X)	C — (H)
	C — (OTS)	C — (H)
(B) At $P^H < 7$ :	Aldehyde	Alcohol
	Ketone	Alcohol
	Epoxide	Alcohol
	Tosyl hydrazone	Hydrocarbon
	Immines	Amines
	Imminium ion	Amines

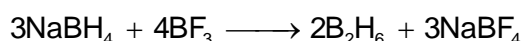
Some typical examples are –



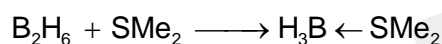
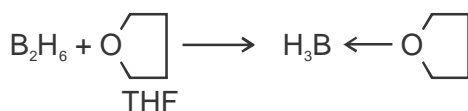
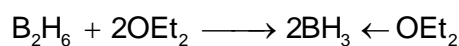


#### 4. Diborane : $\text{B}_2\text{H}_6$

It is weak and selective reducing agent derived from  $\text{NaBH}_4$

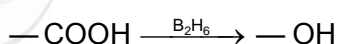


Diboranes are stable in the monomeric form in presence of lewis acid.

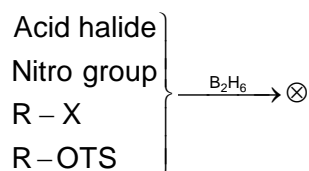


#### Applications :

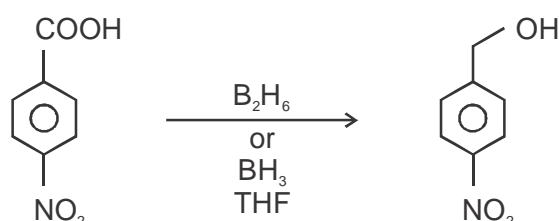
- It reduces carbonyl group to alcohol but is less reactive towards other functional group.
- A number of other reagents derived from diboranes are called organoborane and useful as reducing agents.
- $\text{B}_2\text{H}_6$  is the powerful reagent in the reduction of carboxylic acid as compare to  $\text{LiAlH}_4$

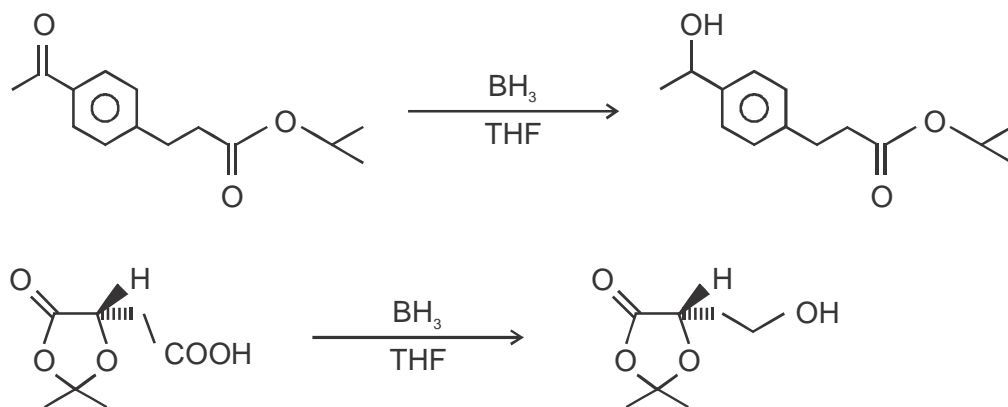


- Diborane reacts with olefins to give monoalkyl borane, dialkylborane, and trialkylborane, which are used as reducing agent.
- $\text{BH}_3$  does not reduce - Acid halide, nitro group, alkyl halide, etc.



Some typical examples are –



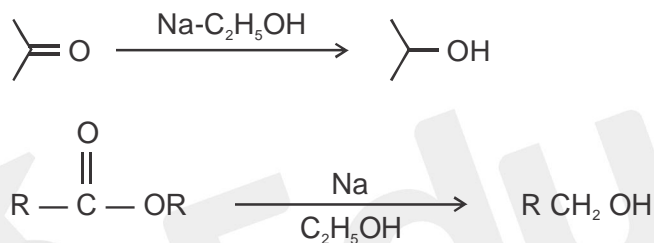


### Reduction by dissolving Metals :

These reductions take place by the transfer of electrons from the metal and a proton donor which may be water, alcohol or an acid.

#### 1. Sodium Alcohol :

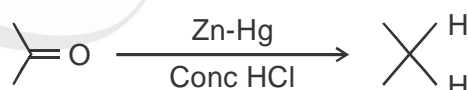
It is used for the reduction of ketones and esters



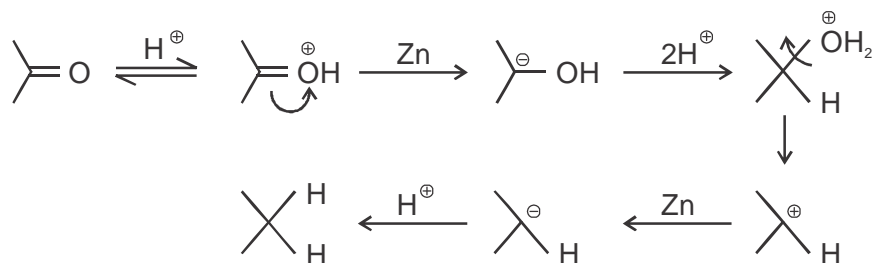
This reaction also known as Bouveault-Blanc-reduction.

#### 2. Zinc-hydrochloric acid :

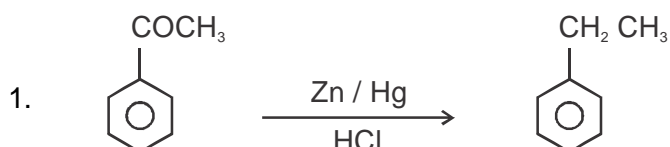
It is used for the reduction of carbonyl compounds give the corresponding hydrocarbons this reaction is known as Clemmensen reduction.

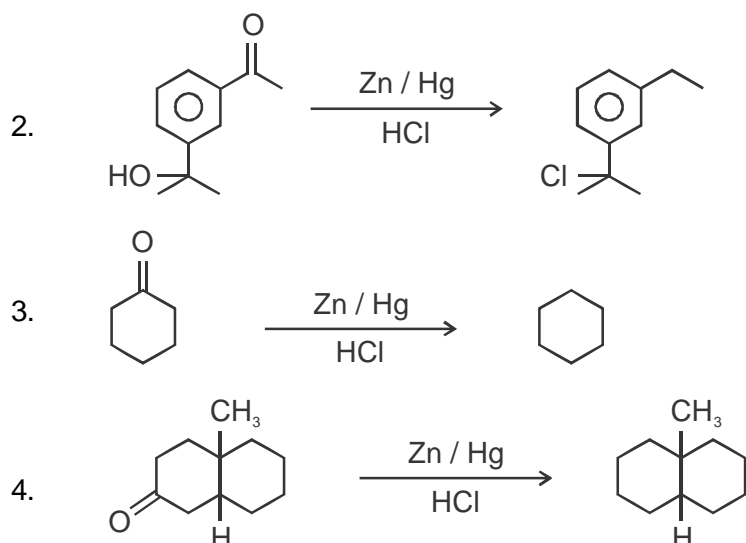


#### Mechanism :



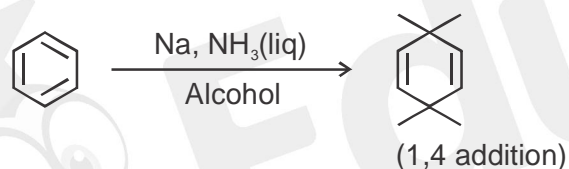
#### Applications :



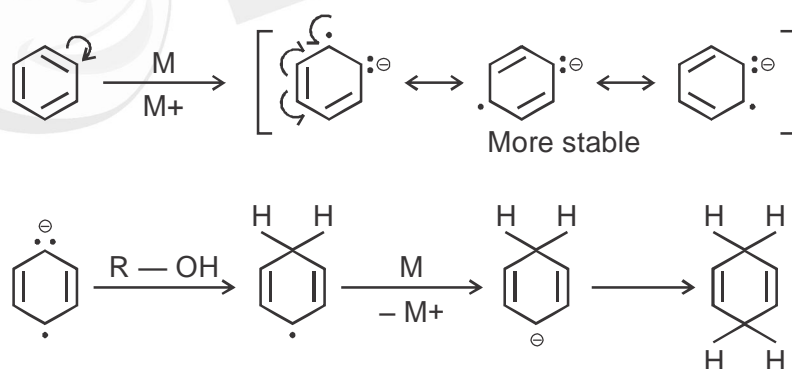


### 3. Sodium-Liquid ammonia :

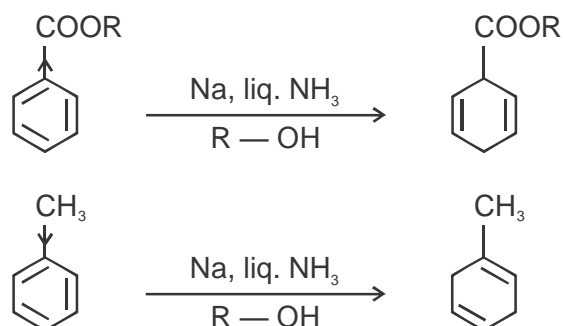
- This reduction is also known as Birch reduction.
- Sodium and liquid ammonia with alcohol reduce aromatic ring to give mainly unconjugated dihydro derivatives.
- Aromatic rings and conjugated dienes are reduced by this method while isolated double bonds are normally not affected.

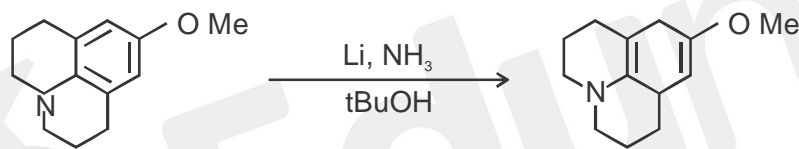
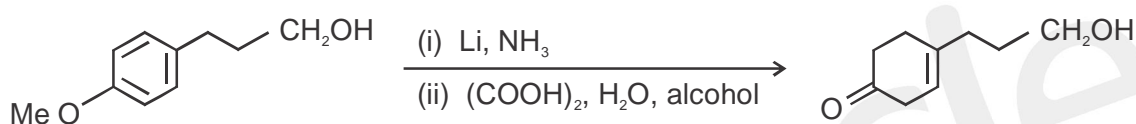
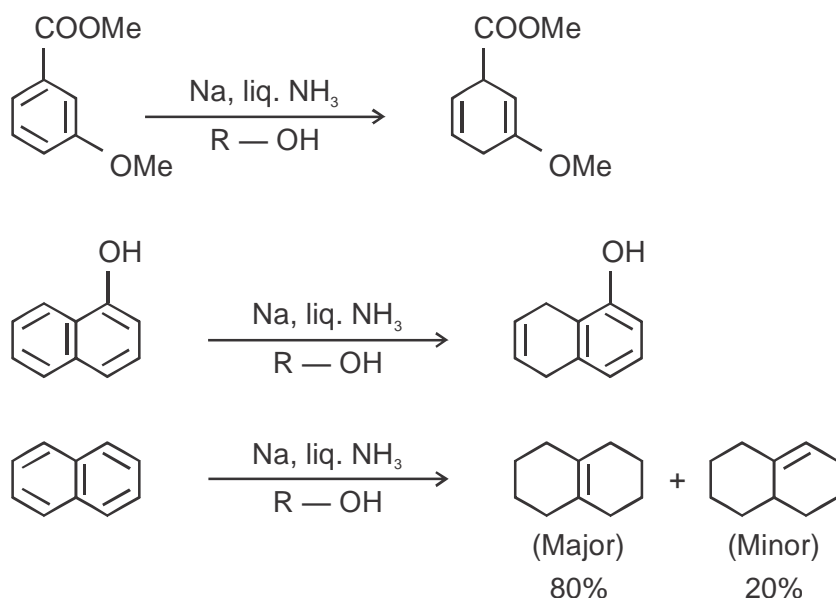


#### Mechanism :



#### Applications :

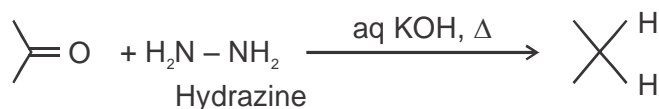




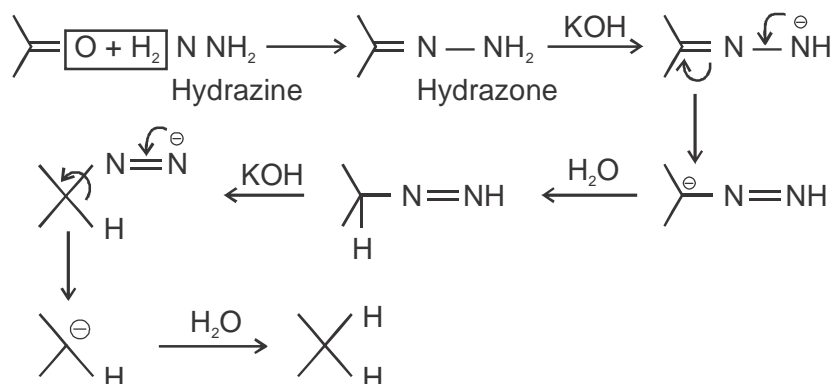
### Reduction by miscellaneous reducing agents :

#### 1. Reduction by hydrazine :

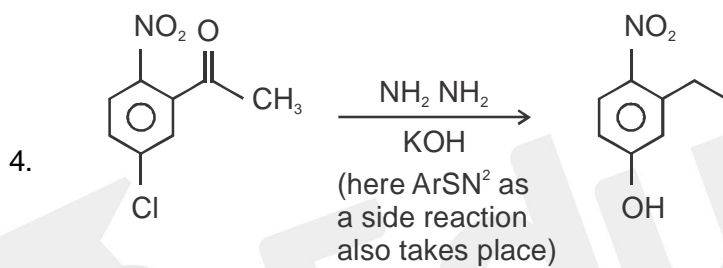
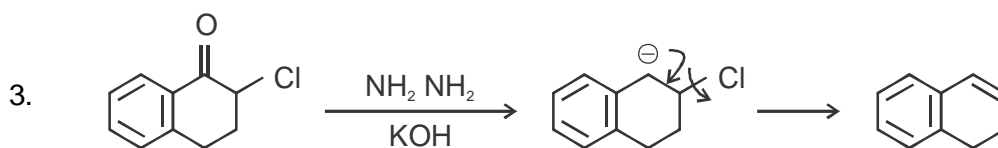
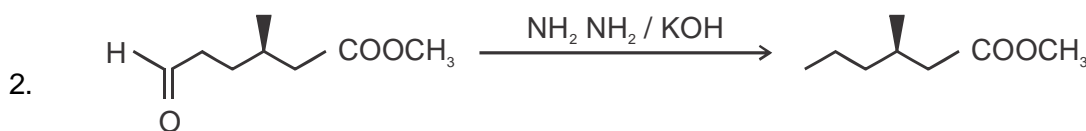
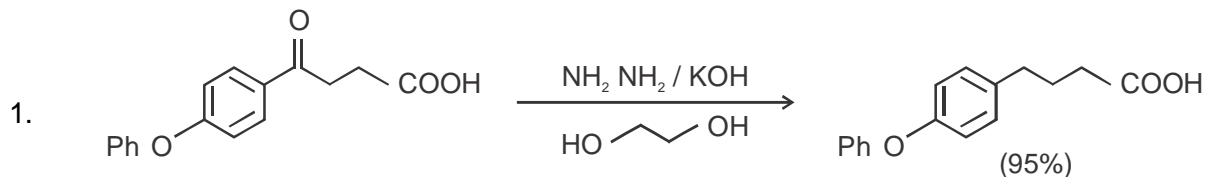
- It is known as Wolff-Kishner reduction
- The aldehydes and ketones can be reduced to corresponding hydrocarbons by Wolff-Kishner reduction.



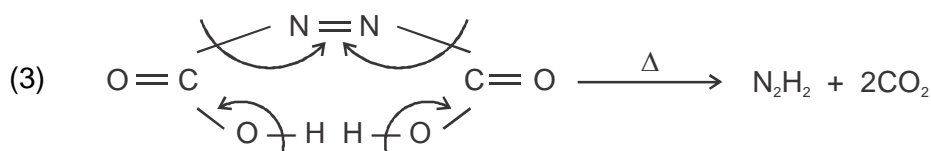
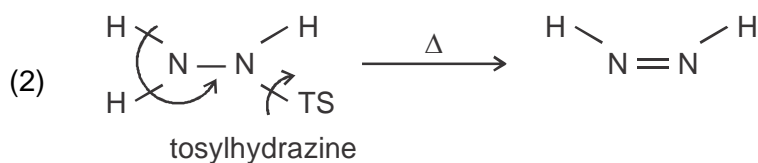
#### Mechanism :



In the Hunang-Minlon modification of the above reaction, diethylene glycol is used as a solvent.

**Applications :**

**2. Reduction by Di-imide :**

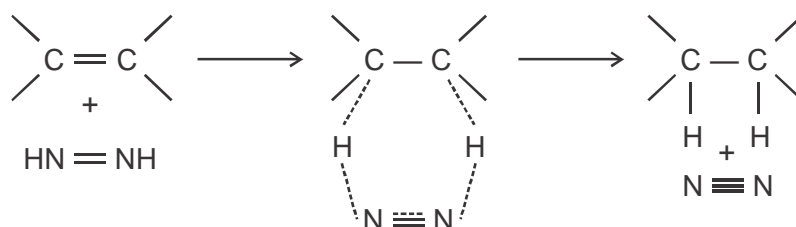
- Di-imide is a highly selective reagent
- This reagent is prepared in situ usually by the oxidation of hydrazine by an oxidizing agent like hydrogen peroxide or by thermal decomposition of tosyl hydrazine or diazodicarboxylic acid.


**Applications :**

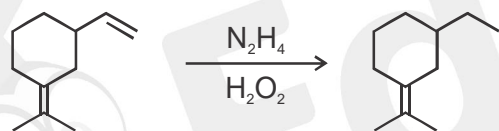
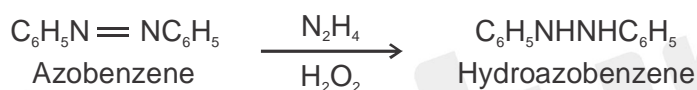
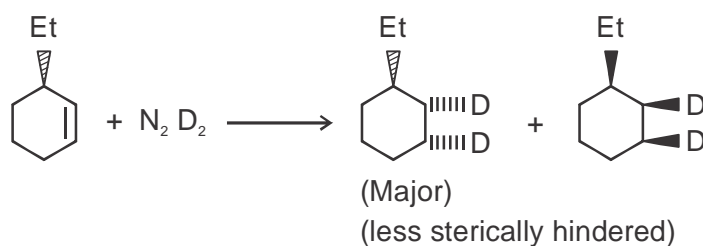
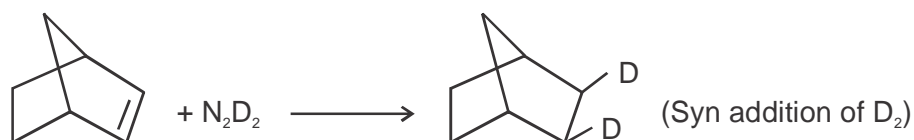
It is useful for the reduction of symmetrical multiple bonds like carbon carbon multiple bond, N=N and O=O. The unsymmetrical multiple bonds like S=O, C=O, C=S are not reduced.



For ex -

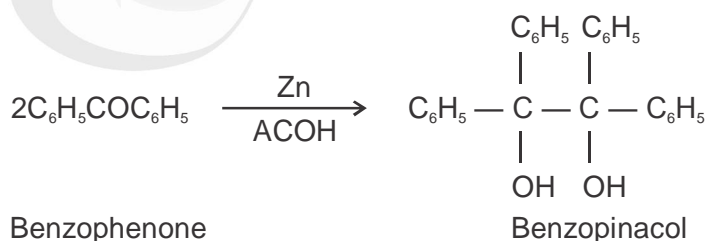


Some typical examples are -



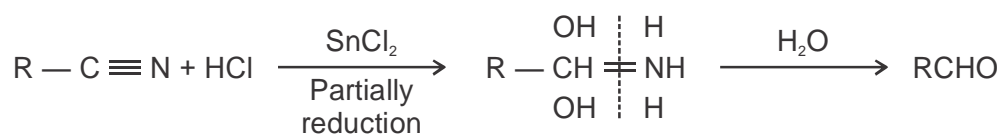
### 3. Reduction by Zinc - Acetic Acid :

It is used for the reductive coupling of ketones -

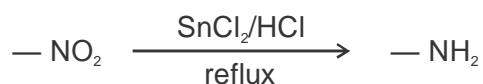


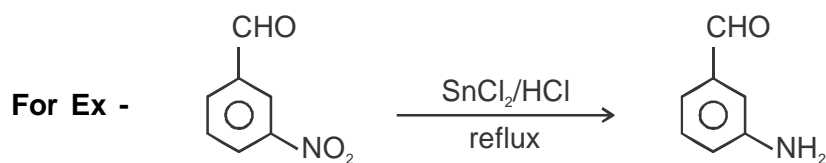
### 4. Reduction by Stannous Chloride :

Stannous chloride and HCl converts nitriles into aldehyde this reaction is also known as 'stephen reduction'.



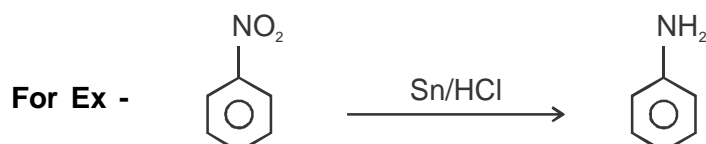
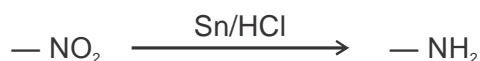
The reduction of nitro group to amino group can also be effected by refluxing with SnCl<sub>2</sub>/HCl





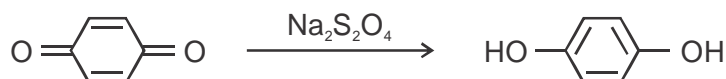
### 5. Reduction by Tin-hydro chloric acid :

This reagent is used for the reduction of nitro group to amino group.



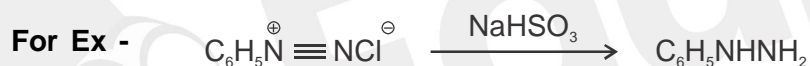
### 6. Reduction by dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ ) :

It is usually used for the reduction of p-benzoquinone to hydroquinone



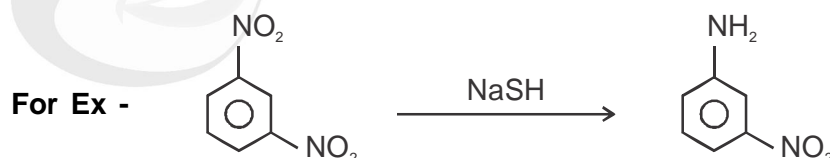
### 7. Reduction by Sodium Metabisulphite :

It is used for the reduction of diazonium salt to the corresponding hydrazines.



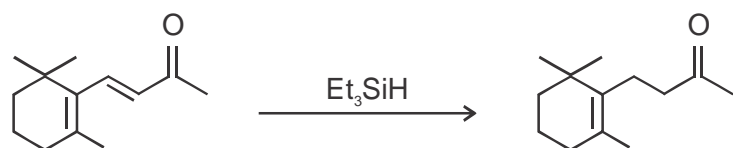
### 8. Reduction by sodium hydrogen sulphide :

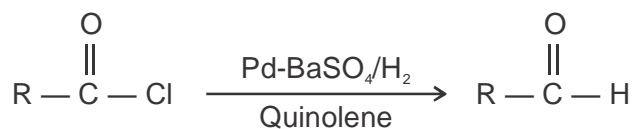
It is used for the selective reduction of one nitro group into amino group.



### 9. Reduction by Silanes :

Silanes can be used for the reduction of carbonyls and alkenes.



**10. Rosenmund reduction :**

**11. Reduction by Red P + HI :**

It is used for the reduction of Acids and Acid derivatives, alkane will be formed.

