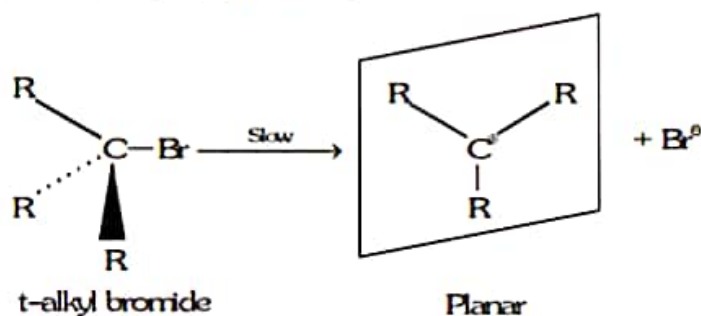


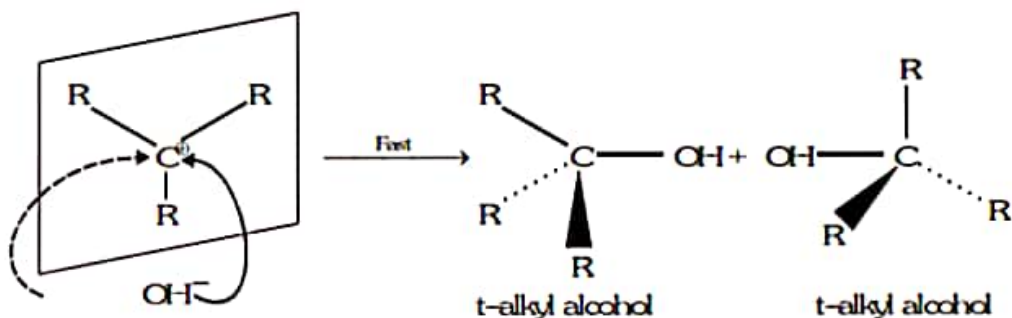
□ Mechanism of S_N1 and S_N2 :

◆ **S_N1 Mechanism** : S_N1 stands for uni molecular nucleophilic substitution. The mechanism involves two steps. Consider the hydrolysis of tert. butyl bromide with aqueous NaOH.

Step 1: The alkyl halide ionises to give a planar carbonium ion. The carbonium ion is planar because the central positively charged carbon is sp^2 hybridized.



Step-2 : The nucleophile can attack the planar carbonium ion from either side to give the product.



(i) Ionisation is the rate determining step because it is the slow step. In other words, the rate at which alcohol is formed should depend upon the concentration of tertiary alkyl halide alone.

$$\therefore \text{Rate} = k[R_3C-Br]$$

It is obvious that the reaction follows first order kinetics, therefore reaction is called S_N1 .

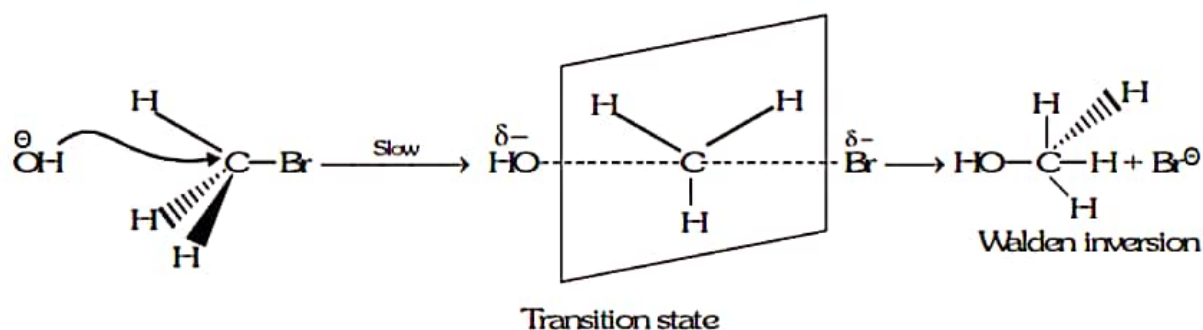
(ii) The reactivity order for S_N1 reaction \propto stability of carbocations formed by halides.

\therefore reactivity order of halides (S_N1) varies as follows :

Benzyl halide > Allylhalide > 3 halide > 2 halide > 1 halide > methyl halide.

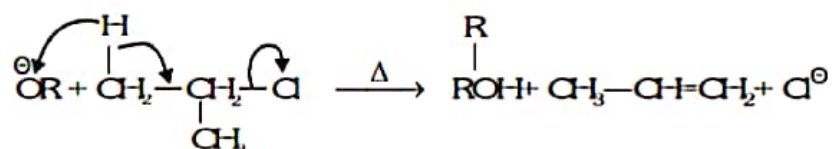
(iii) Remember that in case alkyl halide is optically active, S_N1 reactions lead to racemisation.

- ◆ **S_N² mechanism** : S_N² stands for bimolecular nucleophilic substitution. In this type of nucleophilic substitution reaction, there occurs bond making and bond breaking simultaneously.



- (i) Reactivities of alkyl halides in S_N² substitution is governed by steric factors. The bulkier the group, that less reactive it will be.
- (ii) Reactivity order of alkyl halide varies as follows : **CH₃X > 1 halide > 2 halide > 3 halide**
- (iii) The order of reactivity among 1 alkyl halides is : **CH₃X > C₂H₅X > C₃H₇X** etc.
Remember that in case alkyl halide is optically active, S_N² reactions lead to Walden inversion.
- (iv) Thus in short 3 alkyl halides react by S_N¹, 1 by S_N² and 2 by either or both of them S_N¹ and S_N² depend upon the nature of the alkyl halide and the reagent.
- (v) For a given alkyl group the order of reactivity is - (for S_N¹ and S_N² both) : **RI > RBr > RCl > RF**
- (vi) In addition to substitution reaction alkyl halide also undergo elimination reactions to form alkene with the removal of a molecule of hydrogen halide (dehydrohalogenation). In dehydrohalogenation, hydrogen and halogen atoms are eliminated from two adjacent carbon atoms, the reaction also known as β-elimination may proceed by E₁ & E₂ mechanism (analogous to S_N¹ and S_N² mechanism).
The order of elimination reaction is : **3 halides > 2 halides > 1 halides**
- (vii) In general 3 halides tend to react by elimination; 1 halides by substitution and 2 halides by either or both of the reactions.

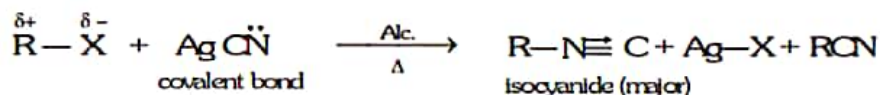
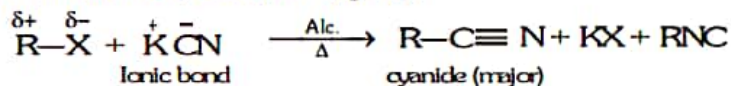
3. **Elimination Reactions (ER)** : Alkyl halides also undergo ER in the presence of base as Nu[⊖] (Loss of H-X and formation of = bond)



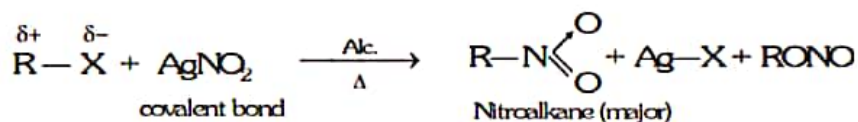
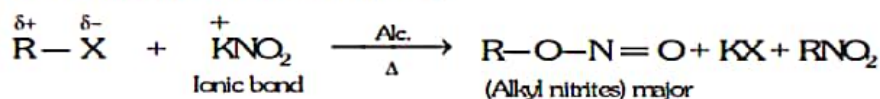
1. **Nucleophilic substitution reaction (S_N)** :

	Replacement of	Product
(a)	$\begin{array}{l} \text{HOH(Bal)} \\ \text{X by - OH} \end{array}$	R-OH (alcohol) + HX
(b)	$\begin{array}{l} \text{KOH aq. } \Delta \\ \text{X by - OH} \end{array}$	R-OH (alcohol) + KX
(c)	$\begin{array}{l} \text{moist Ag}_2\text{O} \\ \text{X by - OH} \end{array}$	R-OH (alcohol) + AgX
(d)	$\begin{array}{l} \text{KSH alc. } \Delta \\ \text{X by - SH} \\ \text{(Mercapto Gp.)} \end{array}$	R-SH + KX Alkane thiol (Mercaptane)
(e)	$\begin{array}{l} \text{NaSR} \\ \text{X by SR} \end{array}$	RSR' + NaX Thioether
(f)	$\begin{array}{l} \text{R' COOAg } \Delta \\ \text{X by (R'COO)} \end{array}$	R' COOR + AgX (Alkyl alkanoate) ester

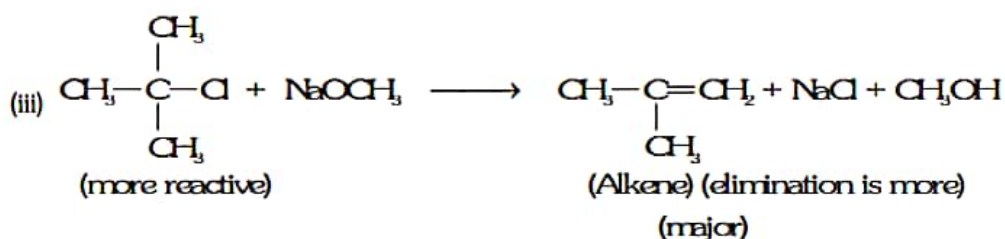
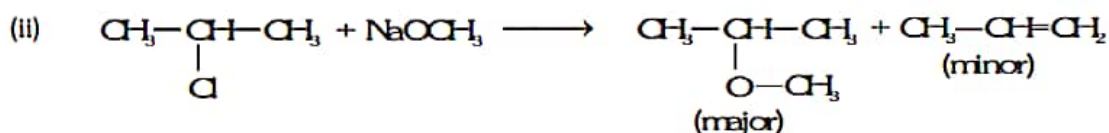
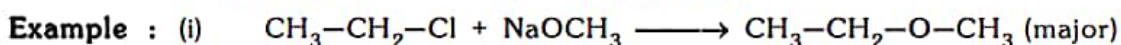
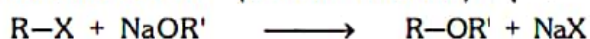
(g) Reaction with KCN and AgCN :



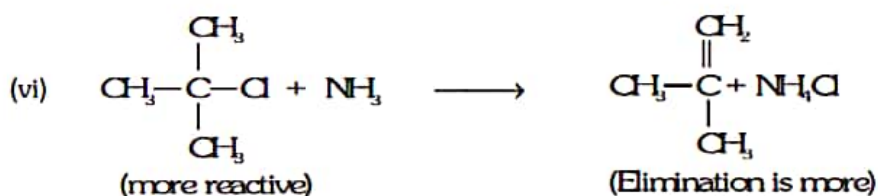
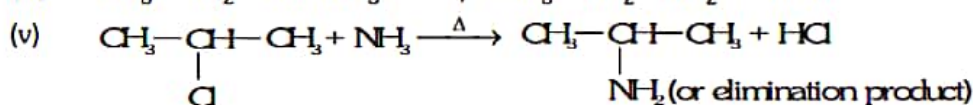
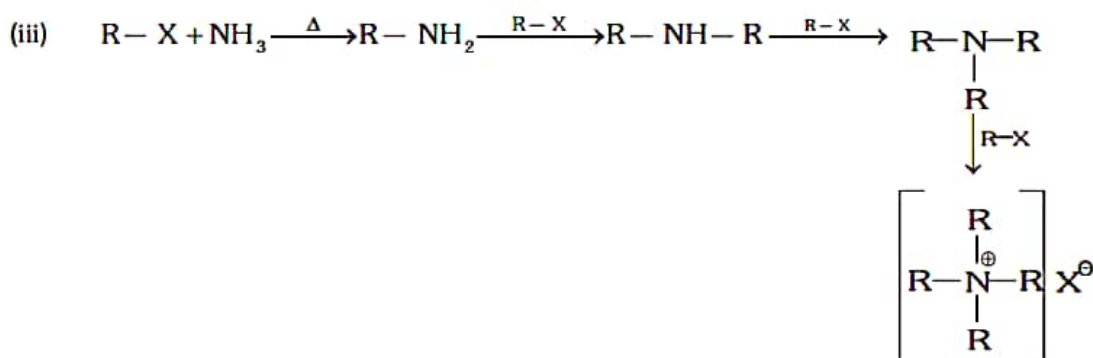
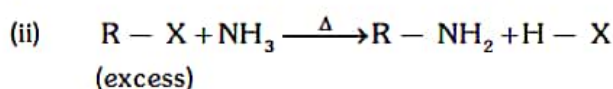
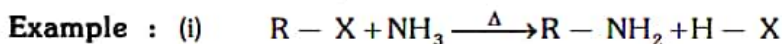
(h) Reaction with KNO₂ and AgNO₂



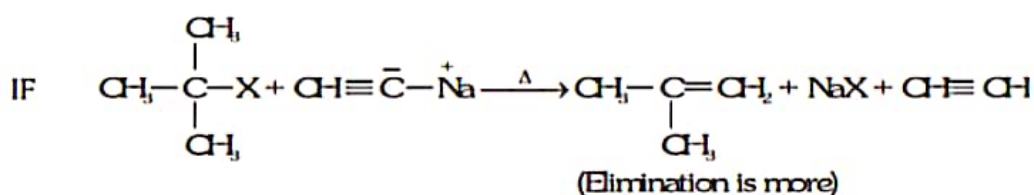
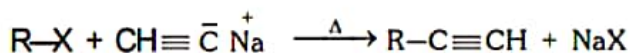
(i) Reaction with NaOR' (Sodium alkoxide) : (williamson synthesis reaction)



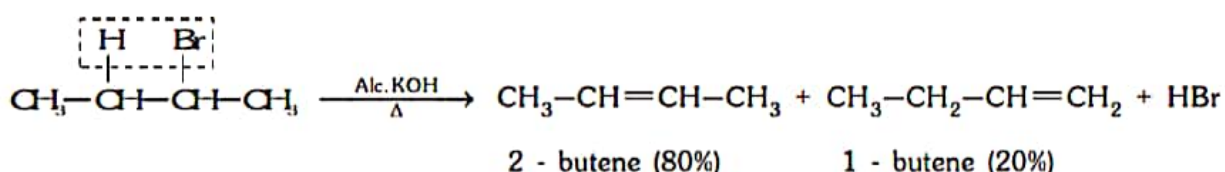
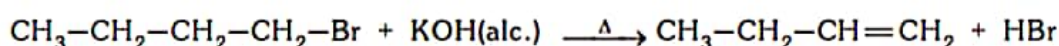
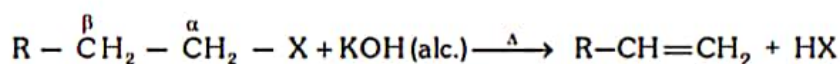
(j) Reaction with NH₃ :



(k) Reaction with $\text{CH}\equiv\bar{\text{C}}\text{Na}^+$:



2. **Elimination Reaction** : (Dehydrohalogenation) Alkyl halides undergo β - elimination on treatment with KOH (alc.)



◆ **Competition between substitution and elimination reactions :**

Reactivity order of alkyl halides : E_1 - Reaction : 1 < 2 < 3

E_2 - Reaction : 1 < 2 < 3

$\text{S}_{\text{N}}1$ - Reaction : 1 < 2 < 3

$\text{S}_{\text{N}}2$ - Reaction : 1 > 2 > 3

Alkyl halides	$\text{S}_{\text{N}}2/\text{E}_2$	$\text{S}_{\text{N}}1/\text{E}_1$
1 Alkyl halides	Mainly give substitution unless sterically hindered alkyl halide or sterically hindered base in which case elimination is favoured	Can not undergo $\text{S}_{\text{N}}1/\text{E}_1$
2 Alkyl halides	Both substitution and elimination, stronger base/ bulkier base or high temp. greater percentage of elimination.	Both substitution and elimination high temp. greater of percentage of elimination
3 Alkyl halides	Mainly elimination	Both substitution and elimination, high temp greater percentage of elimination.

(i) $\text{S}_{\text{N}}2/\text{E}_2$ is favoured by high conc. of good nucleophile or strong base. ($\text{CH}_3\text{O}^\ominus$, HO^\ominus)

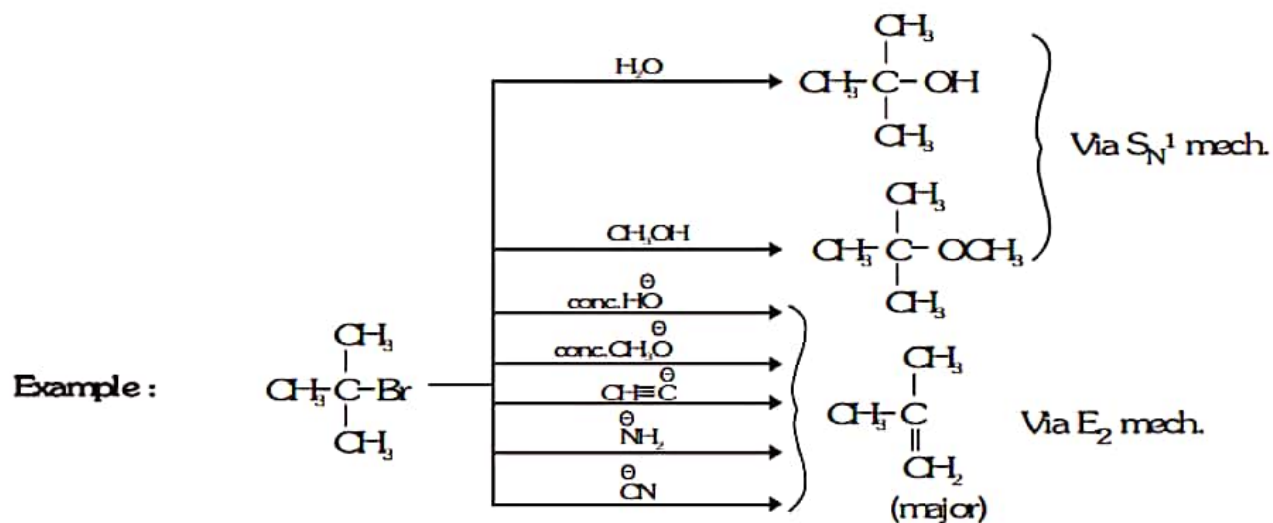
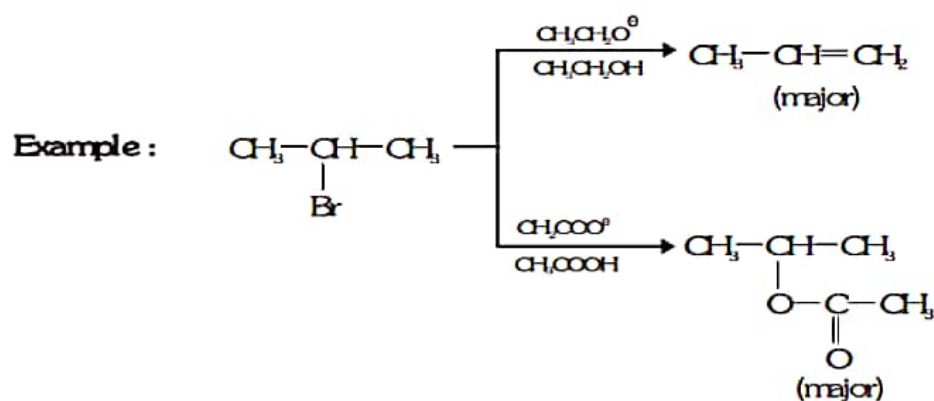
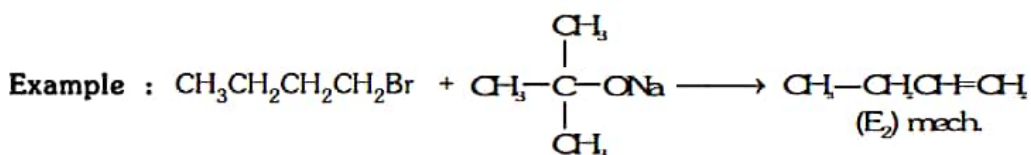
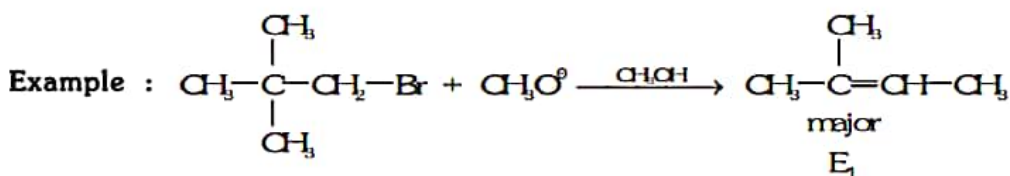
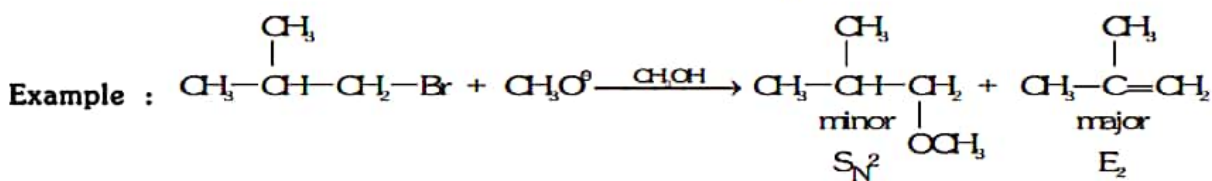
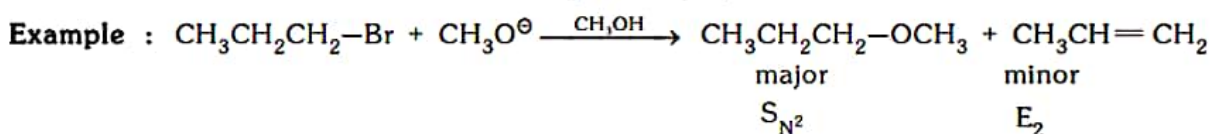
Rate of Reaction \propto (Substrate) (Reagent)

(ii) $\text{S}_{\text{N}}1/\text{E}_1$ is favoured by low conc. of poor nucleophile or weak base (CH_3OH , H_2O)

(iii) If an alkyl halide, undergoes $\text{S}_{\text{N}}2/\text{S}_{\text{N}}1$ - Reaction then $\text{S}_{\text{N}}2$ will be favoured by high conc. of good nucleophile (negatively charged) in presence of polar aprotic solvent . where as $\text{S}_{\text{N}}1$ - reaction is favoured by low conc. of poor nucleophile (neutral) in presence of polar protic solvent.

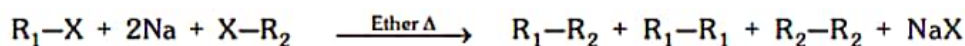
Polar protic solvent : H_2O , CH_3OH , HCOOH .

Polar aprotic solvent : DMSO , CH_3CN , $\text{C}_2\text{H}_5\text{-O-C}_2\text{H}_5$



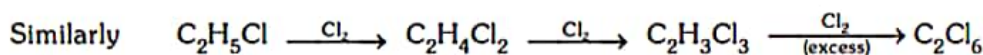
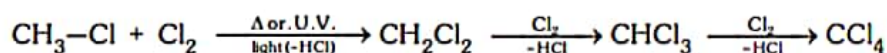
Saytzeff rule : According to this rule "The dehydrohalogenation of an alkyl halide results preferentially in the production of more alkylated alkene i.e. more stable alkene.

3. **Wurtz Reaction** : When a mixture of different alkyl halides, ($R_1 - X$) and ($R_2 - X$) is used a mixture of alkane is formed -

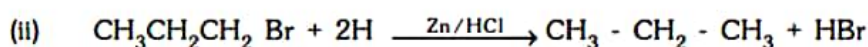


If 'Zn' is used in place of 'Na' the reaction is called **Frankland's Reaction**.

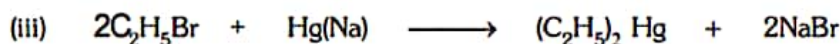
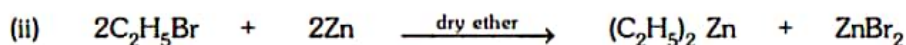
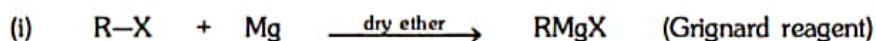
4. **Halogenation of alkyl halides** :



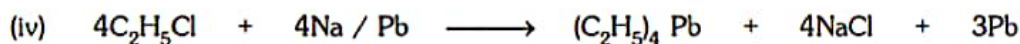
5. **Reduction** : $R - X$ are reduced to corresponding alkane.



6. **Formation of Organometallic compounds** :



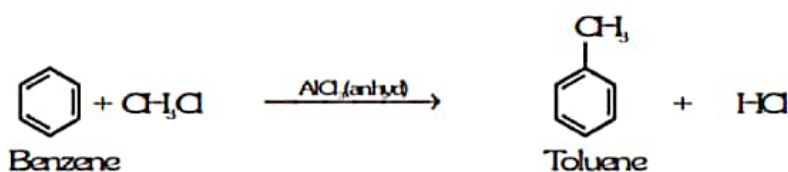
Sodium Amalgam



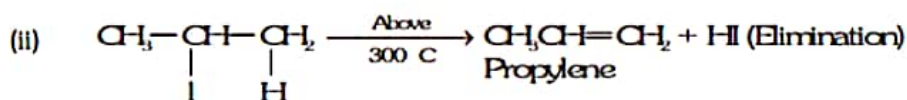
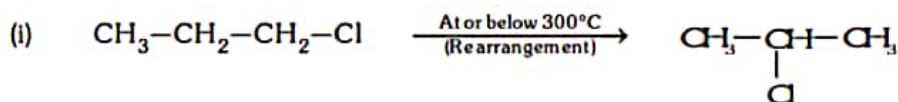
Sodium lead Alloy

Tetra ethyl lead (used as antiknocking agent)

7. **Friedel - Crafts reaction** :



8. **Action of heat** :



◆ **Uses** :

- As alkylation agent (Wurtz reaction)
- As synthetic reagent
- Lower members used as anaesthetic agent, refrigerent or solvent.

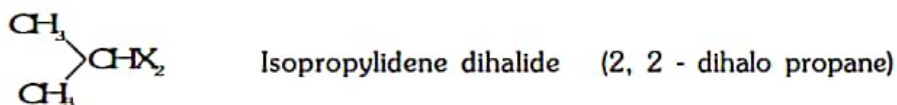
General formula $C_nH_{2n}X_2$. Two H - atom of alkanes, replaced by two halogen atoms to form dihalides.

Dihalides are classified as :

(a) **Gem dihalide** : The term Gem is derived from geminal means - same position.

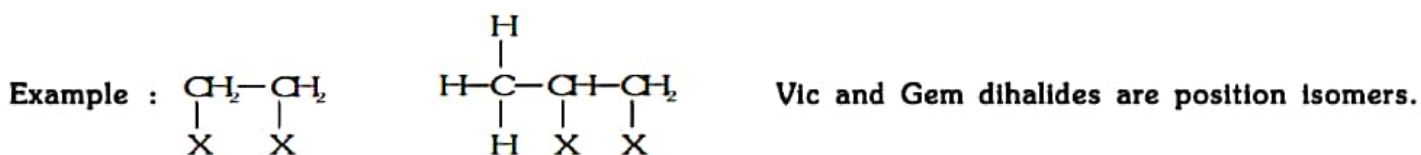
Two similar halogen atoms are attached to same C - atom

Example : CH_3CHX_2 ethylidene dihalide (1, 1 - dihalo ethane)



(b) **Vic dihalides** : Vic term from - Vicinal means adjacent C - atoms

Two halogen atoms are attached on adjacent carbon atom.



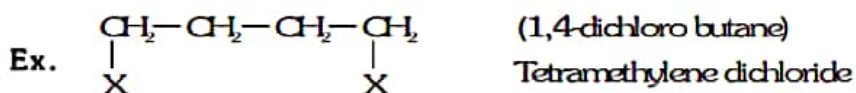
ethylene dihalide

(1,2-dihaloethane)

Propylene dihalide

(1,2-dihalo propane)

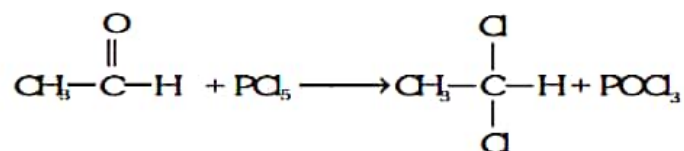
(c) **α, ω dihalides** : Halogen atoms are attached with terminal C - atom. They are separated by 3 or more C - atom . They are also known as polymethylene halides.



I General Method of Preparation :

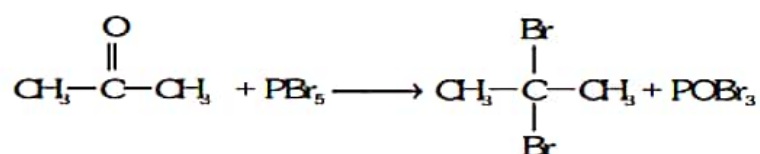
(a) **Gem dihalides** :

(i) By the reaction of PCl_5 on carbonyl compound.



Acetaldehyde

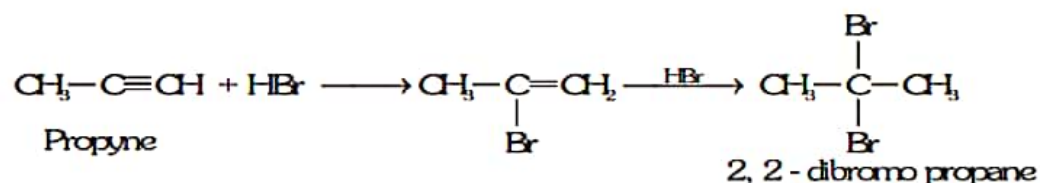
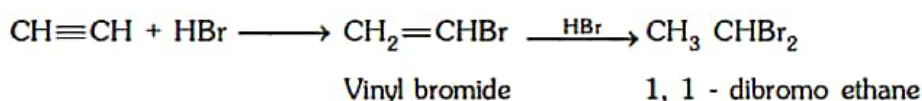
Ethylidene chloride



Acetone

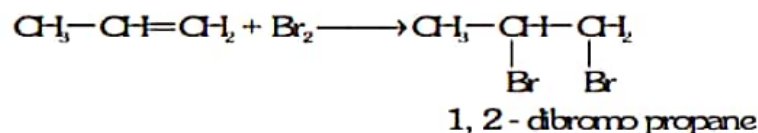
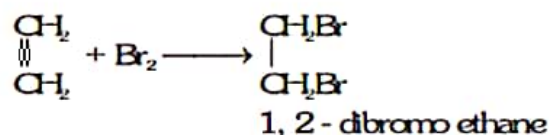
2, 2 - dibromo propane

(ii) By addition of halogen acids on alkynes :

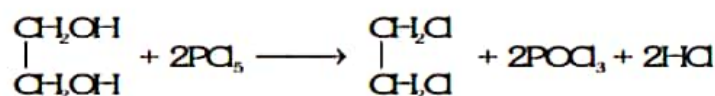


(b) Vic-dihalides :

(i) By the addition of halogens to alkenes :

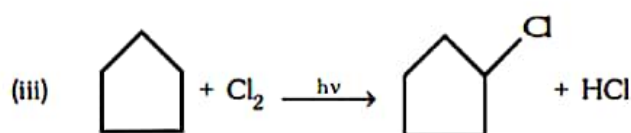
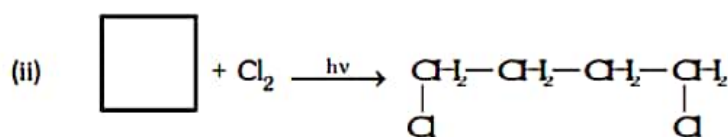
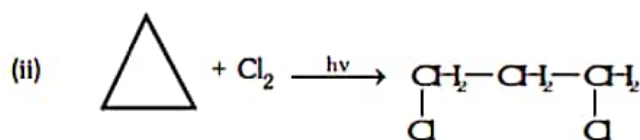



(ii) By the action of PCl_5 on glycols :



(c) $\alpha - \omega$ dihalides :

(i) $\text{CH}_2=\text{CH}-\text{CH}_2\text{Br} + \text{HBr} \longrightarrow \text{Br}-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{Br}$
1, 3 - dibromo propane



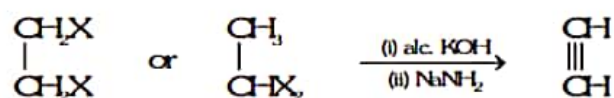
Note : Here  has less tendency to open the ring.

1 Physical Properties :

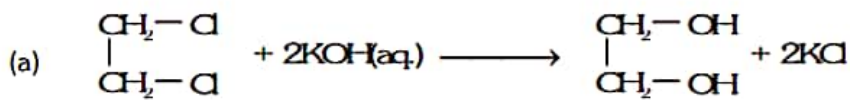
- (i) Lower members are colourless, oily liquids with sweet smell. Higher members are solid.
- (ii) The reactivity of gemdihalides is lesser than vicinal or mono halides. [Reason - in presence of one halogen atom (Strong attracting $-I$ effect) the other halogen atom can not be so easily replaced.]
- (iii) These are heavier than water.

1 Chemical Properties :

(I) **Action of $\text{KOH}(\text{alc.})$:** (Dehydrohalogenation)



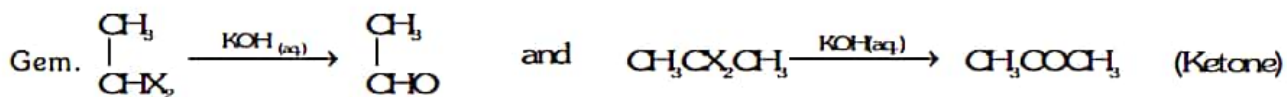
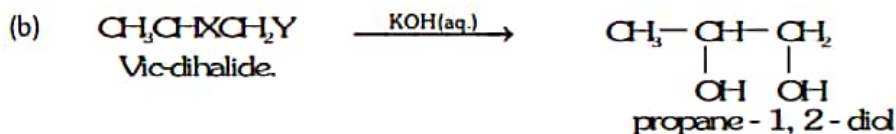
(II) **Action of $\text{KOH}(\text{aq.})$:** (Hydrolysis) It is a distinction test for gem and vic dihalides.



Glycol

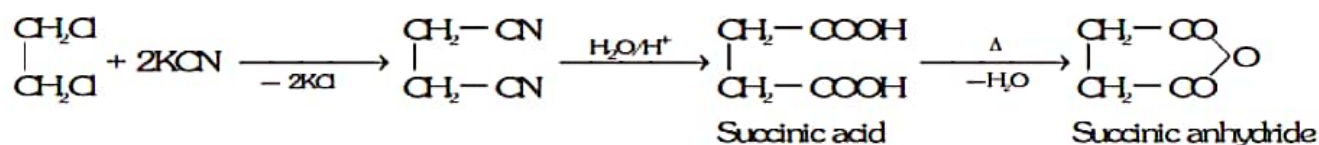
Vic - dihalide.

1, 2 - ethane diol.

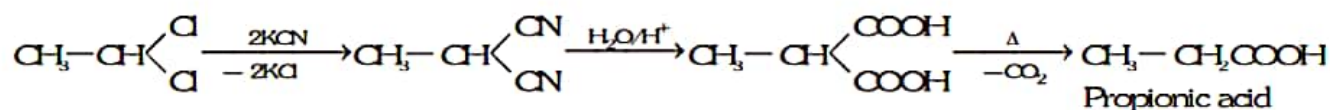


(iii) Reaction with KCN : Gem and Vic dihalide gives different products

Vic. :

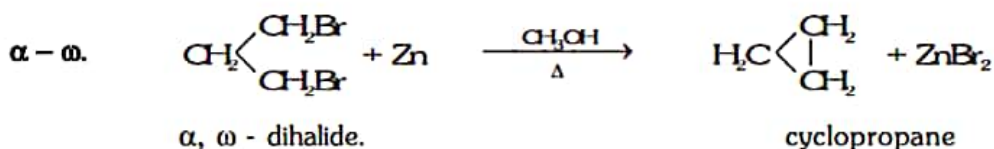
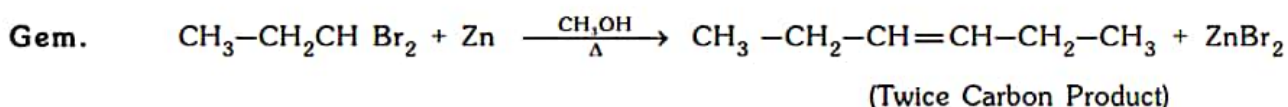
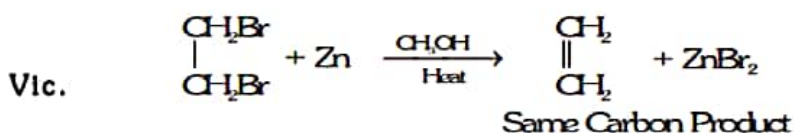


Gem. :



- (i) - CN group on acid hydrolysis gives - COOH
- (ii) Two - COOH group on one C - atom on heating always lose CO₂ to form monocarboxylic acid.
- (iii) Two - COOH group on vic. C - atom on heating lose H₂O to form anhydride.

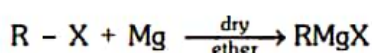
(iv) Dehalogenation :



GRIGNARD REAGENT

General Method of Preparation :

Grignard reagents are prepared in the laboratory by the action of alkyl halides on magnesium metal in the presence of dry ether.




(Grignard reagent)

(Alkyl magnesium halide)

The ease of formation of Grignard reagent is in the order $\text{RI} > \text{RBr} > \text{RCI}$
 Ether is used to dissolved the Grignard reagent by coordination.

□ **Chemical Reactions :**

RMgX	(i) O_2 (ii) H_3O^+	R-OH	1 Alcohol
	$\text{H}_2\text{CO}/\text{H}_3\text{O}^+$	$\text{RCH}_2\text{-OH}$	1 Alcohol
	 $\text{CH}_2\text{-CH}_2/\text{H}_3\text{O}^+$	$\text{R-CH}_2\text{-CH}_2\text{-OH}$	1 Alcohol
	$\text{RCHO}/\text{H}_3\text{O}^+$	R_2CHOH	1 Alcohol
	$\text{HCOOEt}/\text{H}_3\text{O}^+$	R_2CHOH	2 Alcohol
	$\text{RCOR}/\text{H}_2\text{O}$	$\text{R}_3\text{C-OH}$	3 Alcohol
	$\text{RCOOEt}/\text{H}_2\text{O}$	$\text{R}_3\text{C-OH}$	3 Alcohol
	HCOOEt	RCHO	aldehyde
	$\text{RCN}/\text{H}_2\text{O}$	RCOR	Ketone
	RCOOEt	RCOR	Ketone
	$\text{CO}_2 + \text{H}_2\text{O}$	RCOOH	Acids
	HOH or ROH or NH_3 or Ph-OH or R-NH_2 or RNH-R or $\text{CH}\equiv\text{CH}$ or Ph-NH_2	R-H	Alkane
	R-X	R-R	Alkane
	R_3N	No reaction	
	$\text{Cl-CH}_2\text{-Cl-CH}_2$	$\text{R-CH}_2\text{-CH=CH}_2$	Alkene
	Cl-NH_2	R-NH_2	1 Amine
	Cl-CN	R-CN	Cyanides
	X_2	R-X	Alkyl halide
	ClCOOEt	RCOOEt	Ester