4.0 TYPE OF REACTIONS :

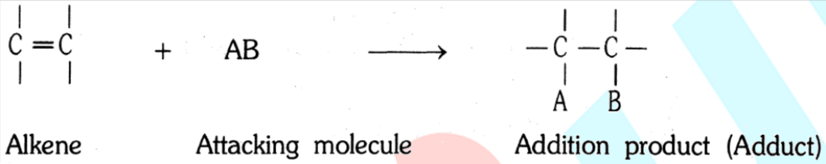
Reaction are of mainly four types :

1. Addition reactions.
2. Substitution reactions.
2. Elimination reactions.
4. Isomerisation reactions

4.1 ADDITION REACTIONS : It is also of three types :

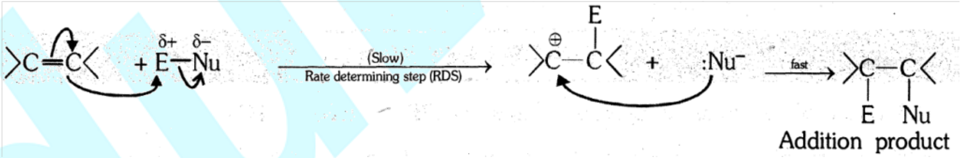
(A) Electrophilic addition reactions
(B) Free radical addition reactions
(C) Nucleophilic addition reactions

(A) Electrophilic addition reaction :- Because of the presence of >C=C< bond in molecules, alkenes generally take part in the addition reactions.



From mechanism point of view, the addition in alkenes is generally **electrophilic in nature** which means that attacking reagent which carries the initial attack is an electrophile (E^+). This is quite expected also as there is high electron density in the double bond. The mechanism proceeds in two steps.

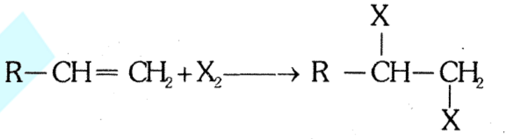
Step I : The π-electron cloud of the double bond causes the polarisation of the attacking molecule (E-Nu) which cleaves to release the electrophile (E^+) for the attack The double bond simultaneously undergoes electromeric effect and the attack by the electrophile is accomplished in slow step (also called rate determining step) to form a **carbocation** intermediate.



Step II : The nucleophile (:Nu^-) released in the slow step combines with the carbocation to give the desired addition product in the fast step.

Reactivity for Electrophilic addition reaction ∝ stability of carbocation formed in RDS

(1) Addition of Halogen : It is a electrophilic addition reaction.

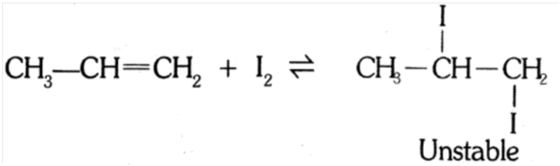


$$R-CH=CH_2+X_2 \longrightarrow R-\underset{X}{\overset{X}{CH}}-CH_2$$

(Vicinal halides)

(a) The addition of Br_2 on alkenes provides a useful test for unsaturation in molecule. The brown colour of the bromine being rapidly discharged. Thus decolarization of 5% Br_2 in $CC1_4$ by a compound suggest unsaturation in it. Colourless dibromo compound is formed.

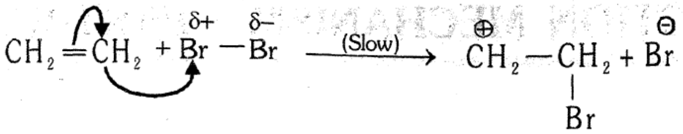
(b) 12 reacts with alkenes to form Vicinal di-iodides which are unstable and I_2 gets eliminated to give original alkene.



$$CH_3-CH=CH_2 + I_2 \rightleftharpoons CH_3-\underset{}{\overset{I}{CH}}-\underset{I}{CH_2}$$

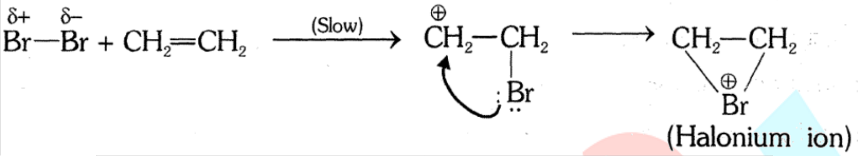
Unstable

Mechanism :



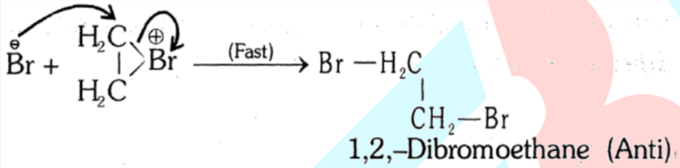
$$CH_2=CH_2 + \overset{\delta+}{Br}-\overset{\delta-}{Br} \xrightarrow{(Slow)} \overset{\oplus}{C}H_2-\underset{Br}{CH_2} + \overset{\ominus}{Br}$$

It is interesting to note that product which is mainly formed as a result of addition is **trans** in nature whereas the cis isomer is obtained in relatively smaller proportions. Since carbocation intermediate is planar (sp^2 hybridised), both cis and trans addition products must be formed almost in equal proportions. The trans product can be justified in case a cyclic halonium ion is formed by the initial electrophile attack.



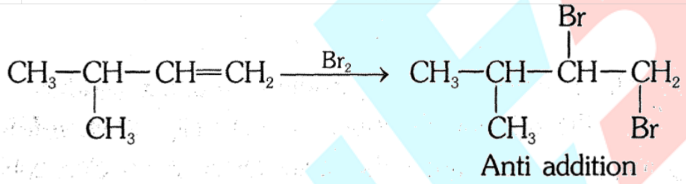
$$\overset{\delta+}{Br}-\overset{\delta-}{Br} + CH_2=CH_2 \xrightarrow{(Slow)} \overset{\oplus}{C}H_2-\underset{:\ddot{Br}}{CH_2} \longrightarrow CH_2-CH_2\ (\overset{\oplus}{Br})$$

(Halonium ion)



$$\overset{\ominus}{Br} + H_2C\!-\!CH_2\ (\overset{\oplus}{Br}) \xrightarrow{(Fast)} Br-H_2C-CH_2-Br$$

1,2,-Dibromoethane (Anti)

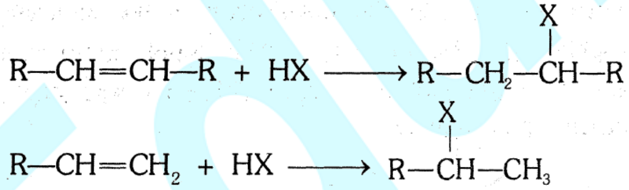


Eg. $$CH_3-\underset{CH_3}{CH}-CH=CH_2 \xrightarrow{Br_2} CH_3-\underset{CH_3}{CH}-\overset{Br}{CH}-\underset{Br}{CH_2}$$

Anti addition

No carbocation rearrangement and anti addition product.

(2) Addition of halogen acid :



$$R-CH=CH-R + HX \longrightarrow R-CH_2-\overset{X}{CH}-R$$

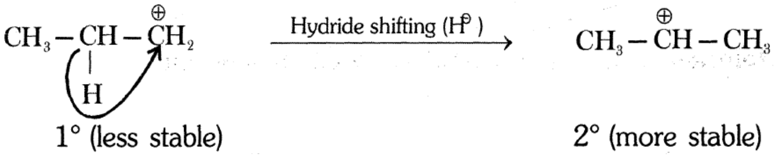
$$R-CH=CH_2 + HX \longrightarrow R-\overset{X}{CH}-CH_3$$

GOLDEN KEY POINTS

- The order of reactivity of hydrogen halide is : **HI > HBr > HCI**
- Addition on alkene proceeds via the formation of more~ stable carbonium ion.
- Addition of HX on unsymmetrical alkenes ($R-CH=CH_2$) takes place according to Markovnikov's rule. Carbocation rearrangement is observed in the reaction.

Rearrangement in. carbocation

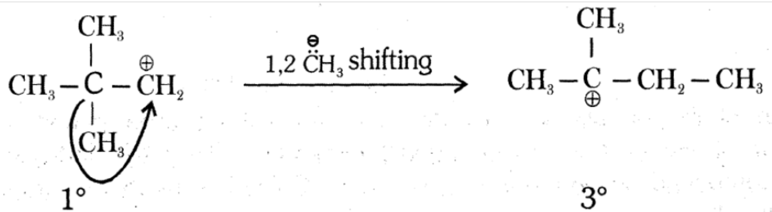
Ex.



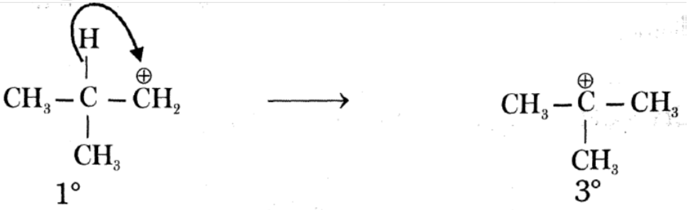
$$CH_3-\underset{H}{CH}-\overset{\oplus}{C}H_2 \xrightarrow{\text{Hydride shifting } (H^{\ominus})} CH_3-\overset{\oplus}{C}H-CH_3$$

1° (less stable) 2° (more stable)

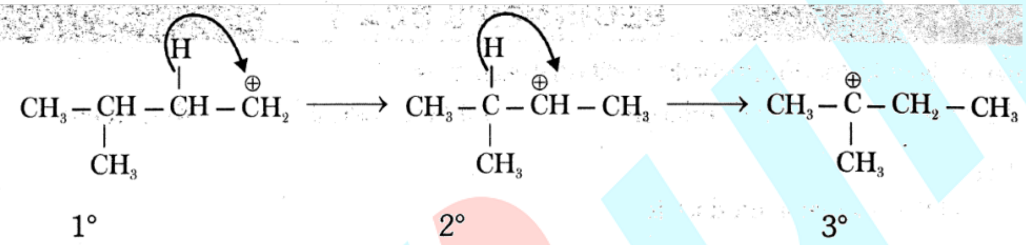
Ex.



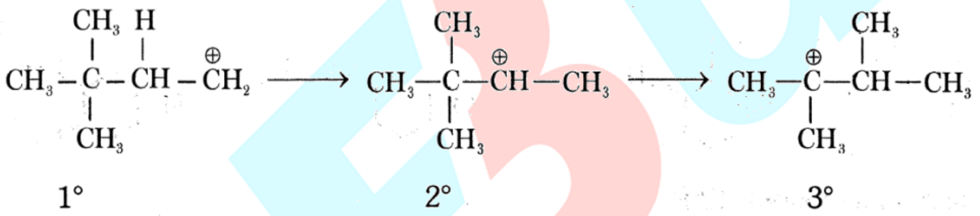
Ex.



Ex.



Ex.

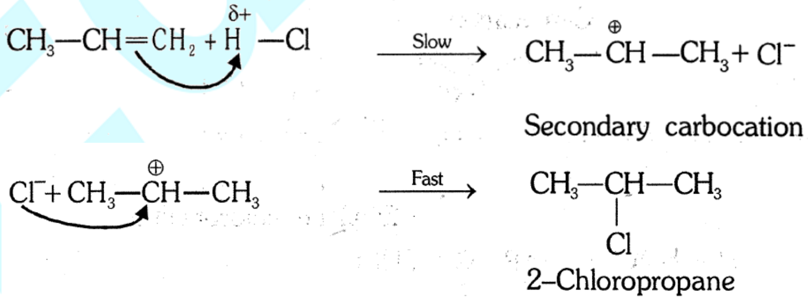


Markovnikov's Rule States :

(a) **First Rule :** When molecule of HX add up on unsymmetrical unsaturated hydrocarbon, the electrophile (H^+) goes to the unsaturated carbon atom bearing more number of hydrogen atoms.

$$CH_3{-}CH{=}CH_2 + HX \longrightarrow CH_3{-}\underset{}{\overset{X}{CH}}{-}\underset{H}{CH_2}$$

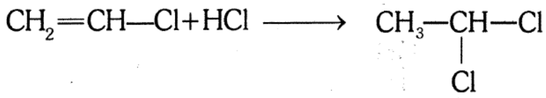
Mechanism : It is electrophilic addition and is illustrated by the action of HCl to propene.



Primary carbocation ($CH_3{-}CH_2{-}\overset{\oplus}{C}H_2$) cis also formed. but only in very small proportion since it less, Stable than the secondary carbocation. Markovnikov's rule is based on stability of carbocation.

Note ; The electrophilic addition of HX to unsymmetrical alkenes always occurs through the formation of a more stable carbocation intermediate.

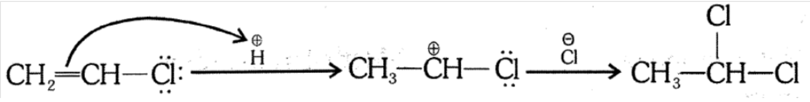
(b) Second Rule : In the addition of HX to vinyl halide and analogous compounds, the halogen attaches itself to the carbon atom, on which the halogen atom is already present.



$$CH_2{=}CH{-}Cl + HCl \longrightarrow CH_3{-}\underset{\displaystyle Cl}{\underset{|}{CH}}{-}Cl$$

Ethylidene chloride

Mechanism :

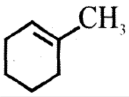


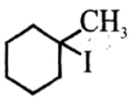
All polar regents of the general structure $\overset{\oplus}{Y}\overset{\ominus}{Z}$ (such as $\overset{\oplus}{Y}-\overset{\ominus}{X}$, $\overset{\oplus}{H}-\overset{\ominus}{OH}$ $\overset{\oplus}{H}-\overset{\ominus}{SO_3H}$, $\overset{\oplus}{X}\overset{\ominus}{OH}$) add on unsymmetrical unsaturated compound in accordance with Markovnikov's rules. Such additions are called normal Markovnikov's rule, where as additions in the opposite manner are referred to as abnormal or **anti Markovnlkov's additions.**

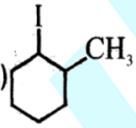
BEGINNER'S BOX-1

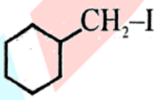
1. The intermediate in the Electrophilic addition-reaction is :-

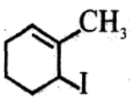
(1) Carbocation (2) Carbanion (3) Free radical (4) Carbene

2.  + HI ⟶ major product is

(1) 

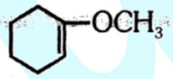
(2) 

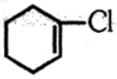
(3) 

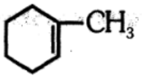
(4) 

3. Give reactivity order towards EAR.

(i) 

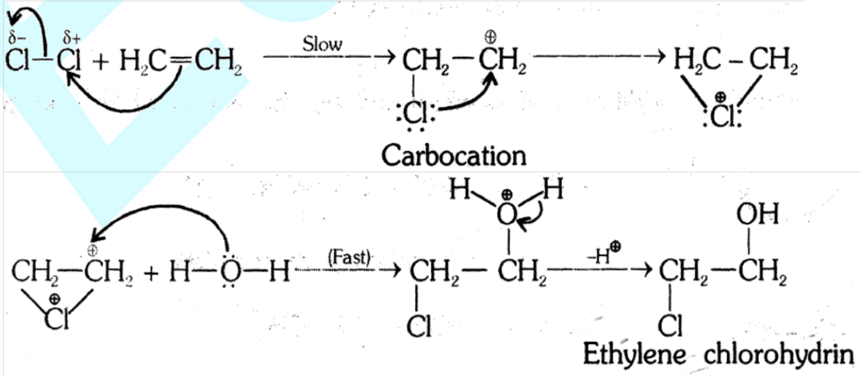
(ii) 

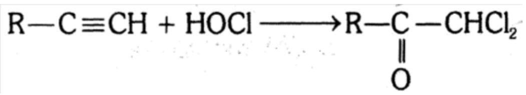
(iii) 

(iv) 

(1) (i) > (ii) > (iii) > (iv)
(2) (iv) > (iii) > (ii) > (i)
(3) (ii) > (iv) > (i) > (iii)
(4) (iii) > (ii) > (iv) > (i)

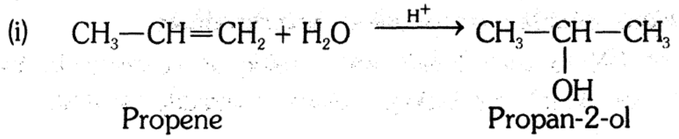
(3) Addition of Hypohalous acid (or X_2/H_2O, or HOX) : It is a electrophilic addition and follows Markovnikov's rule, and anti addition.





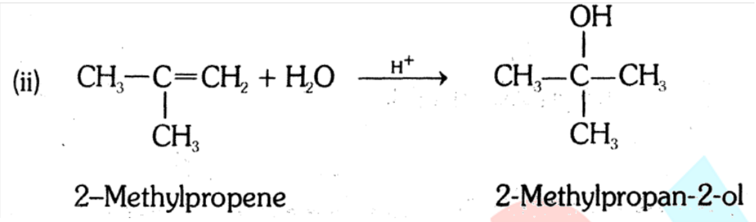
$$R-C\equiv CH + HOCl \longrightarrow R-\underset{\underset{O}{\|}}{C}-CHCl_2$$

(4) **Addition of water (Hydration of alkenes) :** Propene and higher alkenes react with water in the presence of acid to form alcohol This reaction is known as acidic **hydration reaction.** Intermediate in this reaction is carbocation, so rearrangement may take place.



$$\text{(i)}\quad CH_3-CH=CH_2 + H_2O \xrightarrow{H^+} CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$$

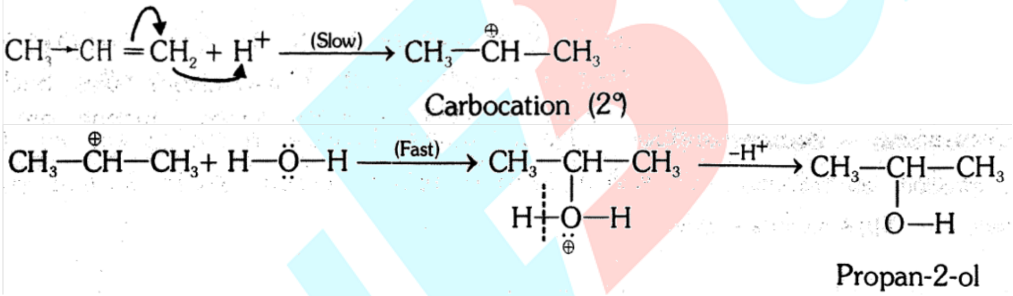
Propene Propan-2-ol



$$\text{(ii)}\quad CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2 + H_2O \xrightarrow{H^+} CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

2–Methylpropene 2-Methylpropan-2-ol

Mechanism :



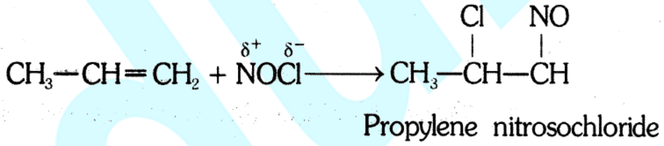
$$CH_3-CH=CH_2 + H^+ \xrightarrow{\text{(Slow)}} CH_3-\overset{\oplus}{C}H-CH_3$$

Carbocation (2°)

$$CH_3-\overset{\oplus}{C}H-CH_3 + H-\ddot{O}-H \xrightarrow{\text{(Fast)}} CH_3-\underset{\underset{H-\underset{\oplus}{O}-H}{|}}{CH}-CH_3 \xrightarrow{-H^+} CH_3-\underset{\underset{O-H}{|}}{CH}-CH_3$$

Propan-2-ol

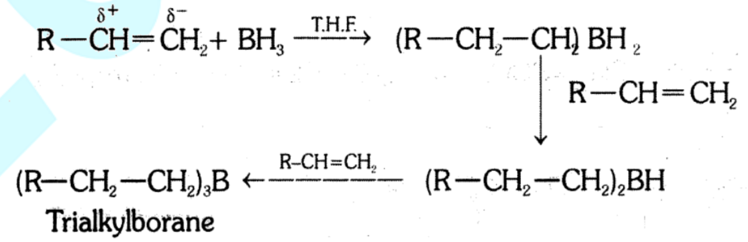
(5) **Addition of NOCl (Tilden reagent) :**



$$CH_3-CH=CH_2 + \overset{\delta+}{NO}\overset{\delta-}{Cl} \longrightarrow CH_3-\overset{\overset{Cl}{|}}{CH}-\overset{\overset{NO}{|}}{CH}$$

Propylene nitrosochloride

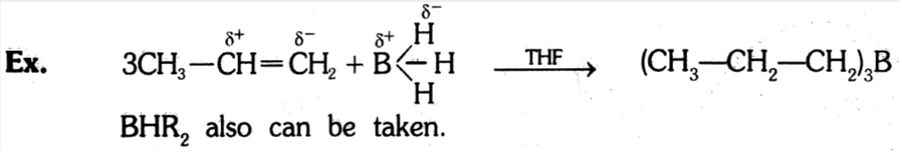
(6) **Hydroboration Oxidation :** Borane readily reacts with alkenes giving trialkyl boranes. The reaction is called hydroboration.



$$R-\overset{\delta+}{CH}=\overset{\delta-}{CH_2} + BH_3 \xrightarrow{\text{T.H.F.}} (R-CH_2-CH_2)BH_2 \xrightarrow{R-CH=CH_2} (R-CH_2-CH_2)_2BH \xrightarrow{R-CH=CH_2} (R-CH_2-CH_2)_3B$$

Trialkylborane

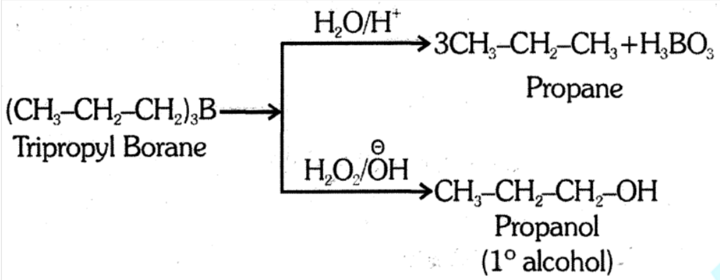
BH_3 does not exist freely as monomer so a solvent THF (tetra hydro furane) is used to stabilised it.

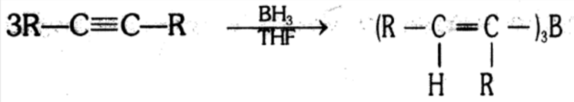


$$\textbf{Ex.}\quad 3CH_3-\overset{\delta+}{CH}=\overset{\delta-}{CH_2} + \overset{\delta+}{B}\overset{\overset{\delta-}{H}}{\leftarrow}H \xrightarrow{THF} (CH_3-CH_2-CH_2)_3B$$

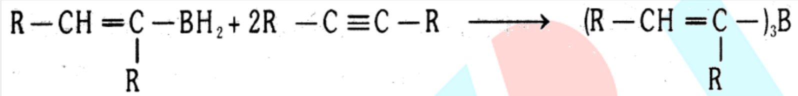
BHR₂ also can be taken.

Ex. $CH_3-\overset{\delta+}{CH}=\overset{\delta-}{CH_2} + BHR_2 \longrightarrow CH_3-CH_2-CH_2-BR_2$

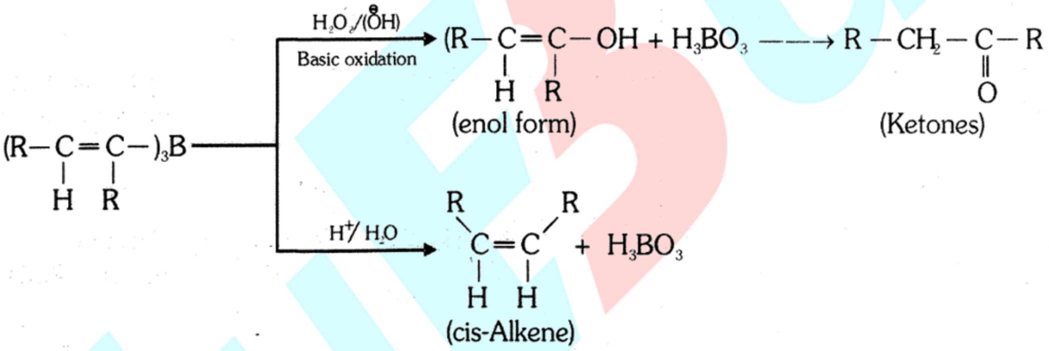




$$3R-C\equiv C-R \xrightarrow[THF]{BH_3} (R-\underset{H}{C}=\underset{R}{C}-)_3B$$



$$R-CH=\underset{R}{C}-BH_2+2R-C\equiv C-R \longrightarrow (R-CH=\underset{R}{C}-)_3B$$



Note : The overall process appears to be addition of water according to anti Markovnikov's rule and involves syn. addition.

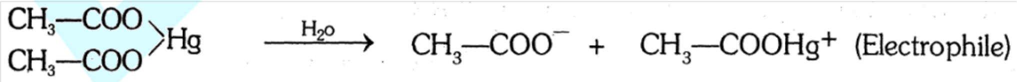
(7) **Oxymercuration- demercuration :** Mercuric acetate in water is treated with an alkene. The addition product on reduction with sodium Boro hydride in aqueous NaOH soulution gives alcohol. It follows the Markovnikov's rule.

$$CH_3-CH=CH_2 \longrightarrow CH_3-\underset{OH}{CH}-CH_3$$

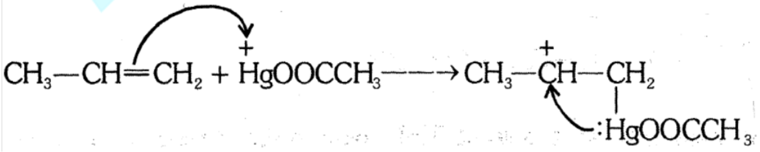
(i) $(AcO)_2$ Hg/H_2O (Mercuric acetate) or $(CH_3COO)_2Hg/H_2O$

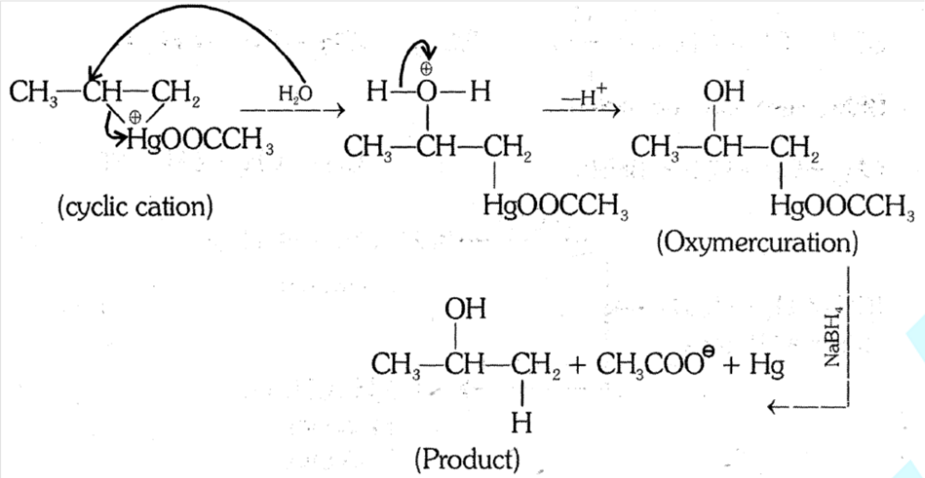
(ii) $NaBH_4$

Mechanism :

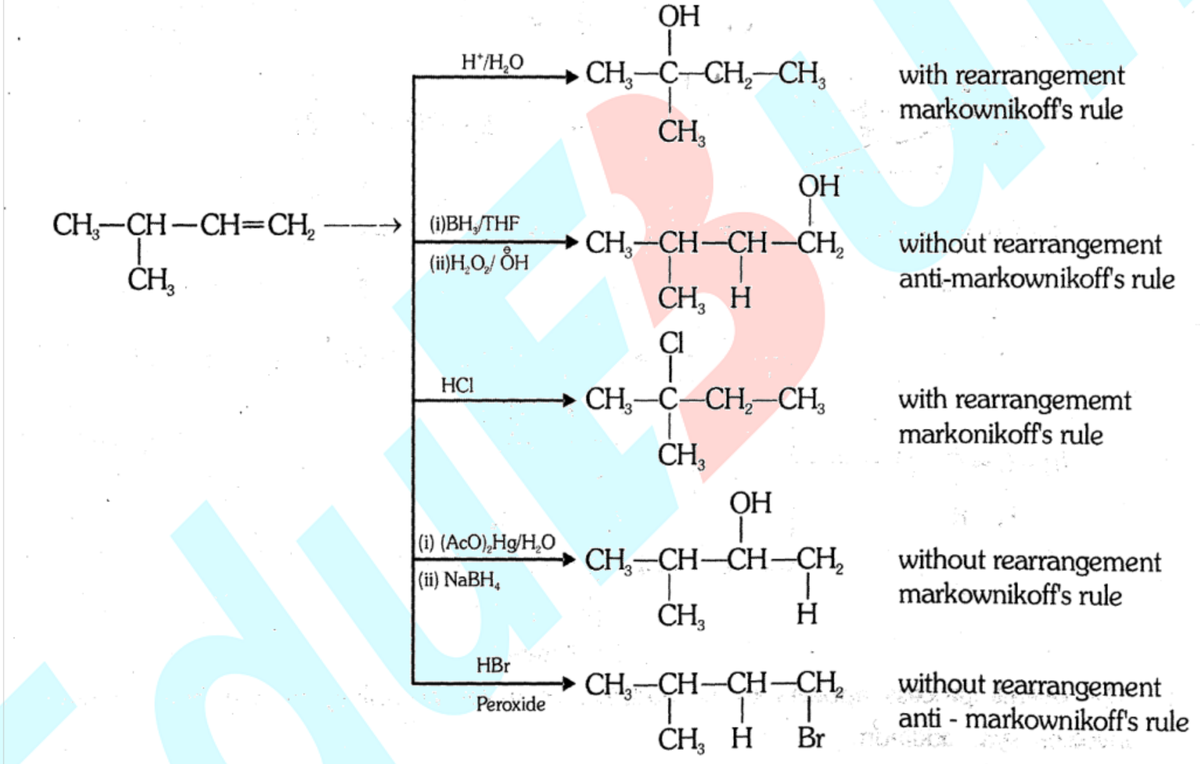


$$\begin{matrix}CH_3-COO\\CH_3-COO\end{matrix}\Big\rangle Hg \xrightarrow{H_2O} CH_3-COO^- + CH_3-COOHg^+ \text{ (Electrophile)}$$





Note : Intermediate is cyclic cation so there is no rearrangement.

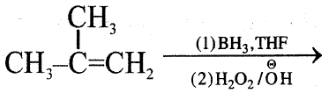


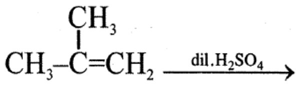
BEGINNER'S BOX-2

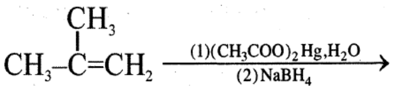
1. What is the product formed when acetylene reacts with hypochlorous acid ?

(1) CH_3COCl (2) $ClCH_2CHO$ (3) Cl_2CHCHO (4) $ClCH_2COOH$

2. Primary alcohol can be formed as major product by

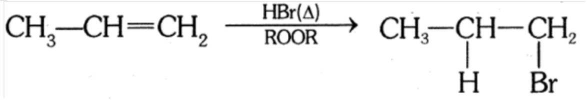
(1) 
$\mathrm{CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 \xrightarrow[(2)H_2O_2/\overset{\ominus}{O}H]{(1)BH_3,THF}}$

(2) 
$\mathrm{CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 \xrightarrow{dil.H_2SO_4}}$

(3) 
$\mathrm{CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 \xrightarrow[(2)NaBH_4]{(1)(CH_3COO)_2Hg,H_2O}}$

(4) 2 & 3 both

(B) Free readical addition reactions :- Addition of HBr on alkene or alkyne in presence of peroxide.



$$CH_3-CH=CH_2 \xrightarrow[\text{ROOR}]{\text{HBr}(\Delta)} \underset{\displaystyle H}{CH_3-CH}-\underset{\displaystyle Br}{CH_2}$$

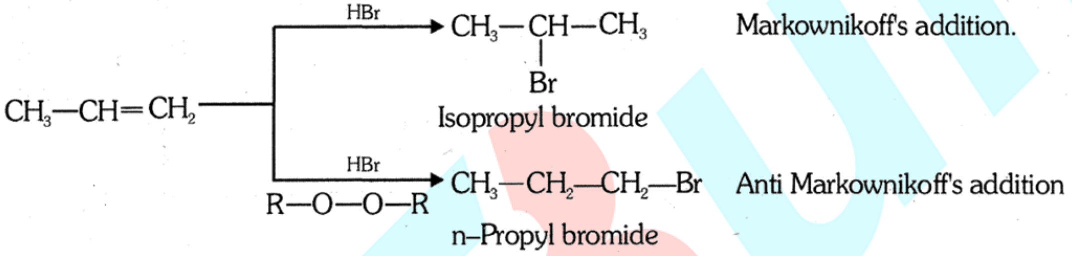
Anti Markovnikov's rule or peroxide effect or Kharasch rule

(i) In the presence of peroxides the addition of HBr on unsaturated unsymmetrical compound takes place contrary to Markovnikov's rule. This is called peroxide effect and is due to the difference in the mechanism of the addition.

(ii) In the normal Markovnikov's addition the mechanism is ionic.

(iii) In the presence of peroxide the addition of HBr takes place via free radicals.

(iv) Peroxide effect is not observed in case of H–F, HCI and HI. Reactions follows electrophilic addition mechanism.



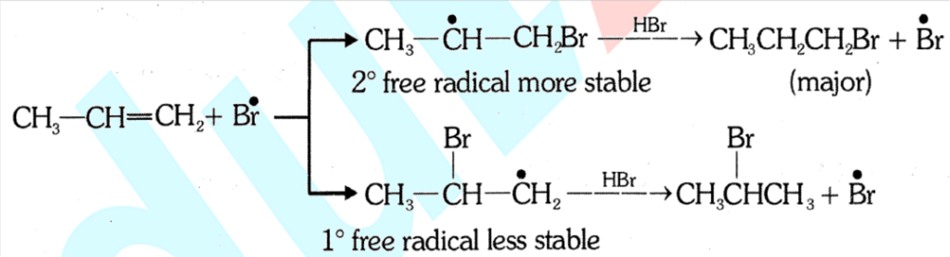
Mechanism :

(i) Chain initiation -

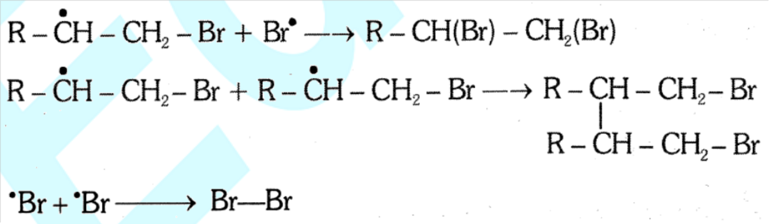
(a) R–O–O–R $\longrightarrow$ 2RO$^\bullet$

HBr + RO$^\bullet$ $\longrightarrow$ ROH + Br$^\bullet$

(ii) Chain propagation



(iii) Chain termination :

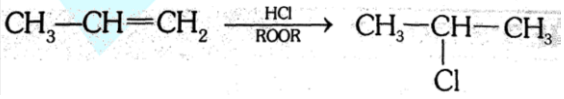


$$R-\dot{C}H-CH_2-Br + Br^\bullet \longrightarrow R-CH(Br)-CH_2(Br)$$

$$R-\dot{C}H-CH_2-Br + R-\dot{C}H-CH_2-Br \longrightarrow \begin{array}{c} R-CH-CH_2-Br \\ | \\ R-CH-CH_2-Br \end{array}$$

$$^\bullet Br + {}^\bullet Br \longrightarrow Br—Br$$

Q :



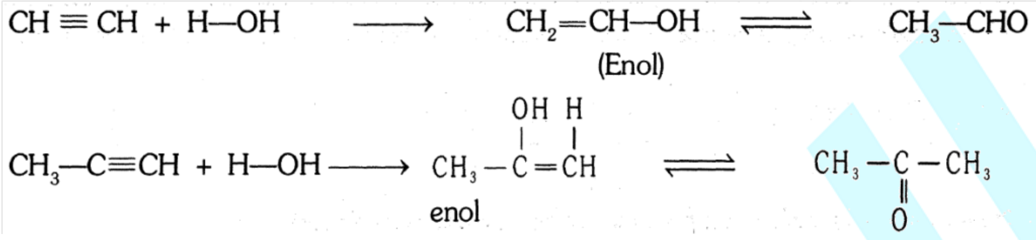
$$CH_3-CH=CH_2 \xrightarrow[\text{ROOR}]{\text{HCl}} CH_3-\underset{\displaystyle Cl}{CH}-CH_3$$

Ans. no effect simple EAR

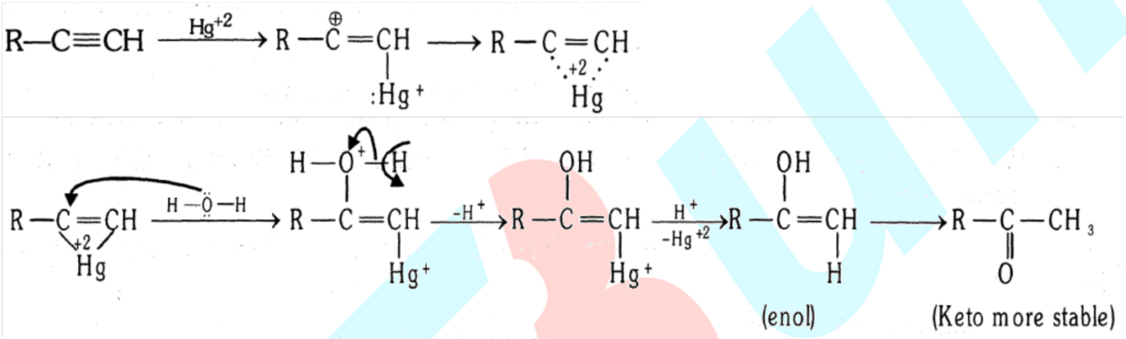
(C) Nucleophilic Addition Reaction :-

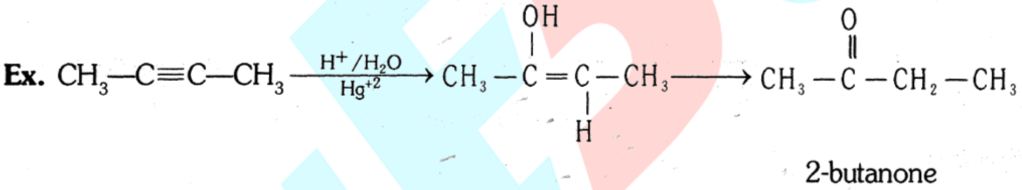
(C_1) NAR in Alkyne : In these reactions some heavy metal cation like Hg^{+2}, Pb^{+2}, Ba^{+2} are used. These cation attracts the π^- e^- of alkynes and decrease the e^- density and hence a nucleophile can attack an alkynes.

(1) Addition of dil. H_2SO_4 (Hydration) : The addition of water takes place inthe presence of Hg^{+2} and H_2SO_4 [1% $HgSO_4$ + 40% H_2SO_4].

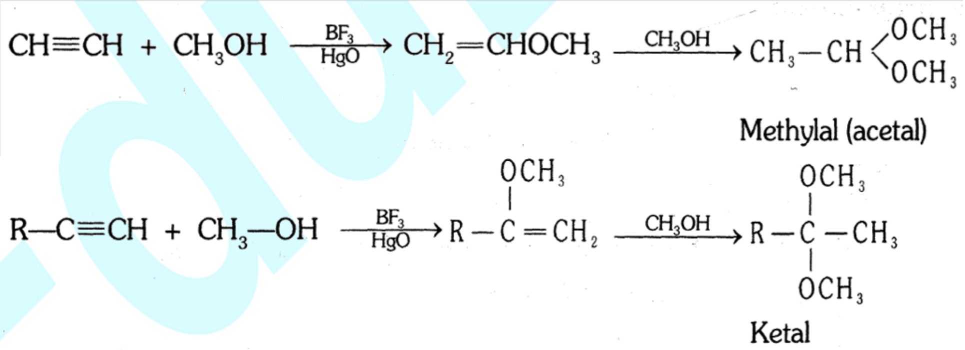

$$CH\equiv CH + H-OH \longrightarrow \underset{(Enol)}{CH_2=CH-OH} \rightleftharpoons CH_3-CHO$$
$$CH_3-C\equiv CH + H-OH \longrightarrow \underset{enol}{CH_3-\overset{OH}{\overset{|}{C}}=\overset{H}{\overset{|}{CH}}} \rightleftharpoons CH_3-\underset{\underset{O}{\|}}{C}-CH_3$$

Mechanism :

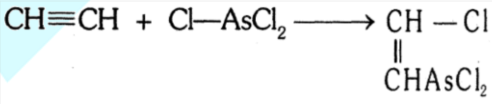



$$\textbf{Ex. } CH_3-C\equiv C-CH_3 \xrightarrow[Hg^{+2}]{H^+/H_2O} CH_3-\overset{OH}{\overset{|}{C}}=\underset{\underset{H}{|}}{C}-CH_3 \longrightarrow \underset{\text{2-butanone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3}$$

(2) Addition of alcohols : In presence of BF_3 and HgO alkynes react with alcohols and form acetal and ketal

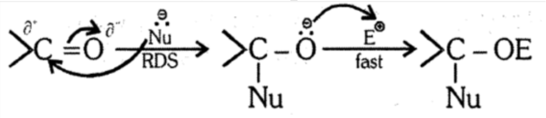

$$CH\equiv CH + CH_3OH \xrightarrow[HgO]{BF_3} CH_2=CHOCH_3 \xrightarrow{CH_3OH} \underset{\text{Methylal (acetal)}}{CH_3-CH\begin{matrix}OCH_3\\OCH_3\end{matrix}}$$
$$R-C\equiv CH + CH_3-OH \xrightarrow[HgO]{BF_3} R-\overset{OCH_3}{\overset{|}{C}}=CH_2 \xrightarrow{CH_3OH} \underset{\text{Ketal}}{R-\overset{OCH_3}{\overset{|}{\underset{\underset{OCH_3}{|}}{C}}}-CH_3}$$

(3) Addition of $AsCl_3$:- In presence of $AlCl_3$ or $HgCl_2$ acetylene combines with $AsCl_3$ to yield Lewisite gas. It is four times poisonous than mustard gas.\


$$CH\equiv CH + Cl-AsCl_2 \longrightarrow \underset{\underset{CHAsCl_2}{\|}}{CH-Cl}$$

2-Chlorovinyl dichloro arsine (Lewisite gas)

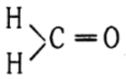
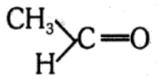
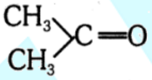
(C_2) NAR ·in Aldehyde & Ketone : Due to strong electronegativity of Oxygen, the mobile π electrons pulled strongly towards oxygen, leaving the carbon atom deficient of electrons. Carbon is thus readily attacked by Nu. The negatively charged oxygen is attacked by electron deficient (electrophile) E^+.



$$\text{Reactivity of carbonyl group} \propto \text{Magnitude of } \partial\text{+ve charge}$$
$$\propto -\text{I effect}$$
$$\propto \frac{1}{+\text{I effect}}$$

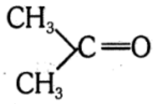
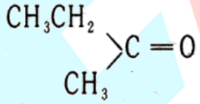
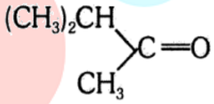
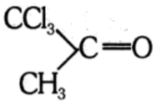
Illustrations

Illustration 1. Arrange the following for reactivity in decreasing order

(a) I.  $H_2C=O$ II.  $CH_3(H)C=O$ III.  $(CH_3)_2C=O$

(b) I. $ClCH_2CHO$ II. NO_2CH_2CHO III. CH_3CHO IV. CH_3CH_2CHO

(c) I. CH_3CHO II. $ClCH_2CHO$ III. $HCCl_2CHO$ IV. CCl_3CHO

(d) I.  $(CH_3)_2C=O$ II.  $CH_3CH_2(CH_3)C=O$ III.  $(CH_3)_2CH(CH_3)C=O$ IV.  $CCl_3(CH_3)C=O$

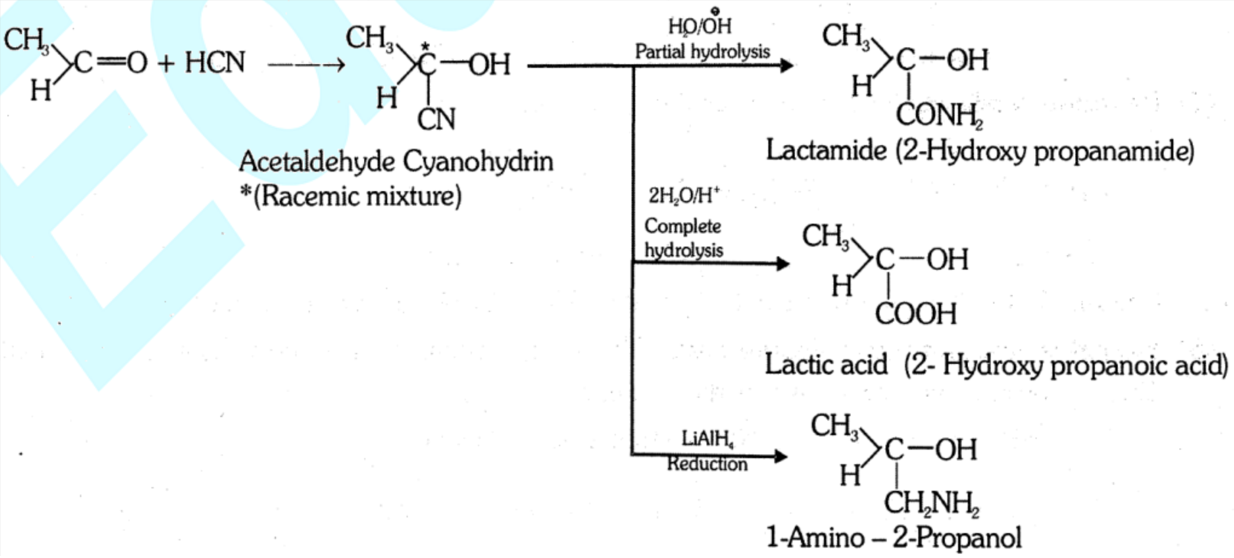
Solution. (a) I > II > III (b) II > l > III > IV

(c) IV > III > II > I (d) IV > I > II > III

CH_3– is +I group, decreases the intensity of δ +ve charge on C-atom of $>C=O$ group.

Cl– is –I group increases the intensity of δ +ve charge on C-atom of $>C=O$ group.

(1) Addition of HCN :



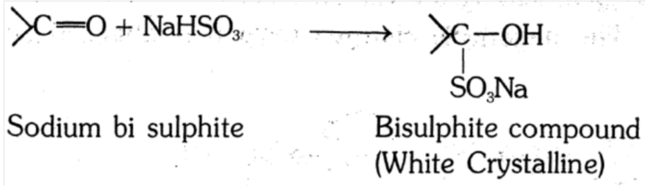
Acetaldehyde Cyanohydrin
*(Racemic mixture)

Lactamide (2-Hydroxy propanamide)

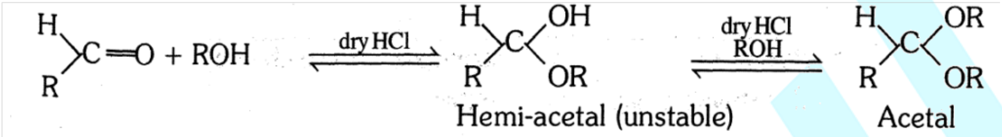
Lactic acid (2- Hydroxy propanoic acid)

1-Amino – 2-Propanol

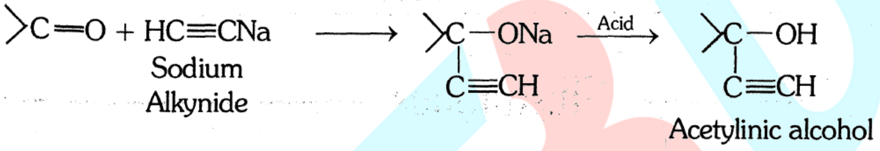
(2) **Addition of $NaHSO_3$:** This reaction is utilized for the separation of carbonyl compounds from non-carbonyl compounds.



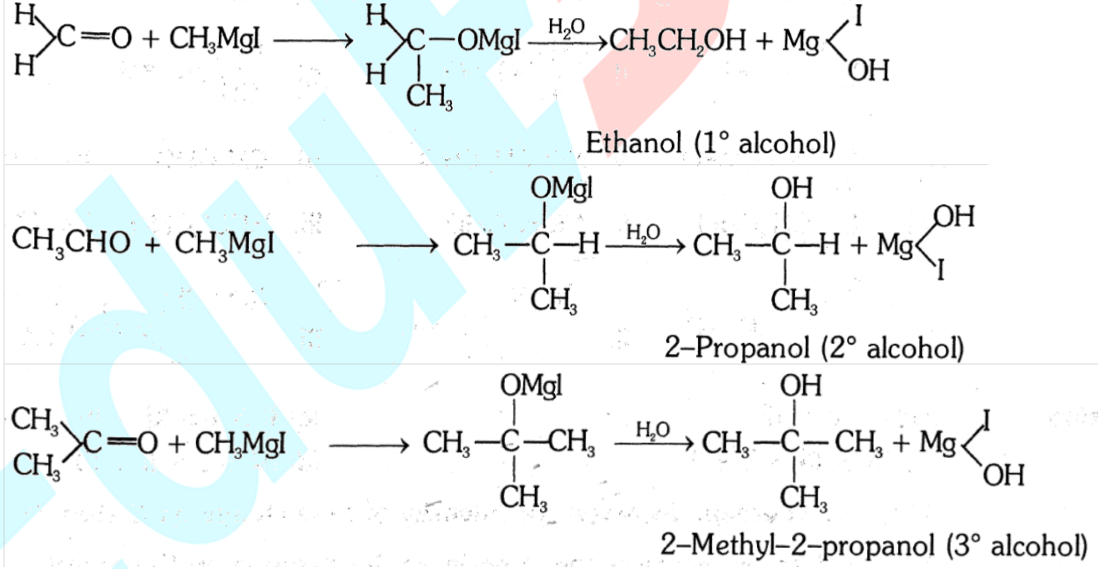
(3) **With Alcohol :**



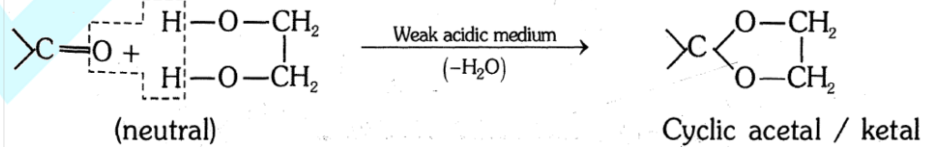
(4) **Reaction with sodium alkynide :**



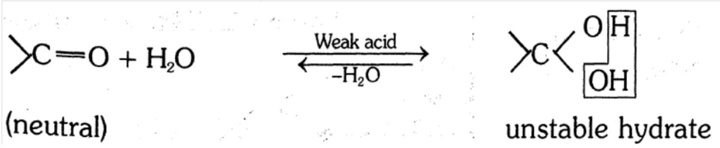
(5) **Reaction with Grignard reagent :**



(6) **Reaction with glycol :**



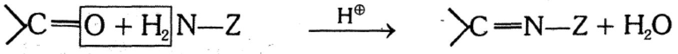
(7) **Reaction with H_2O :** It is a reversible reaction.



Note : Chloral ($Cl_3C–CH=O$) forms stable hydrate [$CCl_3–CH(OH_2)$ (chloral hydrate)]

(8) Reaction with ammoinia derivatives : These are condensation or addition elimination reaction. These prceeds well in weakly acidic medium.

$NH_3 \longrightarrow NH_2Z$ (Ammonia derivative)



Addition- elimination (Condensation)

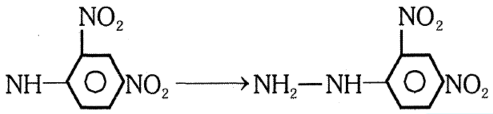
Ammonia derivatives (NH_2Z) :

Z = OH $\longrightarrow$ NHpH (Hydroxyl amine)

Z = $NH_2 \longrightarrow NH_2NH_2$ (hydrazine)

Z = $NHC_6H_5 \longrightarrow NH_2NHC_6H_5$ (Phenyl hydrazine)

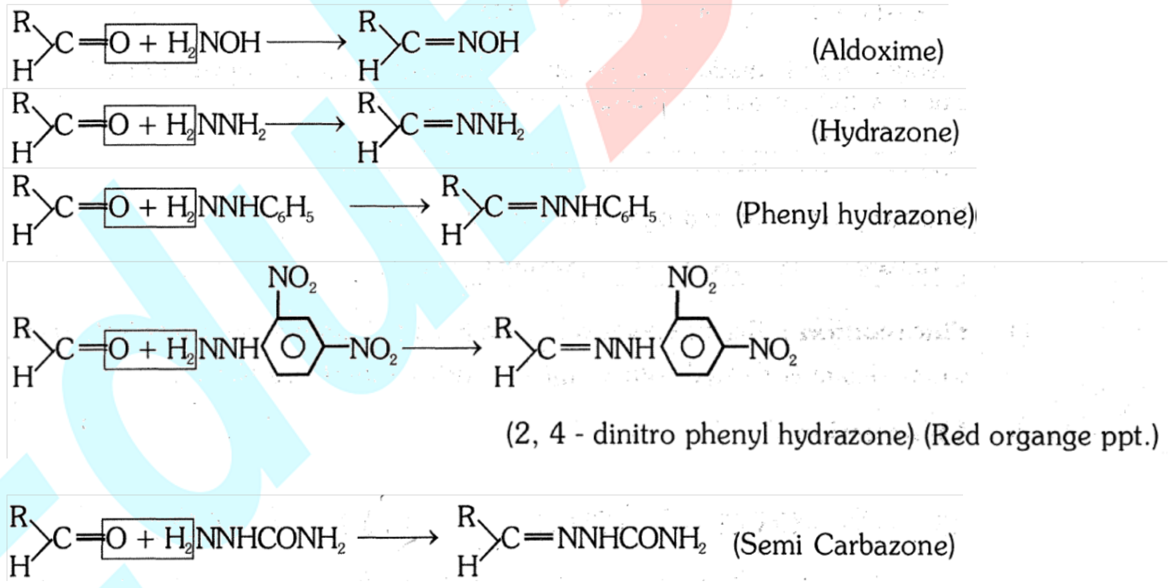
Z =



2, 4-Dinitro phenyl hydrazine (2, 4-DNP) Brady's reagent.

Z = $NHCONH_2 \longrightarrow NH_2NHCONH_2$

Semi Carbazide



BEGINNER'S BOX-3

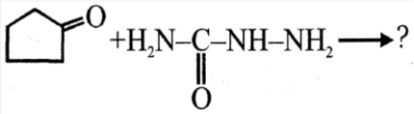
1. Which compound form more stable hydrate with H_2O?

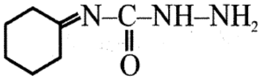
(1) $CC1_3CHO$ (2) CH_3CHO (3) CH_3COCH_3 (4) $CH_3COC_2H_5$

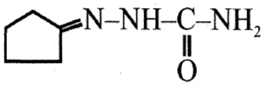
2. The formation of cyanohydrin from a ketone is an example of :-

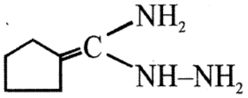
(1) Electrophilic addition (2) Nucleophilic addition

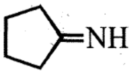
(3) Nucleophilic substitution (4) Electrophilic substitution

3. 

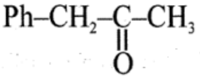
(1) 

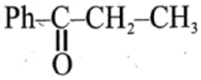
(2) 

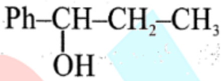
(3) 

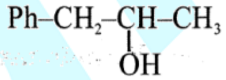
(4) 

4. Ph–C°C–CH$_3$ $\xrightarrow[H_2SO_4]{HgSO_4}$ A, A is

(1) 
$Ph{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}CH_3$

(2) 
$Ph{-}\underset{\underset{O}{\|}}{C}{-}CH_2{-}CH_3$

(3) 
$Ph{-}\underset{\underset{OH}{|}}{CH}{-}CH_2{-}CH_3$

(4) 
$Ph{-}CH_2{-}\underset{\underset{OH}{|}}{CH}{-}CH_3$

4.2 SUBSTITUTION REACTIONS : Reactions in which one atom or a group of substrate is replaced by other atom or group are called as substitution reactions.

On the basis of reaction conditions and attacking species, substitution reaction is also of three types :

(A) Free radical substitution reactions
(B) Electrophilic substitution reactions
(C) Nucleophilic substitution reactions

(A) **Free radical substitution reactions :** Substitution reaction in alkanes show free radical mechanism. They give following substitution reaction.

(a) **Halogenation :** Replacement of H-atom by halogen atom

$$R{-}H + X_2 \longrightarrow R{-}X + HX$$

Halogenation is made on exposure to (halogen + alkane) mixture to UV or at elevated temperature. The reactivity order for halogens shows the order.

$F_2 > Cl_2 > Br_2 > I_2$

Reactivity order of hydrogen atom in alkane is

Tertiary C–H > Sec. C–H > primary C–H

(i) **Fluorination :** Reacts explosively even in dark. Fluorination can be achieved without violence when alkane is treated with F_2 diluted with an inert gas like N_2.

(ii) **Chlorination :**

$$CH_4 \xrightarrow{Cl_2} CH_3Cl \xrightarrow{Cl_2} CH_2Cl_2 \xrightarrow{Cl_2} CHCl_3 \xrightarrow{Cl_2} CCl_4$$

The monochloro derivative of alkane is obtained as major product by taking alkane in large excess.

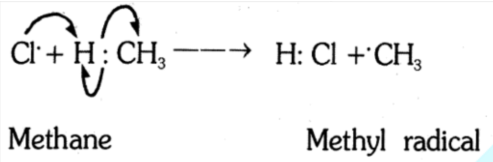
When chlorine is in excess then perchloro derivative is obtained as major product.

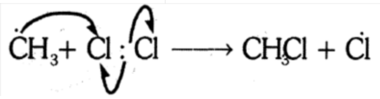
At 12 noon explosively $CH_4 + Cl_2 \longrightarrow C + HCl$

Mechanism for $CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$

Step-I Chain initiation step : $Cl{:}Cl \xrightarrow[\text{or }\Delta]{\text{UV}} Cl^{\bullet} + Cl^{\bullet}$

Step-II Chain propagation step :





Step-III Chain termination step : $Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl_2$, $CH_3^{\bullet} + {}^{\bullet}Cl \longrightarrow CH_3Cl$,

$CH_3^{\bullet} + {}^{\bullet}CH_3 \longrightarrow CH_3CH_3$

(iii) **Bromination :** Br_2 reacts with alkanes in a similar manner but less vigorously.

(iv) **Iodination :** Iodine reacts with alkanes reversibly. HI formed as the by product is a powerful reducing agent and is capable of reducing the CH_3I to CH_4.

Iodination may be carried out in the presence of an oxidising agent such as HIO_3, HNO_3, HgO etc. which decompose HI,

$CH_4 + I_2 \rightleftharpoons CH_3I + HI$

$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$

Iodination is very slow because energy of activation of the reaction is very large

$CH_4 + I^{\bullet} \longrightarrow HI + \dot{C}H_3$

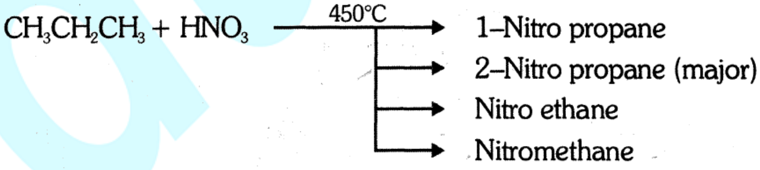
(b) **Nitration :** (Vapour phase nitration) This involves the substitution of a hydrogen atom of alkane with $–NO_2$ group.

At ordinary temperature, alkanes do not react with HNO_3 But reacts with vapours of Conc. HNO_3 at 450ºC and in pressure.

$$R–H + HO–NO_2 \xrightarrow[\text{pressure}]{400–500°C} R–NO_2 + H_2O$$

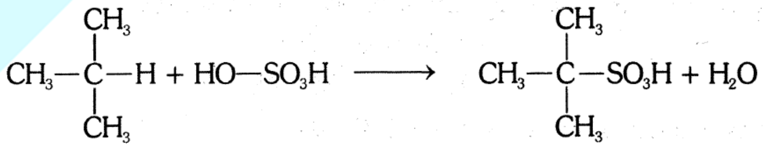
Since the reaction is carried at high temperature and in pressure, so the C–C bonds of alkanes also break during the reaction and a mixture of nitroalkanes is formed.

Ex. $CH_3–CH_3 + HNO_3 \xrightarrow{450°C} CH_3CH_2NO_2 + CH_3NO_2 + H_2O$



(c) **Sulphonation :** Replacement of H atom of alkane by $–SO_3H$ is known sulphonation. Alkane react with fuming H_2SO_4 or oleum ($H_2S_2O_7$).

Ex.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-H + HO-SO_3H \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-SO_3H + H_2O$$

2-Methyl propane

[The reactivity order for sulphonation is tert. H > Sec. H > prim. H]

Note : The reaction is observed in higher alkanes and the alkanes having 3º H.

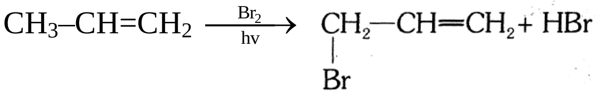
(d) **Chlorosulphonation (Reed reaction) :** Reaction with a mixture of SO_2 and Cl_2 at ordinary temperature in the presence of UV light is called chlorosulphonation.

$$C_3H_8 + SO_2 + Cl_2 \xrightarrow{UV} C_3H_7SO_2Cl + HCl$$

Propanesulphonyl chloride

GOLDEN KEY POINTS

Allylic or benzylic substitution by Br_2 (low concentration)/hv or NBS/hv



$$CH_3–CH=CH_2 \xrightarrow[hv]{Br_2} \underset{Br}{\underset{|}{CH_2}}–CH=CH_2 + HBr$$

Mechanism :

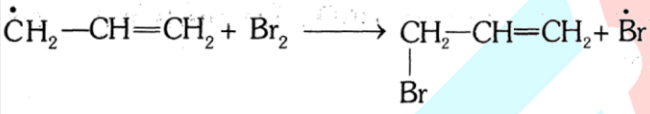
I **Chain initiation step :**

$$Br_2 \xrightarrow{hv} \dot{B}r + \dot{B}r$$

II **Chain propagation step :**

$$CH_3–CH=CH_2 + \dot{B}r \longrightarrow \dot{C}H_2–CH=CH_2 + HBr$$

(stable by resonance)

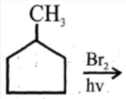


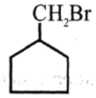
$$\dot{C}H_2–CH=CH_2 + Br_2 \longrightarrow \underset{Br}{\underset{|}{CH_2}}–CH=CH_2 + \dot{B}r$$

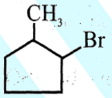
(Product)

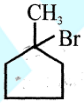
BEGINNER'S BOX-4

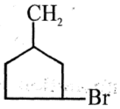
1. In the following reaction, the major product is : -



(1) 

(2) 

(3) 

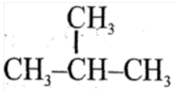
(4) 

2. The bond dissociation energy at the C–H bond for the compound :-

(I) CH_3H (II) $CH_3–CH_2–H$ (III) $CH_2=CH–CH_2–H$ (IV) $C_6H_5–H$

(1) I > II > III > IV (2) IV > III > II > I (3) IV > I > II > III (4) II > I > IV > III

3. Arrange the following in correct order of reactivity towards Cl_2/hv -

(A) CH_4 (B) CH_3CH_3 (C) $CH_3CH_2CH_3$ (D) 

$$CH_3–\overset{\overset{CH_3}{|}}{CH}–CH_3$$

(1) A > B > C > D (2) D > C > B > A (3) B > C > A > D (4) C > B > D > A

4. Which of the following are free radical reactions:-

(a) $CH_3CH=CH_2 + HBr \xrightarrow{perodixe} CH_3CH_2CH_2–Br$

(b) $CH_3CH=CH_2 + HCl \xrightarrow{perodixe} CH_3CH(Cl)CH_3$

(c) $CHFH=CH_2 + Cl_2 \xrightarrow{500°C} Cl–CH_2CH=CH_2$

(d) $CH_3CH_3 + Cl_2 \xrightarrow{hv} CH_3CH_2Cl$

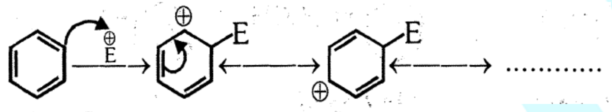
(1) Only d (2) a, c (3) a, b, d (4) a, c, d

(B) Electrophilic substitution reaction [ESR] : Characteristic reaction of arenes is ESR

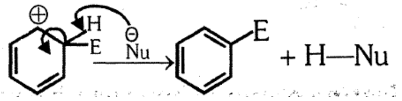
Mechanism :

Formation of $\overset{\oplus}{E}$ $\quad E{-}Nu \xrightarrow{\text{Catalyst}} \overset{\oplus}{E} + \overset{\ominus}{Nu}$

Attack of $\overset{\oplus}{E}$



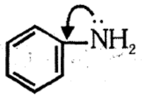
Abstraction of $\overset{\oplus}{H}$



Illustrations

Illustrations 2. Give reactivity order for electrophilic substitution reaction.\

(i)



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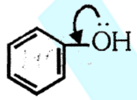
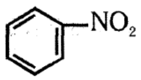


less EN of nitrogen so more +M so more e⁻ density so more reactive

less +M of –OH due to more EN

(ii)



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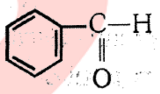
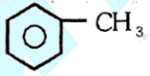
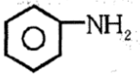


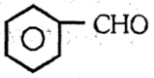
More –M of $-NO_2$ & more –I so e⁻ density decrease (more) so less reactive

less –M of –CHO & less –I so e⁻ density decreases (less) so more reactive.

(iii)







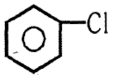
+H ↑

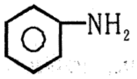
+M ↑

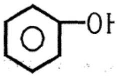
–M ↓

ESR order III > II > I > IV

(iv)







+H ↑

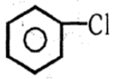
–I > +M ↓

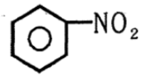
more +M due to less EN ↑

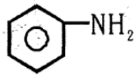
less +M ↑

ESR order III > IV > I > II

(v)







– I

– M

+ M

ESR order III > IV > I > II

(vi)

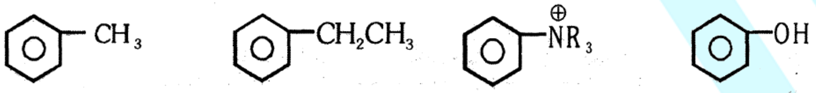

–H +H +M – M

ESR order III > II > I > IV

(vii)


+M –M (more) –I –M (less)

ESR order I > III > IV > II

(viii)


+H(more) +H (less) –I +M

ESR order IV > I > II > III

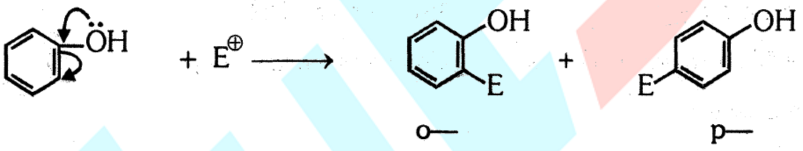
Note :

(1) **ortho/para directing group or activating group:** Group which direct electrophile on ortho and para position is called as o/p directing group.

These group increases electron density or increases reactivity of benzene ring so are called activating group.

These groups are :

$-\ddot{N}H_2$, $-\ddot{N}HR$, $-\ddot{N}R_2$, $-\ddot{O}H$, $-\ddot{O}R$, $-\ddot{N}HCOCH_3$, $-\ddot{S}H$, $-\ddot{O}COR$, $-CH_3$, $-CH_2CH_3$, $-CH(CH_3)_2$



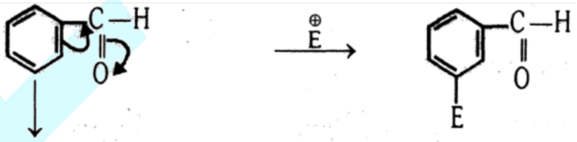
Due to +M/ +H of these groups electron density at ortho and para position is increased so electrophile easily attack on ortho/para position.

(2) **Meta directing or deactivating group :** Due to –M/–H of groups electron density at ortho and para position is less but more at meta position so electrophile attack on meta position. So, groups which direct electrophile on meta position are called as meta directing· groups.

These groups decrease electron density in benzene ring and decrease reactivity of benzene ring so are called as deactivating group.

These groups are :

–CHO, COOH, –COOR, –COR, –CN, $-NO_2$, $-SO_3H$, $-CX_3$

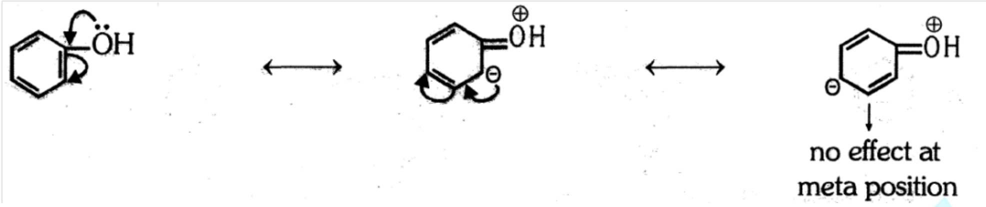


More e$^-$ density at meta position

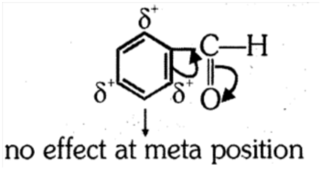
(3) Halogens are o/p directing group due to +M effect but are deactivating group due to –I > +M.

(4) M and H effect does not depend on distance while I–effect depends on distance In given example

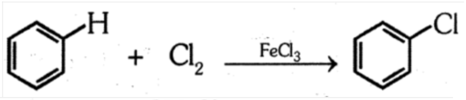
(5) M-effect at meta position is considered zero.

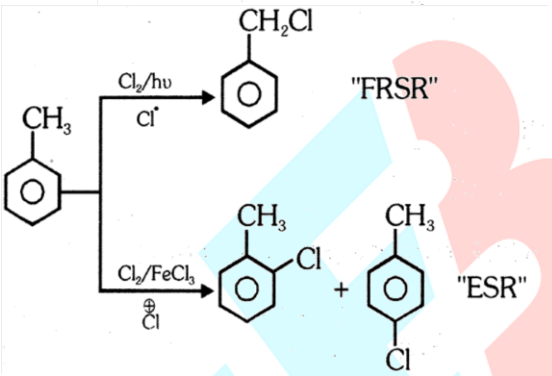


Similarly :



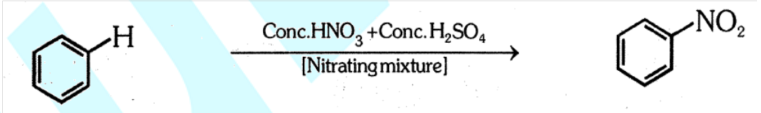
(i) Halogenations :



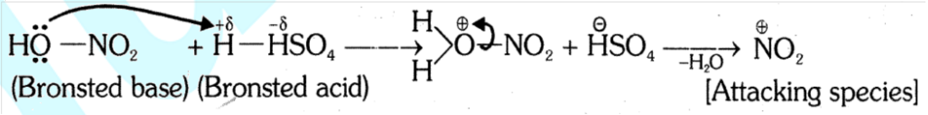


Note : CH_3 group in toluene is o/p directing and activating group.

(ii) Nitration :

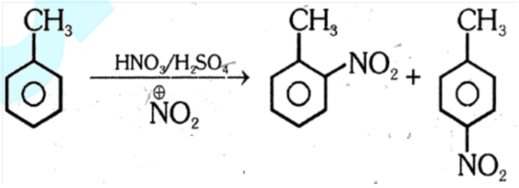


Formation of $\overset{\oplus}{E}$

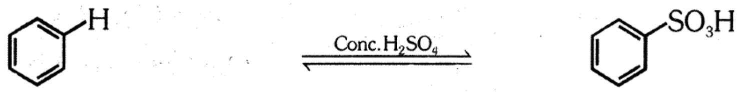


$$H\ddot{O}-NO_2 + \overset{+\delta}{H}-\overset{-\delta}{HSO_4} \longrightarrow \begin{matrix}H\\H\end{matrix}\!>\!\overset{\oplus}{O}-NO_2 + \overset{\ominus}{HSO_4} \xrightarrow[-H_2O]{} \overset{\oplus}{NO_2}$$

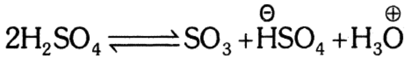
(Bronsted base) (Bronsted acid) [Attacking species]



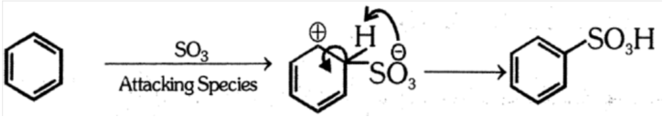
(iii) Sulphonation :

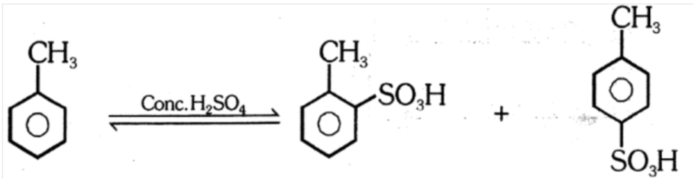


Mechanism :

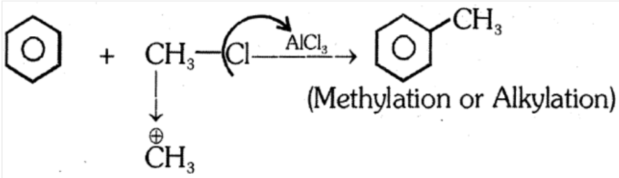


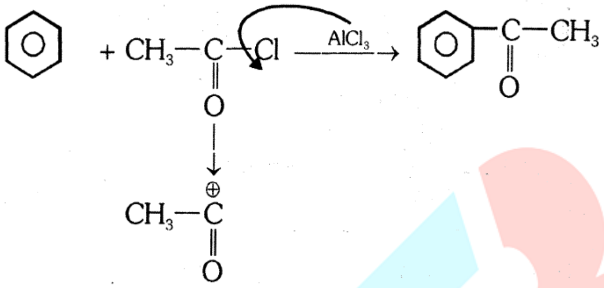
$$2H_2SO_4 \rightleftharpoons SO_3 + \overset{\ominus}{HSO_4} + H_3\overset{\oplus}{O}$$



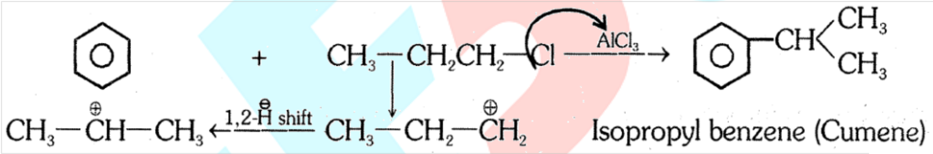


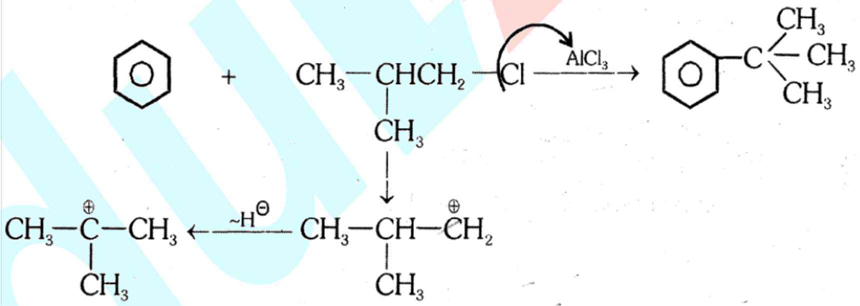
(iv) **Friedel crafts reaction [FCR] :** Alkylation or acylation of arenes in presence of lewis acid [$FeCl_3$, $A1Cl_3$ or $ZnCl_2$ …] is called as FCR.

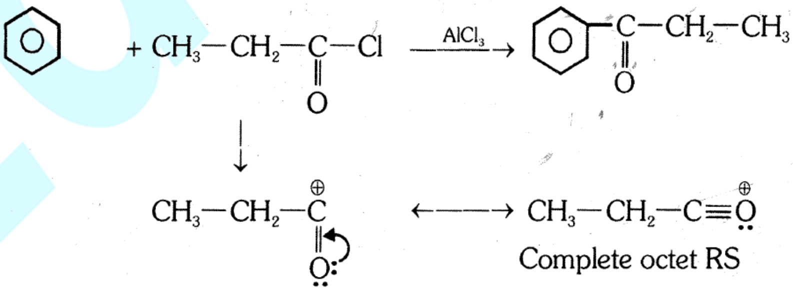


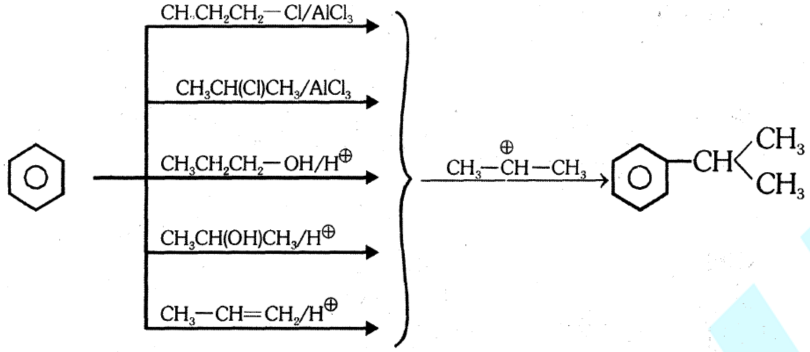


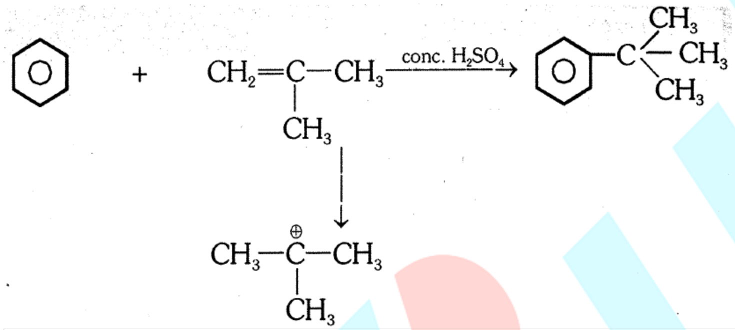
Intermediate carbocation is formed in FCR so rearrangement is possible.

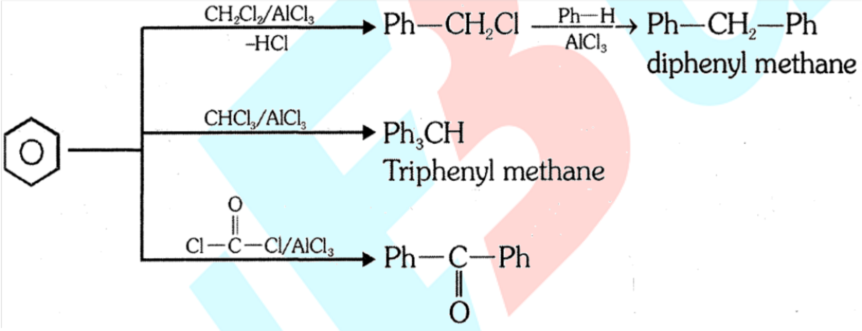




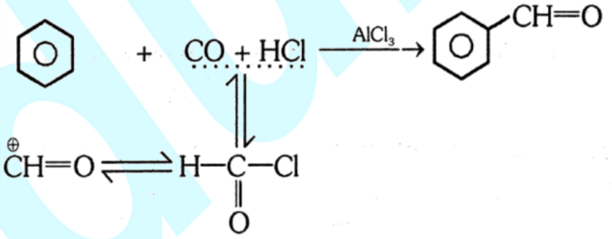




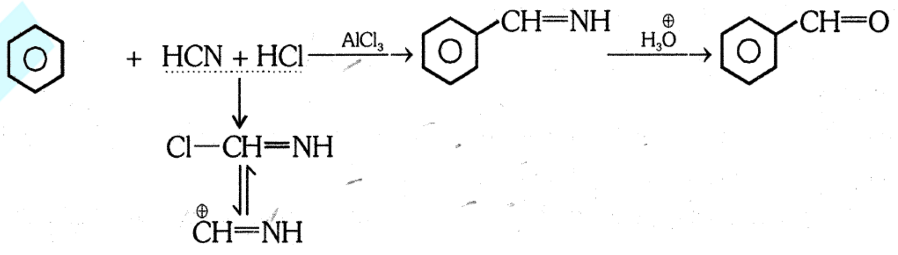




(vi) Gatterman's Koch Reaction :



(vii) Gatterman's Aldehyde synthesis :



GOLDEN KEY POINTS

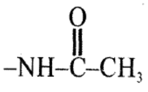
The important electrophiles used in the aromatic substitution are the following -

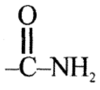
Electrophilic	Source	Name of substitution reaction

Cl^+ (Chloronium)	$Cl_2 + AlCl_3$ or $FeCl_3$	Chlorination
Br^+ (Bromonium)	$Br_2 + AlBr_3$ or $FeBr_3$	Bromination
NO_2^+ (Nitronium)	(conc. $HNO_3 + H_2SO_4$)	Nitration
SO_3 (Sulphertrioxide)	conc. H_2SO_4, fuming sulphuric acid	Sulphonation
R^+ (Alkyl carbonium)	$RX + AlX_3$ (X = Cl or Br) $ROH + H^+$	Friedel crafts (Alkylation)
$R-\overset{\oplus}{C}=O$ (Acyl carbonium)	$RCOCl + AlCl_3$	Friedel crafts (Acylation)

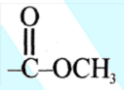
BEGINNER'S BOX-5

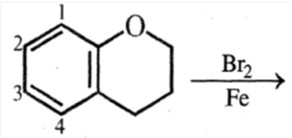
1. Which of the following group is ortho para director :-

(1) 
$-NH-\overset{\overset{O}{\|}}{C}-CH_3$

(2) 
$-\overset{\overset{O}{\|}}{C}-NH_2$

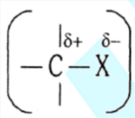
(3) $-C\equiv N$

(4) 
$-\overset{\overset{O}{\|}}{C}-OCH_3$

2. 

Substitution takes place at the position.

(1) 1 (2) 2 (3) 3 (4) Both (1) and (3)

(C) Nucleophilic substitution reaction (S_N) : Due to electronegativity difference the $-\overset{|}{\underset{|}{C}}-$ bond is polarised bond. 

Thus the C-atom of the $\overset{\delta+}{C}-\overset{\delta-}{X}$ bond becomes centre of attack by a nucleophile $(\overset{\ominus}{Nu})$.

$X^{\ominus}$ ion from R–X molecule is substituted by a $\overset{\ominus}{Nu}$. i.e.S_N reaction are the most common reactions in R–X.

$R-X + \overset{\ominus}{Nu} \longrightarrow R-Nu + X^{\ominus}$

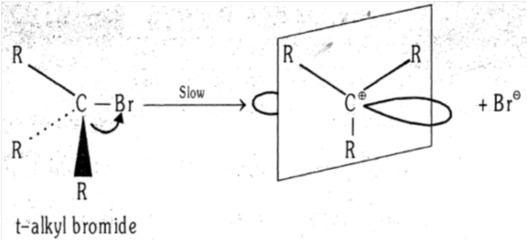
Two mechanism are observed in S_N reaction :

(a) S_{N^1} mechanism (b) S_{N^2} mechanism

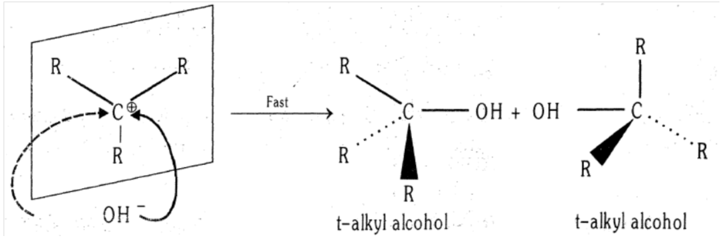
Mechanism of S_{N^1} and S_{N^2} :

S_{N^1} **Mechanism :** S_{N^1} 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 depends upon the concentration of tertiary alkyl halide alone.

∴ Rate= K[R_3C–Br]

It is obvious that the reaction follows first order kinetics, therefore reaction is called S_{N^1} .

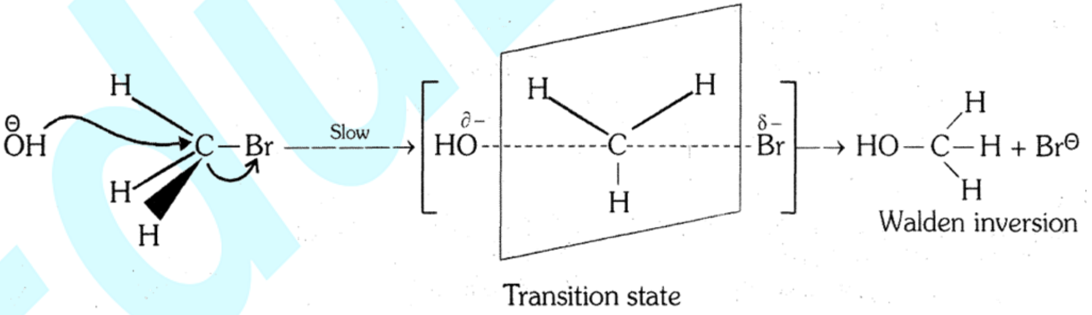
(ii) The reactivity order for S_{N^1} reaction ∝ stability of carbocations formed by halides.

∴ reactivity order of halides (S_{N^1}) varies as follows :

Benzyl halide > Allyl3° halide > Allyl 2° halide > Allyl 1° halide > 3° halide > 2° halide > 1° halide > methyl halide.

(iii) Remember that in case alkyl halide is optically active, S_{N^1} reactions lead to racemisation.

S_{N^2} **mechanism :** S_{N^2} stands for bimolecular nucleophilic substitution. In this type of nucleophilic substitution reaction, bond making and bond breaking process occur simultaneously.



(i) Reactivity of alkyl halides in S_{N^2} 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 :

allyl halide > CH_3f > 1° halide > 2°halide > 3° halide

(iii) The order of reactivity among 1° alkyl halides is: $CH_3X > C_2H_5X > C_3H_7X$ etc.

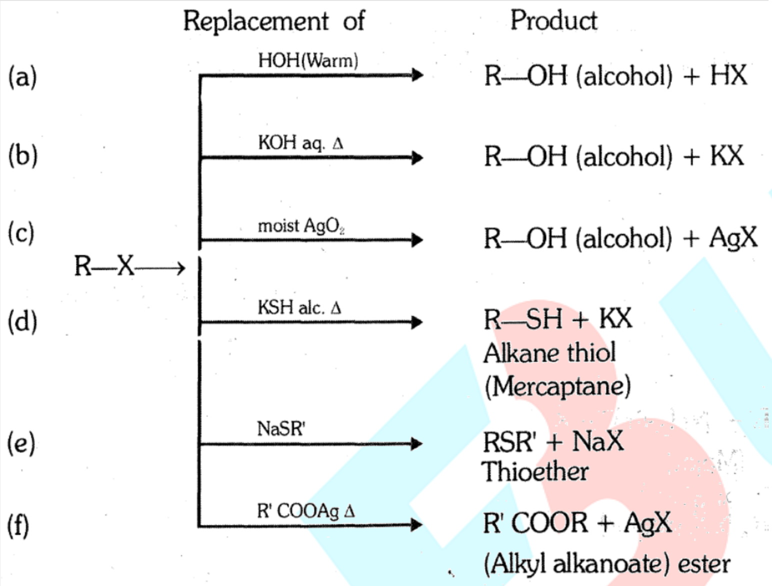
Remember that in case alkyl halide is optically active, S_{N^1} reactions lead to Walden inversion.

(iv) For a given alkyl group the order of reactivity is- (for S_{N^1} and S_{N^2} both) : **RI > RBr > RCI > RF**

(v) 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 it may proceed by E^1 or E^2 mechanism (analogous, to S_{N^1} and S_{N^2} mechanism).

The order of elimination reaction is : **3º halides > 2º halides > 1º halides**

(1) Nucleophilic substitution reaction (S_N) in alkyl halide :



(g) Reaction with KCN and AgCN :

$$\overset{\delta+}{R}-\overset{\delta-}{X} + \overset{+}{K}\overset{-}{C}N \xrightarrow[\Delta]{\text{Alc.}} R-C\equiv N + KX$$

Ionic bond　　　cyanide (major)

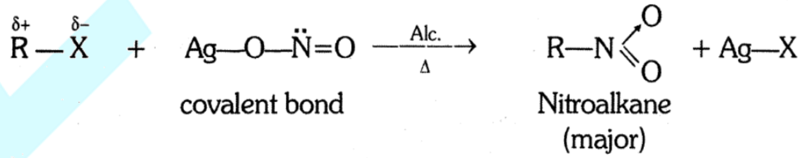
$$\overset{\delta+}{R}-\overset{\delta-}{X} + Ag-C\ddot{N} \xrightarrow[\Delta]{\text{Alc.}} R-N\rightleftarrows C + Ag-X$$

covalent bond　　　isocyanide (major)

(h) Reaction with KNO_2 and $AgNO_2$:

$$\overset{\delta+}{R}-\overset{\delta-}{X} + \overset{+}{K}\,\overset{-}{O}-N=O \xrightarrow[\Delta]{\text{Alc.}} R-O-N=O + KX$$

Ionic bond　　　(Alkyl nitrites) (major)



$$\overset{\delta+}{R}-\overset{\delta-}{X} + Ag-O-\ddot{N}=O \xrightarrow[\Delta]{\text{Alc.}} R-N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix} + Ag-X$$

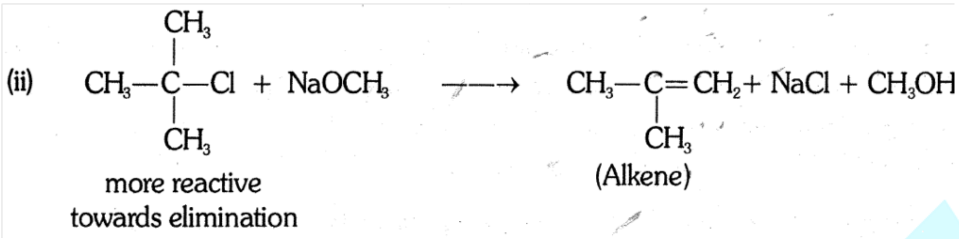
covalent bond　　　Nitroalkane (major)

(i) Reaction with NaOR' (Sodium alkoxide) :

$R-X + NaOR' \longrightarrow R-OR' + NaX$

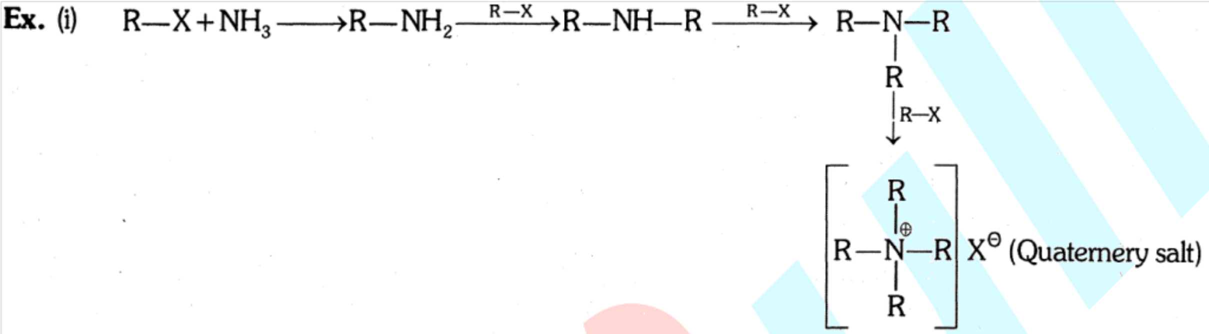
(Williamson ether synthesis reaction)

Ex. (i) $CH_3-CH_2-Cl + NaOCH_3 \longrightarrow CH_3-CH_2-O-CH_3$



$$\text{(ii)}\quad \underset{\substack{\text{more reactive}\\ \text{towards elimination}}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-Cl} + NaOCH_3 \longrightarrow \underset{(\text{Alkene})}{CH_3-\underset{\underset{\displaystyle CH_3}{|}}{C}=CH_2} + NaCl + CH_3OH$$

(j) Reaction with NH_3 :

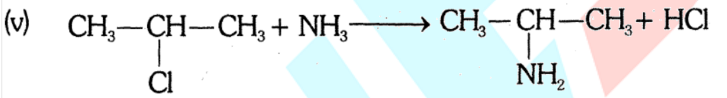


Ex. (i) $$R-X+NH_3 \longrightarrow R-NH_2 \xrightarrow{R-X} R-NH-R \xrightarrow{R-X} R-\underset{\underset{\displaystyle R}{|}}{N}-R \xrightarrow{R-X} \left[R-\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle R}{|}}{\overset{\oplus}{N}}}-R\right]X^{\ominus}\ (\text{Quaternery salt})$$

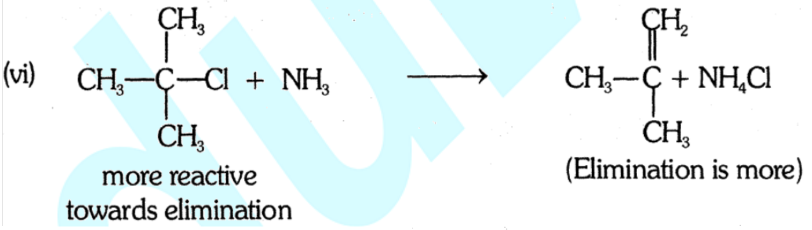
(ii) $$R-X+\underset{(\text{excess})}{NH_3} \longrightarrow \underset{(\text{Major})}{R-NH_2}+H-X$$

(iii) $$R-X+\underset{(\text{excess})}{NH_3} \longrightarrow R_4\overset{\oplus}{N}\overset{\ominus}{X}\ (\text{major})$$

(iv) $CH_3-CH_2-Cl+NH_3 \longrightarrow CH_3-CH_2-NH_2+HCl$



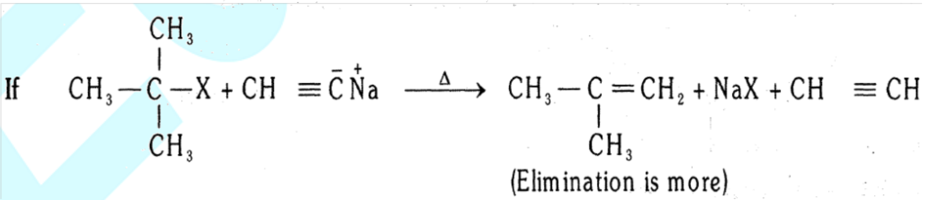
(v) $$CH_3-\underset{\underset{\displaystyle Cl}{|}}{CH}-CH_3+NH_3 \longrightarrow CH_3-\underset{\underset{\displaystyle NH_2}{|}}{CH}-CH_3+HCl$$



(vi) $$\underset{\substack{\text{more reactive}\\ \text{towards elimination}}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-Cl} + NH_3 \longrightarrow \underset{(\text{Elimination is more})}{CH_3-\overset{\overset{\displaystyle CH_2}{\|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}} + NH_4Cl$$

(k) Reaction with $CH\equiv CNa$:

$$R-X+CH\equiv CNa \xrightarrow{\Delta} R-C\equiv CH+NaX$$

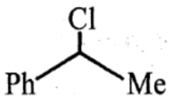


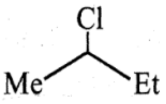
If $$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-X+CH\equiv\overset{-}{C}\overset{+}{Na} \xrightarrow{\Delta} \underset{(\text{Elimination is more})}{CH_3-\underset{\underset{\displaystyle CH_3}{|}}{C}=CH_2} + NaX + CH\equiv CH$$

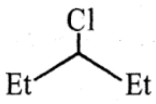
BEGINNER'S BOX-6

1. Which is most reactive for S_N1 reaction:-

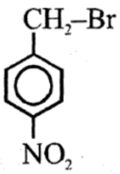
(1) 

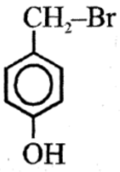
(2) 

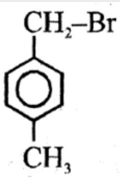
(3) 

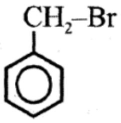
(4) 

2. Which is most reactive SN^1 ?

(1) 

(2) 

(3) 

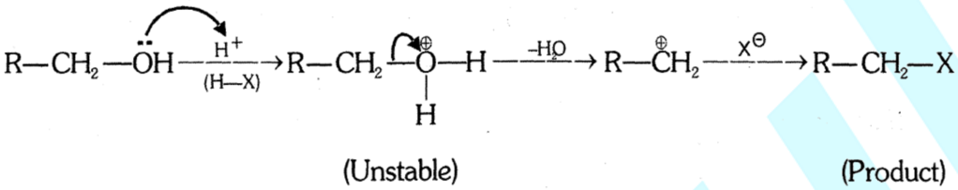
(4) 

NSR reaction of alcohol :-

(a) Reaction with HX :

eg. $R–CH_2–OH \xrightarrow[\text{anhy.ZnCl2}]{\text{H–X}} RCH_2–X$

Mechanism :



In this reaction, intermediate carbocation is formed so rearrangement can take place.
anhy. $ZnCl_2$ act as dehydrating agent and absorbs H_2O from the reaction so good yield of halide is obtained.
Also it generates H^+ from HCI.

$$HCl + ZnCl_2 \longrightarrow ZnCl_3^{\ominus} + H^{\oplus}$$

Reactivity order for alcohol :
[Reactivity ∝ stability of intermediate carbocationl], so reactivity order: **Tert. ale. > Sec. ale. > Pri. alc.**
Reactivity order of H–X is : **HI > HBr > HCl**
HI is maximum reactive so it reacts readily with 1°, 2° and 3° alcohols.

$$R–OH + HI \longrightarrow R–I + HP$$

HCl and also 1° alcohol are less reactive so $ZnCl_2$ or some amount of H_2SO_4 is needed to increase the reactivity.

eg. $CH_3–CH_2–OH + HCl \xrightarrow[\Delta]{ZnCl_2} CH_3–CH_2–Cl$

At normal condition :

$$CH_3–CH_2–OH + HCl \longrightarrow \times \text{ (no reaction)}$$

Note : [$HCl_{(conc)} + ZnCl_{2(anhydrous)}$ is called as **lucas reagent**, alcohol gives turbidity with lucas reagent.

Reactivity towards lucas reagent (difference in 1°, 2° and 3° alcohol).

	1° alcohol	2° alcohol	3° alcohol
Time to give turbidity	in 30 min. on heating	in 5 min.	in 2-3 second

(b) Reaction with phosphorus halides :-

$$R–OH + PCl_5 \longrightarrow R–Cl + POCl_3 + HCI$$
$$3R–OH + PCl_3 \longrightarrow 3RCl + H_3PO_3$$

PBr_3 and PI_3 are less stable, thus for bromides and Iodides, ($P + Br_2$) Or ($P + I_2$) mixture is used.

(c) Reaction with thionyl chloride-(Darzen's procedure) :-

$$R–OH + SOCl_2 \xrightarrow[\text{(1mole)}]{\text{Pyridine}} R–Cl + SO_2 + HCI$$

One mole One mole

NSR reaction in ether :-

Reaction with HX : Reactivity of HX [HI > HBr > HCl]

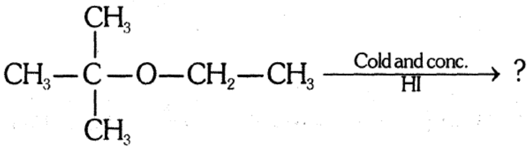
(A) **Reaction with cold cone. HX :** Ethers forms ox:bnium. salt with cold and cone. HCI (less reactive) Cold cone. HI and HBr (more reactive) break C–O bond.

(B) **Reaction with cone. HI or cone. HBr :**

$CH_3CH_2–O–CH_3 \xrightarrow{\text{hot and conc. HI}} CH_3CH_2–I + CH_3–I$

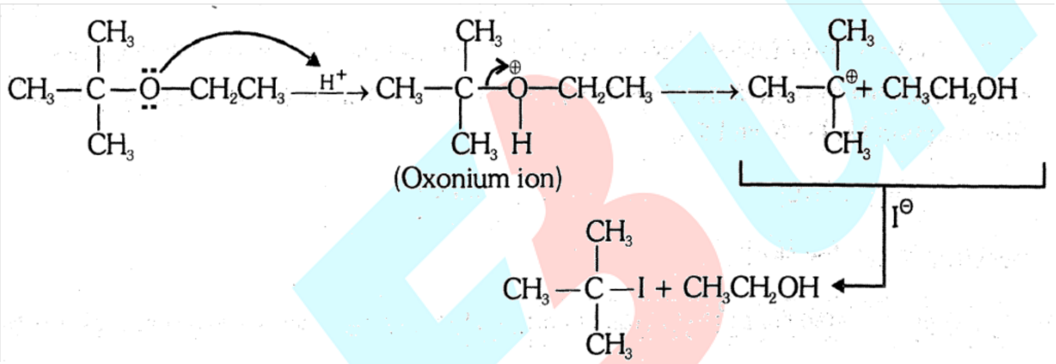
Illustrations

Illustrations 3.



$CH_3–\overset{CH_3}{\underset{CH_3}{C}}–O–CH_2–CH_3 \xrightarrow[\text{HI}]{\text{Cold and conc.}} ?$

Solution. **Mechanism**



If oxonium ion gives more stable carbocation $[Ph\overset{\oplus}{C}H_2$, $CH_2=CH–\overset{\oplus}{C}H_2$, $(CH_3)_3\overset{\oplus}{C}$] then SN^1 reaction occurs.

If oxonium ion gives less stable carbocation [$\overset{\oplus}{Ph}$, $CH_2=\overset{\oplus}{C}H_2$, $CH_3\overset{\oplus}{C}H_2$, $(CH_3)_2\overset{\oplus}{C}H$] then SN^2 reaction occurs, and $X^{\ominus}$ attacks at less hindered carbon

Illustration 4. $CH_3CH_2–O–CH_2Ph \xrightarrow[\text{HI}]{\text{Cold conc.}} CH_3CH_2–OH + PhCH_2–I$, write mechanism of given reaction.

Solution **Mechanism :**

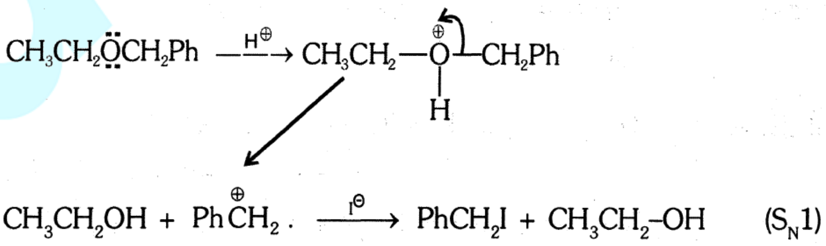
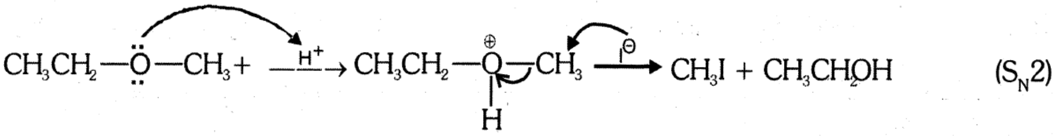


Illustration 5. $CH_3CH_2–O–CH_3 \xrightarrow{\text{conc. and cold HI}} ?$

Solution.

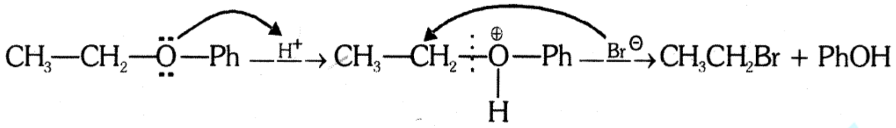


Oxonium ion gives less stable carbocation

SN^2 reaction $I^{\ominus}$ attacks at less hinderd carbon.

Illustration 6. $CH_3–CH_2–O–Ph \xrightarrow[\text{HBr}]{\text{cold and conc.}} ?$

Solution. **Mechanism :**



Note : If excess of HI/Δ is used then two moles of alkyl halides are formed.

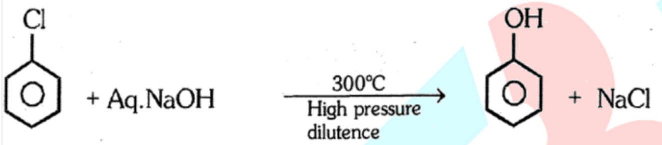
$CH_3CH_2–O–CH_2Ph \xrightarrow[\Delta]{\text{HI}} CH_3CH_2OH + PhCH_2I \xrightarrow[\Delta]{\text{HI}} CH_3CH_2–I + PhCH_2–I$

Illustration 7. $C_2H_5–O–C_2H_5 \xrightarrow{\text{hot and conc. HBr}} ? + ?$

Solution. $C_2H_5–Br + C_2H_5–Br$

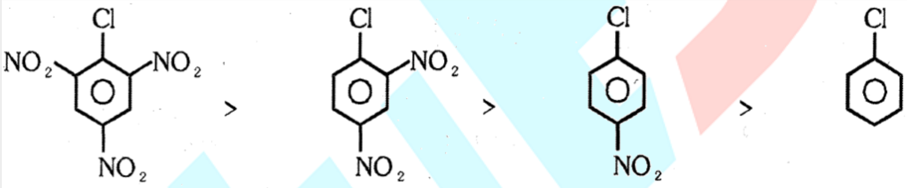
Aromatic nucleophilic substitution :

NSR reaction in halobenzene :-



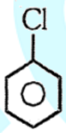
Presence of deactivating group at ortho and para position makes the nucleophilic substitution easier.

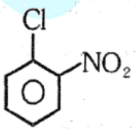
Reactivity Order : (Towards nucleophilic substatitution)

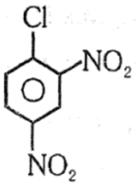


Illustrations

Illustration Which of the following undergoes Hydrolysis most easily :

(1)


(2)


(3)


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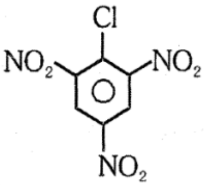


Solution. If there is more e- withdrawing groups then there will be more nuclephilic substitution reaction.

Ans. **(4)**

Illustration The product in the following reaction is :

$Ph–Cl + Fe/Br_2 \longrightarrow \text{Product}$

(1) o- bromo-chloro benzene

(2) p- bromo-chloro benzene

(3) (1) and (2) both

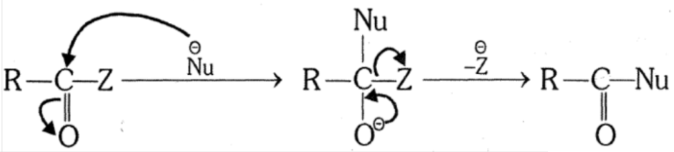
(4) 2, 4, 6-tribromo chloro benzene

Solution. Since –Cl group is deactivating and o/p directing group so o– and p– products are formed.

Ans. **(3)**

NSR in Acid derrivatives :

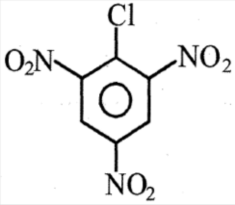
Example : Hydrolysis of acid derivatives :

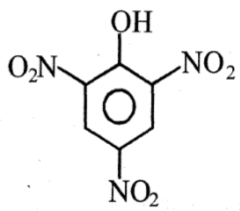


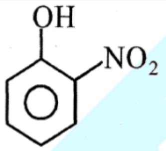
Where Z= —Cl, —OR, —NH$_2$, $-O-\underset{\underset{O}{\|}}{C}-R$

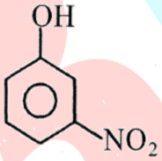
Here Z is a good leaving group

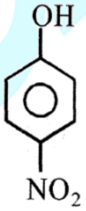
BEGINNER'S BOX-7

1.  $\xrightarrow[\Delta,\text{pressure}]{NaOH}$?

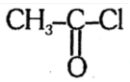
(1) 

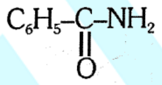
(2) 

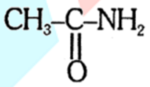
(3) 

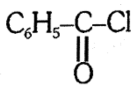
(4) 

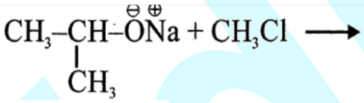
2. Which one of the following is least reactive with water.

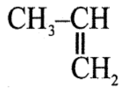
(1)  $CH_3-\underset{\underset{O}{\|}}{C}-Cl$

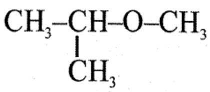
(2)  $C_6H_5-\underset{\underset{O}{\|}}{C}-NH_2$

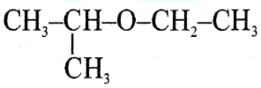
(3)  $CH_3-\underset{\underset{O}{\|}}{C}-NH_2$

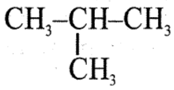
(4)  $C_6H_5-\underset{\underset{O}{\|}}{C}-Cl$

3.  $CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\ominus}{O}\overset{\oplus}{Na} + CH_3Cl \longrightarrow$

(1)  $CH_3-\underset{\underset{CH_2}{\|}}{C}H$

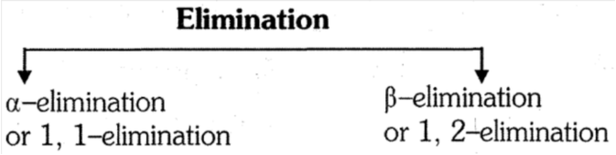
(2)  $CH_3-\underset{\underset{CH_3}{|}}{CH}-O-CH_3$

(3)  $CH_3-\underset{\underset{CH_3}{|}}{CH}-O-CH_2-CH_3$

(4)  $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3$

4.3 ELIMINATION REAC TIONS :

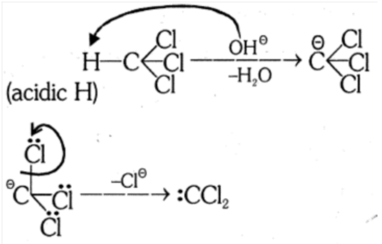
These reaction are involve elimination of small molecule from the substrate



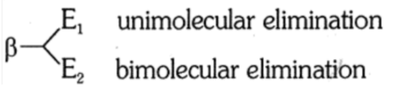
α-Elimination (1, 1-Elimination) : Removal of H and X from one C-atom

Example : $CHCl_3 \xrightarrow{KOH}$ $:CCl_2$ (dichloro carbine)

Mechanism :



α, β Elimination (b-elimination) : Removal of H and X from adjacent C-atoms

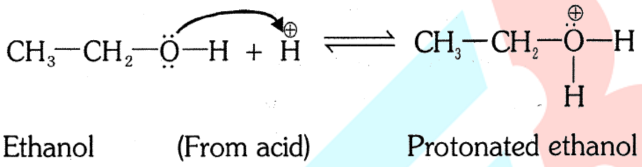


(a) Unimolecualr elimination (E_1) :-

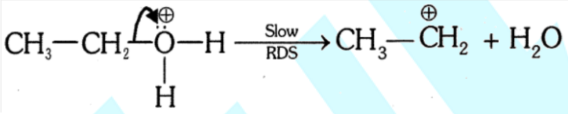
$CH_3–CH_2–OH \xrightarrow[443°K]{95\%H_2SO_4} CH_2=CH_2$

Mechanism of Reaction: The acidic dehydration of alcohol proceeds through the formation of a carbocation intermediate and is explained as follows :

Step I : Alcohol being a Lewis base accepts a proton (H^+) from the acid in a reversible step as follows:



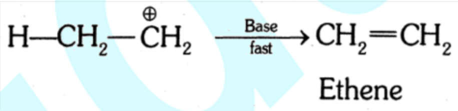
Step II : Due to presence of positive charge on electronegative oxygen, its electron accepting tendency increases. As a result C–O bond becomes weak and cleaves as follows :



Ethyl carbocation

This is a slow and is regarded as **rate determining step in E1 reaction.**

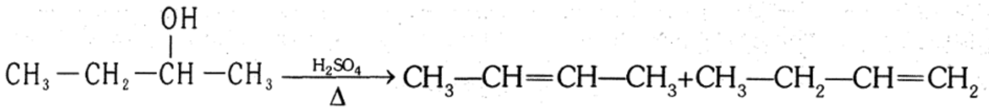
Step III : base removes Hα (proton) form carbocation and changes it into ethene in a fast step as follows:



Saytzeff rule : When two possible alkenes are obtained by the elimination reaction then that alkene containing maximum number of alkyl group on double bonded C-atoms is called Saytzeff's product and formed as major product.

Note : The alkene having less number of alkyl groups on double bonded C-atoms is called Hofmann's product.

Example : (i)



$$CH_3-CH_2-\overset{OH}{CH}-CH_3 \xrightarrow[\Delta]{H_2SO_4} CH_3-CH=CH-CH_3 + CH_3-CH_2-CH=CH_2$$

2–butanol

main product 2–butene 80% (Saytzeff's product)

1–butene 20% (Hoffmann's product)

(ii) $CH_3-CH_2-CH_2-CH_2-OH \xrightarrow[\Delta]{H_2SO_4} CH_3-CH=CH-CH_3 + CH_3CH_2CH=CH_2$

1–butanol

2–butene80% Main product

1–butene 20%

Mechanism : Acid catalyzed dehydration of alkanols proceeds via the formation of more stable carbonium ion.

$$CH_3-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{\oplus}{C}}-H \xrightarrow[\text{1, 2 hydride ion shift}]{\text{Rearrangement by}} CH_3-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{\oplus}{C}}-\underset{H}{\overset{H}{C}}-H$$

1⁰ Carbonium

2⁰ Carbonium more stable

$CH_3CH_2CH_2-CH_2-\ddot{\underset{\cdot\cdot}{O}}-H + \overset{\oplus}{H} \longrightarrow CH_3CH_2CH_2CH_2\overset{\oplus}{O}H_2$

$CH_3CH_2CH_2CH_2\overset{\oplus}{O}H_2 \longrightarrow CH_3CH_2CH_2-\overset{\oplus}{CH_2} + H_2O$

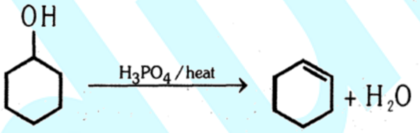
Primary carbonium ion

$$CH_3-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{\oplus}{C}}-\underset{H}{\overset{H}{C}}-H \xrightarrow[\text{a proton}]{\text{Elimination of}} \begin{cases} CH_3-CH=CH-CH_3 \\ CH_3-CH_2-CH=CH_2 \end{cases}$$

2- butene (major Product)

1–butene (minor product)

(iii)



Cyclohexanol Cyclohexene

Reactivity order of acidic dehydration of alcohols is 3° > 2° > 1° R–OH

- Rate of reaction ∝ [substrate]
- Molecularity of reaction = 1 (So reaction is called as E_1)
- In reaction intermediate carbocation is formed, so carbocation rearrangement is possible.

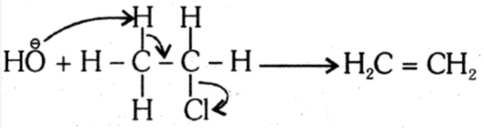
(b) Bimolecular elimination (E_2) :

Example:

(i) Dehydrohalogenation of halides by alcoholic KOH/NaNH$_2$:

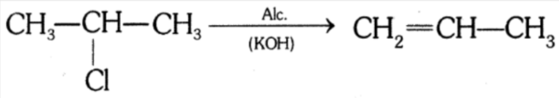
$$CH_3-CH_2-Cl + KOH_{(alc)} \longrightarrow CH_2=CH_2 + KCl + H_2O$$

Mechanism:

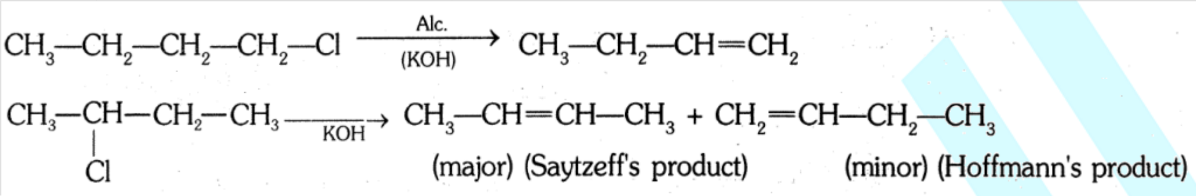


$$H\overset{\ominus}{O} + H-\underset{H}{\overset{H}{C}}-\underset{Cl}{\overset{H}{C}}-H \longrightarrow H_2C=CH_2$$

- ♦ Rate of reaction a [substrate] [base]
- ♦ Order of reaction = 2 (So reaction is E_2)
- ♦ In E_2 reaction intermediate (carbocation) is not formed. So there will be no carbocation rearrangement.



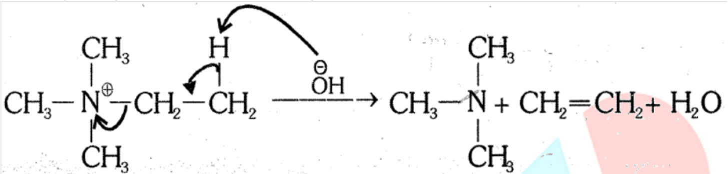
$$CH_3-\underset{\substack{|\\Cl}}{CH}-CH_3 \xrightarrow[(KOH)]{Alc.} CH_2=CH-CH_3$$



$$CH_3-CH_2-CH_2-CH_2-Cl \xrightarrow[(KOH)]{Alc.} CH_3-CH_2-CH=CH_2$$

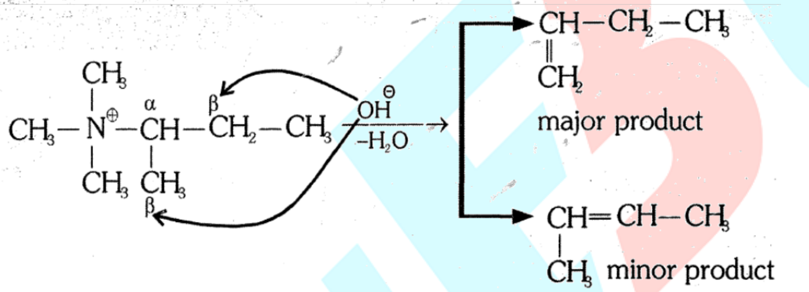
$$CH_3-\underset{\substack{|\\Cl}}{CH}-CH_2-CH_3 \xrightarrow[KOH]{} \underset{\text{(major) (Saytzeff's product)}}{CH_3-CH=CH-CH_3} + \underset{\text{(minor) (Hoffmann's product)}}{CH_2=CH-CH_2-CH_3}$$

(ii) Pyrolysis of tetra alkyl ammonium ion :



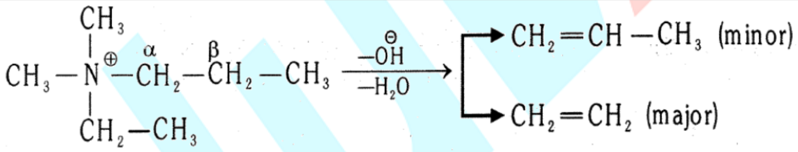
$$CH_3-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{N^{\oplus}}}-CH_2-\overset{\substack{H\\|}}{CH_2} \xrightarrow{\overset{\ominus}{O}H} CH_3-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{N}} + CH_2=CH_2 + H_2O$$

Ex.



$$CH_3-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{N^{\oplus}}}-\overset{\alpha}{\underset{\substack{|\\CH_3\ \beta}}{CH}}-\overset{\beta}{CH_2}-CH_3 \xrightarrow[-H_2O]{\overset{\ominus}{O}H} \begin{cases} \underset{\substack{\|\\CH_2}}{CH}-CH_2-CH_3 & \text{major product} \\ \underset{\substack{|\\CH_3}}{CH}=CH-CH_3 & \text{minor product} \end{cases}$$

Ex.



$$CH_3-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_2-CH_3}}{N^{\oplus}}}-\overset{\alpha}{CH_2}-\overset{\beta}{CH_2}-CH_3 \xrightarrow[-H_2O]{-\overset{\ominus}{O}H} \begin{cases} CH_2=CH-CH_3 & \text{(minor)} \\ CH_2=CH_2 & \text{(major)} \end{cases}$$

Note : Hoffmann's product is formed as major product.

Competition between substitution and elimination reactions

Reactivity order of alkyl halides : E_1- Reaction : $1° < 2° < \boxed{3°}$

E_2- Reaction : $1° < 2° < \boxed{3°}$

S_N1-Reaction : $1° < 2° < \boxed{3°}$

S_N2-Reaction : $\boxed{1°} > 2° > 3°$

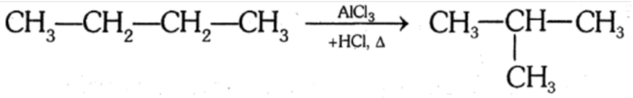
GOLDEN KEY POINTS

- SN^2/E^2 is favoured by high conc. of good neucleophile or strong base. ($CH_3O^{\ominus}$, $HO^{\ominus}$)
  Rate of Reaction ∝ (Substrate) (Reagent)
- SN^1/E^1 is favoured by low conc. of poor neucleophile or weak base (CH_3OH, H_2O)

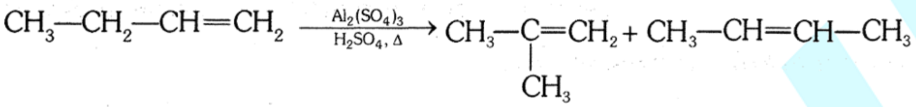
- If an alkyl halide, undergoes SN^2/SN^1 then SN^2 reaction will be favoured by high conc. of good neucleophile (negetively charged) in presence of polor aprotic solvent where as SN^1–reaction is favoured by low conc. of poor neucleophile (neutral) in presence of polar protic solvent.
  Polar protic solvent: H_2O, CH_3OH, HCOOH
  Polar aprotic solvent: DMSO, CH_3CN, $C_2H_5–O–C_2H_5$, DMF

4.4 ISOMERIZATION REACTIONS : These reaction involves the interconversion of one isomer into the another isomer.

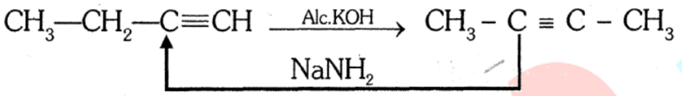
For example :

(i) 

$$CH_3-CH_2-CH_2-CH_3 \xrightarrow[+HCl,\ \Delta]{AlCl_3} CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

(ii) 

$$CH_3-CH_2-CH=CH_2 \xrightarrow[H_2SO_4,\ \Delta]{Al_2(SO_4)_3} CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2 + CH_3-CH=CH-CH_3$$

(iii) 

$$CH_3-CH_2-C\equiv CH \xrightarrow{Alc.KOH} CH_3-C\equiv C-CH_3$$

NaNH₂

BEGINNER'S BOX-8

1. Acidic dehydration of alcohol involves :

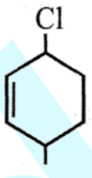
(1) E_1 elimination

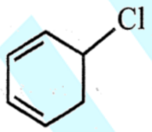
(2) Carbocation rearrangement if possible

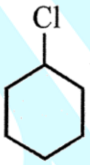
(3) Saytzeff's product is formed as major product

(4) All

2. Arrange the following in order of their reactivity toward dehydrohalogenation :-


I


II


III


IV

(1) II > I > III > IV (2) III > II > I > IV

(3) IV > III > I > II (4) I > II > III > IV

REACTION AT A GLANCE :

S.N	Class of compounds	Types of reactions
(i)	Alkane	Free radical substitution
(ii)	Alkene, alkyne	Electrophilic addition
(iii)	Alkyl halide	Nucleophilic substitution
(iv)	Aldehyde, ketone	Nucleophilic addition
(v)	Acid and their derivatives	Nucleophilic substitution
(vi)	Aromatic compounds	Electrophilc substitution

ANSWER KEY

BEGINNER'S BOX-1

1. (1) **2.** (1) **3.** (3)

BEGINNER'S BOX-2

1. (3) **2.** (1)

BEGINNER'S BOX-3

1. (1) **2.** (2) **3.** (2) **4.** (2)

BEGINNER'S BOX-4

1. (3) **2.** (3) **3.** (2) **4.** (4)

BEGINNER'S BOX-5

1. (1) **2.** (4)

BEGINNER'S BOX-6

1. (2) **2.** (2)

BEGINNER'S BOX-7

1. (1) **2.** (2) **3.** (2)

BEGINNER'S BOX-8

1. (4) **2.** (1)