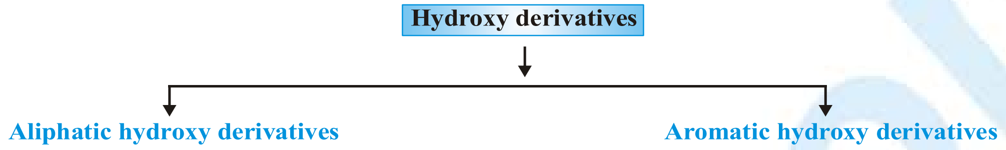
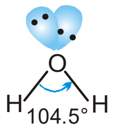
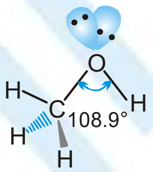
ALCOHOL, PHENOL & ETHER



Alcohols have sp^3 hybridized oxygen atoms, but the C – O – H bond angle in methanol (108.9°) is considerably larger than the H – O – H bond angle in water (104.5°) because the methyl group is much larger than a hydrogen atom. The bulky methyl group counteracts the bond angle compression caused by oxygen's nonbonding pairs of electrons. The O – H bond lengths are about the same in water and methanol (0.96 Å), but the C – O bond is considerably longer (1.4 Å), reflecting the larger covalent radius of carbon compared to hydrogen.



water



methyl alcohol

(I) ALIPHATIC HYDROXY DERIVATIVES :

Hydroxy derivatives in which —OH is directly attached to sp^3 C (Alcoholic compounds).

(II) Aromatic hydroxy derivatives :

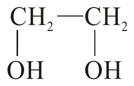
Hydroxy derivatives in which —OH is directly attached to sp^2 C or benzene ring (Phenolic compounds).

ALIPHATIC HYDROXY DERIVATIVES

(a) Classification according to number of —OH groups :

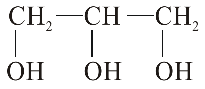
(i) Monohydric [one –OH] ⟶ $CH_3CH_2—OH$

(ii) Dihydric [two –OH] ⟶



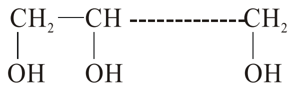
$$\underset{OH}{\underset{|}{CH_2}}—\underset{OH}{\underset{|}{CH_2}}$$

(iii) Trihydric [three –OH] ⟶



$$\underset{OH}{\underset{|}{CH_2}}—\underset{OH}{\underset{|}{CH}}—\underset{OH}{\underset{|}{CH_2}}$$

(iv) Polyhydric [n –OH] ⟶



$$\underset{OH}{\underset{|}{CH_2}}—\underset{OH}{\underset{|}{CH}}\text{------------}\underset{OH}{\underset{|}{CH_2}}$$

(b) Classification according to nature of carbon :

(i) p or 1° – alcohol $\longrightarrow$ CH_3CH_2-OH

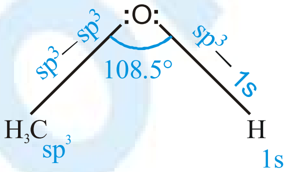
(ii) s or 2° – alcohol $\longrightarrow$ $(CH_3)_2CH-OH$

(i) t or 3° – alcohol $\longrightarrow$ $(CH_3)_3C-OH$

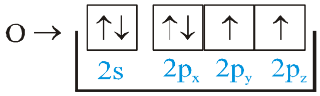
ALCOHOLS

Structure of alcohol

Alcohols are bent molecules. The carbon atom (linked with 'O' atom of –OH group) is sp^3 hybridised. The central 'O' atom is also in sp^3 state of hybridisation. The bond angle is 108.5^0. In sp^3 hybridisation of O - $2s^2,2p_x^2\,2p_y^1\,2p_z^1$ orbitals hybridised to form sp^3 orbitals



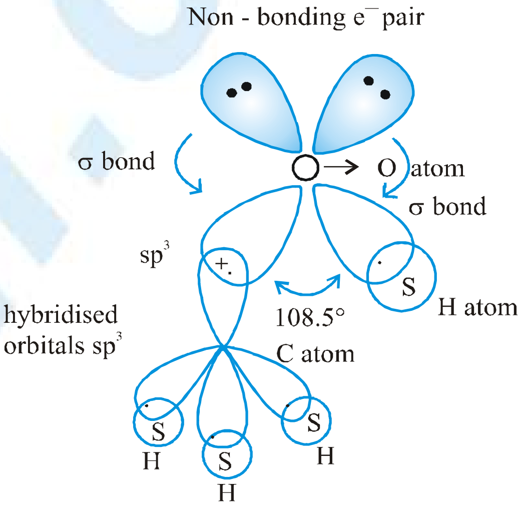
Structure of CH_3OH



sp^3 hybridisation

In these four orbitals two containing one electron each and two containing two electrons each. Orbitals containing two electrons do not take part in bonding. Other two half filled orbitals form σ bond with s-orbitals of H -atom and hybridised orbital of C-atom (O—C).

Due to lone pair effect the bond angle of tetrahedral oxygen atom is lesser than normal tetrahedral structure ($109^028'$).



MONOHYDRIC ALCOHOL

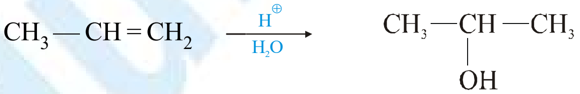
GENERAL METHODS OF PREPARATION

(a) From alkanes (By oxidation) :

$$(CH_3)_3\,C—H \xrightarrow[\Delta]{H^{\oplus}/KMnO_4} (CH_3)_3\,C—OH$$

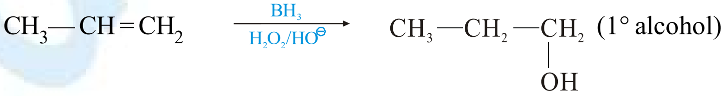
(b) From alkenes :

(i) By hydration :



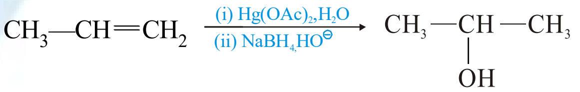
$$CH_3—CH=CH_2 \xrightarrow[H_2O]{H^{\oplus}} CH_3—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_3$$

(ii) By hydroboration oxidation :



$$CH_3—CH=CH_2 \xrightarrow[H_2O_2/HO^{\ominus}]{BH_3} CH_3—CH_2—\underset{\displaystyle OH}{\underset{|}{CH_2}}\ (1°\text{ alcohol})$$

(iii) By oxymercuration demercuration :



$$CH_3—CH=CH_2 \xrightarrow[\text{(ii) }NaBH_4,HO^{\ominus}]{\text{(i) }Hg(OAc)_2,H_2O} CH_3—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_3$$

(c) From alkyl halides (By hydrolysis) :

$$CH_3—CH_2—Cl \xrightarrow[\text{or Moist } Ag_2O]{\text{Aq. KOH}} CH_3CH_2—OH$$

(d) From carbonyl compounds (By reduction) :

$$>C{=}O \xrightarrow{\text{Reducing agent}} >CH—OH$$

Reducing agents may be,

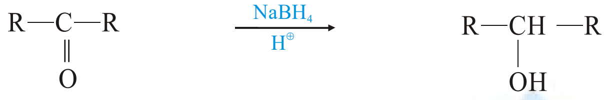
$LiAlH_4/H^{\oplus}$, $NaBH_4/H^{\oplus}$

Na + EtOH [Bouveault-blanc Reduction]

NaH [Darzen reduction]

Ni / H_2

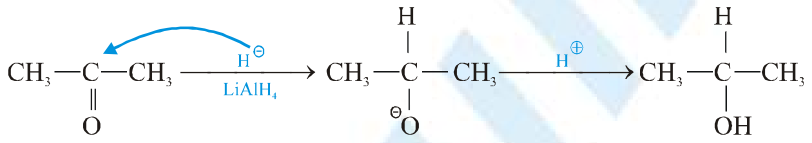
$$R—CHO \xrightarrow[H^{\oplus}]{LiAlH_4} R—CH_2—OH$$

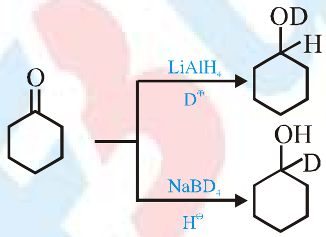


$$R—\underset{\underset{O}{\|}}{C}—R \xrightarrow[H^{\oplus}]{NaBH_4} R—\underset{\underset{OH}{|}}{CH}—R$$

$$CH_3—\underset{\underset{O}{\|}}{C}—CH_3 \xrightarrow[H^{\oplus}]{LiAlH_4} ?$$

MECHANISM :





$$\underset{\text{Crotonaldehyde}}{CH_3—CH{=}CH—CHO} \xrightarrow[H^{\oplus}]{LiAlH_4} CH_3—CH{=}CH—CH_2—OH$$

$$\underset{\text{Cinnamaldehyde}}{Ph—CH{=}CH—CHO} \xrightarrow[H^{\oplus}/OH^{-}]{LiAlH_4} Ph—CH_2—CH_2—CH_2—OH$$

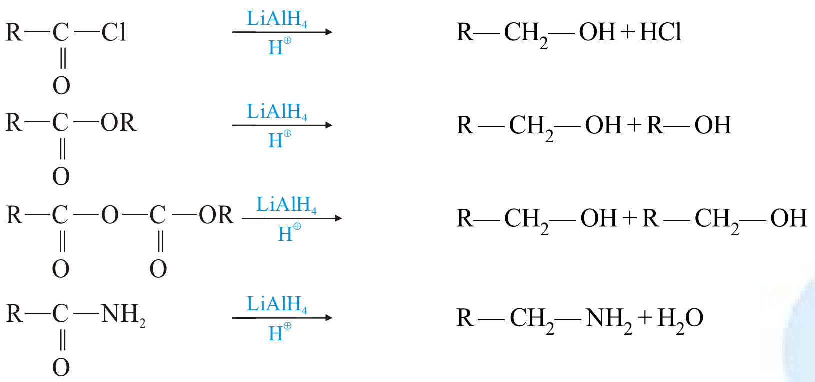
(e) From ethers :

$$R—O—R \xrightarrow{\text{dil. } H_2SO_4} R—OH + R—OH$$

$$CH_3—O—CH_2CH_3 \xrightarrow{\text{dil. } H_2SO_4} CH_3—OH + CH_3CH_2—OH$$

(f) From acid and derivatives (By reduction) :

$$R—COOH \xrightarrow[H^{\oplus}]{LiAlH_4} R—CH_2—OH + H_2O$$



$$R-\underset{\underset{O}{\|}}{C}-Cl \xrightarrow[H^{\oplus}]{LiAlH_4} R-CH_2-OH+HCl$$

$$R-\underset{\underset{O}{\|}}{C}-OR \xrightarrow[H^{\oplus}]{LiAlH_4} R-CH_2-OH+R-OH$$

$$R-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-OR \xrightarrow[H^{\oplus}]{LiAlH_4} R-CH_2-OH+R-CH_2-OH$$

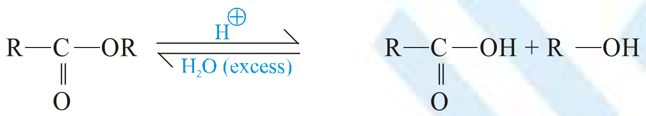
$$R-\underset{\underset{O}{\|}}{C}-NH_2 \xrightarrow[H^{\oplus}]{LiAlH_4} R-CH_2-NH_2+H_2O$$

(g) From esters (By hydrolysis) :

(i) By alkaline hydrolysis :

$$R-\underset{\underset{O}{\|}}{C}-OR \xrightarrow{NaOH} R-\underset{\underset{O}{\|}}{C}-ONa + R-OH$$

(ii) By acidic hydrolysis :



$$R-\underset{\underset{O}{\|}}{C}-OR \underset{H_2O\ (excess)}{\overset{H^{\oplus}}{\rightleftharpoons}} R-\underset{\underset{O}{\|}}{C}-OH + R-OH$$

$$CH_3-\underset{\underset{O}{\|}}{C}-\overset{18}{O}C_2H_5 \overset{H_3O^{\oplus}}{\rightleftharpoons} CH_3-\underset{\underset{O}{\|}}{C}-OH + C_2H_5\overset{18}{O}H$$

This reaction is reversible reaction and it's order is 1 and it is also called Pseudo-Unimolecular reaction.

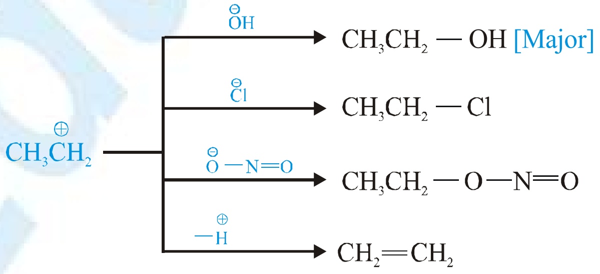
(h) From p-amines :

$$R-NH_2 \xrightarrow[\text{or } HNO_2]{NaNO_2+HCl} R-OH+N_2+H_2O$$

$$CH_3CH_2-NH_2 \xrightarrow{HNO_2} CH_3CH_2-OH+N_2+H_2O$$

MECHANISM :

$$CH_3CH_2-NH_2 \xrightarrow{NaNO_2+HCl} \underset{\text{Unstable}}{CH_3CH_2-\overset{\oplus}{N_2}\overset{\ominus}{Cl}} \longrightarrow CH_3\overset{\oplus}{C}H_2+N_2+\overset{\ominus}{Cl}$$



$$CH_3\overset{\oplus}{C}H_2 \xrightarrow{\overset{\ominus}{O}H} CH_3CH_2-OH\ \text{[Major]}$$

$$CH_3\overset{\oplus}{C}H_2 \xrightarrow{\overset{\ominus}{Cl}} CH_3CH_2-Cl$$

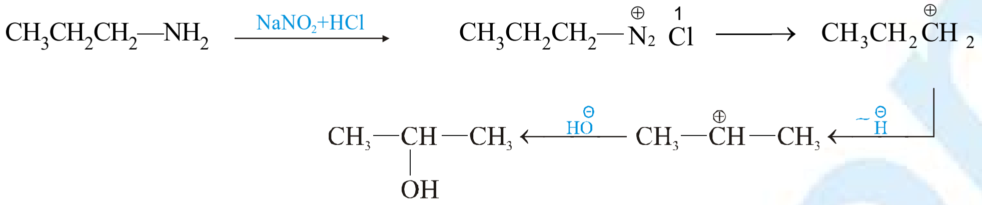
$$CH_3\overset{\oplus}{C}H_2 \xrightarrow{\overset{\ominus}{O}-N=O} CH_3CH_2-O-N=O$$

$$CH_3\overset{\oplus}{C}H_2 \xrightarrow{-\overset{\oplus}{H}} CH_2=CH_2$$

Inter mediate is carbocation so rearrangement may be possible.

Ex. $CH_3CH_2CH_2—NH_2 \xrightarrow{NaNO_2+HCl} ?$

Sol. **Mechanism :**



$$CH_3CH_2CH_2—NH_2 \xrightarrow{NaNO_2+HCl} CH_3CH_2CH_2—\overset{\oplus}{N_2}\ \overset{1}{Cl} \longrightarrow CH_3CH_2\overset{\oplus}{CH}{}_2$$

$$\underset{\displaystyle OH}{CH_3—\underset{|}{CH}—CH_3} \xleftarrow{\overset{\ominus}{HO}} CH_3—\overset{\oplus}{CH}—CH_3 \xleftarrow{\sim\overset{\ominus}{H}}$$

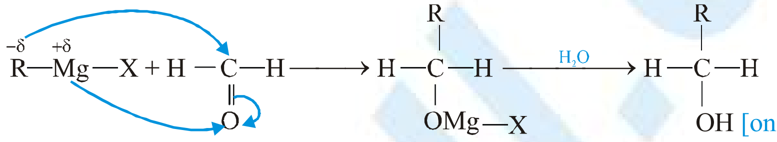
Exception : $CH_3 - NH_2 \xrightarrow{HNO_2} CH_3 - O - CH_3$

(i) From Grignard reagent :

(i) p-alcohol :

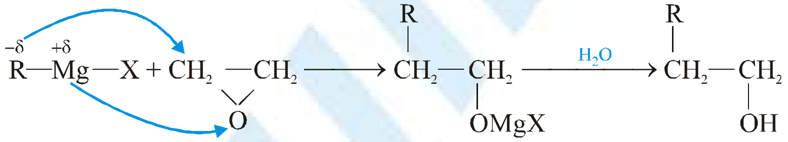
$R—Mg—X + [O] \longrightarrow R—O—MgX \xrightarrow{H_2O} R—OH$

[Same C-p-alcohol]



$$\overset{-\delta}{R}—\overset{+\delta}{Mg}—X + H—\underset{\underset{\displaystyle O}{\|}}{C}—H \longrightarrow H—\underset{\underset{\displaystyle OMg—X}{|}}{\overset{\overset{\displaystyle R}{|}}{C}}—H \xrightarrow{H_2O} H—\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle R}{|}}{C}}—H$$

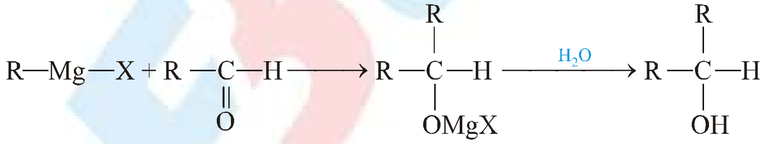
[one C more p-alcohol]



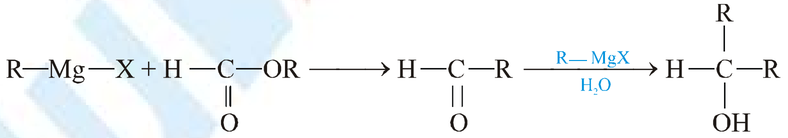
$$\overset{-\delta}{R}—\overset{+\delta}{Mg}—X + \underbrace{CH_2—CH_2}_{\displaystyle O} \longrightarrow \overset{\overset{\displaystyle R}{|}}{CH_2}—\underset{\underset{\displaystyle OMgX}{|}}{CH_2} \xrightarrow{H_2O} \overset{\overset{\displaystyle R}{|}}{CH_2}—\underset{\underset{\displaystyle OH}{|}}{CH_2}$$

[two C more p-alcohol]

(ii) s-alcohol :

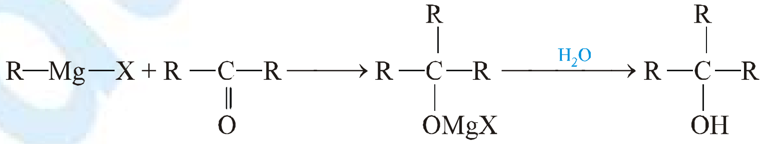


$$R—Mg—X + R—\underset{\underset{\displaystyle O}{\|}}{C}—H \longrightarrow R—\underset{\underset{\displaystyle OMgX}{|}}{\overset{\overset{\displaystyle R}{|}}{C}}—H \xrightarrow{H_2O} R—\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle R}{|}}{C}}—H$$

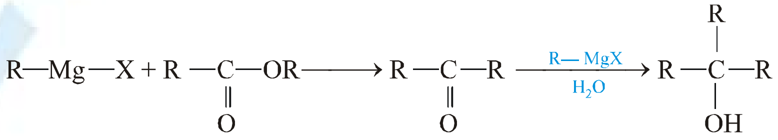


$$R—Mg—X + H—\underset{\underset{\displaystyle O}{\|}}{C}—OR \longrightarrow H—\underset{\underset{\displaystyle O}{\|}}{C}—R \xrightarrow[H_2O]{R—MgX} H—\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle R}{|}}{C}}—R$$

(iii) t-alcohol :



$$R—Mg—X + R—\underset{\underset{\displaystyle O}{\|}}{C}—R \longrightarrow R—\underset{\underset{\displaystyle OMgX}{|}}{\overset{\overset{\displaystyle R}{|}}{C}}—R \xrightarrow{H_2O} R—\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle R}{|}}{C}}—R$$



$$R—Mg—X + R—\underset{\underset{\displaystyle O}{\|}}{C}—OR \longrightarrow R—\underset{\underset{\displaystyle O}{\|}}{C}—R \xrightarrow[H_2O]{R—MgX} R—\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle R}{|}}{C}}—R$$

PHYSICAL PROPERTIES

(i) C_1 to C_{11} are colourless liquids and high alcohols are solids.

(ii) Density of monohydric alcohol is less than H_2O.

(iii) Density $\propto$ mol. wt. (for monohydric alcohol).

(iv) **Solubility :**

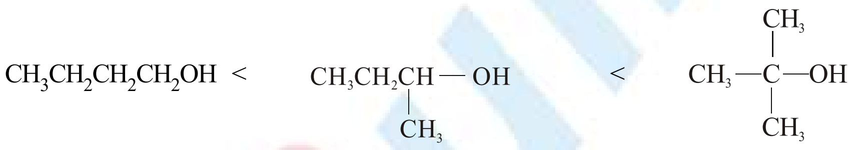
- The first three members are completely miscible with water. The higher members are almost insoluble in water but are soluble in organic solvents like benzene, ether etc.
- The solubility of lower alcohols is due to the existence of hydrogen bonds between water and polar O–H groups of alcohol molecules.
- The solubility of alcohols in water decreases with increase in molecular mass.
- Among the isomeric alcohols the solubility decrease with branching of chain increases.

C_1 to C_3 and t-butyl alcohol is completely soluble in H_2O due to H–bonding.

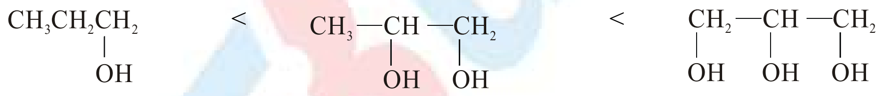
$$\boxed{\text{solubility} \propto \text{No. of side chains} \propto \frac{1}{\text{molecular weight}}}$$

Order of solubility :

$C_4H_9OH > C_5H_{11}OH > C_6H_{13}OH$



$CH_3CH_2CH_2CH_2OH < CH_3CH_2CH(CH_3)-OH < CH_3-C(CH_3)_2-OH$



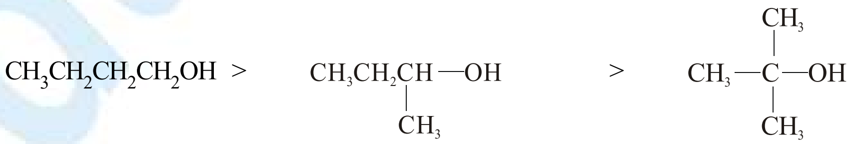
$CH_3CH_2CH_2OH < CH_3-CH(OH)-CH_2OH < CH_2(OH)-CH(OH)-CH_2OH$

[Number of —OH increases, H-bonding increases]

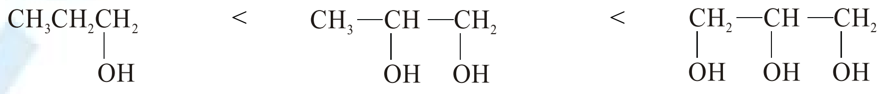
(v) **Boiling points :** B.P. $\propto$ molecular weight

If molecular wt. is same then B.P. $\propto \frac{1}{\text{branching}}$

Order of BP : $C_4H_9OH < C_5H_{11}OH < C_6H_{13}OH$



$CH_3CH_2CH_2CH_2OH > CH_3CH_2CH(CH_3)-OH > CH_3-C(CH_3)_2-OH$

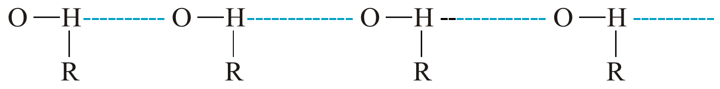


$CH_3CH_2CH_2OH < CH_3-CH(OH)-CH_2OH < CH_2(OH)-CH(OH)-CH_2OH$

[Number of OH increases, H-bonding increases]

Ex. Boiling point of alcohol is more than corresponding ether. Why ?

Sol. **Reason :** H-bonding in alcohol.



Ex. Boiling point of alcohol is less than corresponding carboxylic acid. Why ?

Sol. **Reason :** Dimer formation in carboxylic acid.

CHEMICAL PROPERTIES

Monohydric alcohol show following reactions

(A) Reaction involving cleavage of O ⌇ H

(B) Reaction involving cleavage of C ⌇ OH

(C) Reaction involving complete molecule of alcohol

(A) **Reaction involving cleavage of O ⌇ H:** Reactivity order (Acidic nature) is

$$CH_3—OH > CH_3CH_2—OH > (CH_3)_2CH—OH > (CH_3)_3C—OH$$

(i) **Acidic nature :**

$$H_2O > R—OH > CH\equiv CH > NH_3 \quad \text{(Acidic strength)}$$

Alcohols are less acidic than H_2O and neutral for litmus paper and gives H_2 with active metals (Na, K)

$$R—OH + Na \longrightarrow R—ONa + \frac{1}{2}H_2$$

$$R—OH + K \longrightarrow R—OK + \frac{1}{2}H_2$$

(ii) **Reaction with CS_2 :**

$$R—OH + Na \longrightarrow R—ONa + \frac{1}{2}H_2$$

$$R—ONa + S{=}C{=}S \longrightarrow R—O—\underset{\underset{\displaystyle S}{\|}}{C}—S—Na$$

Sodium alkyl xanthate (Used as floating agent)

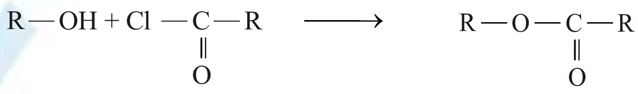
(iii) **Alkylation:**

$$R—OH \xrightarrow{CH_2N_2/\Delta} R—O—CH_2—H$$

$$R—OH \xrightarrow{Na} R—ONa \xrightarrow{R-X} R—O—R$$

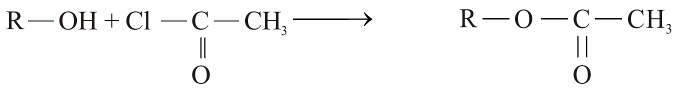
(Williamson synthesis)

(iv) **Acylation :**



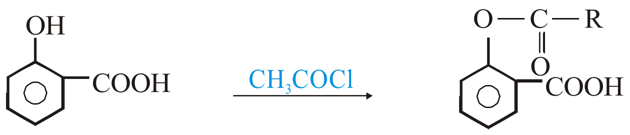
$$R—OH + Cl—\underset{\underset{\displaystyle O}{\|}}{C}—R \longrightarrow R—O—\underset{\underset{\displaystyle O}{\|}}{C}—R$$

(Acylation)



$$\mathrm{R-OH + Cl-\underset{\underset{O}{\|}}{C}-CH_3 \longrightarrow R-O-\underset{\underset{O}{\|}}{C}-CH_3}$$

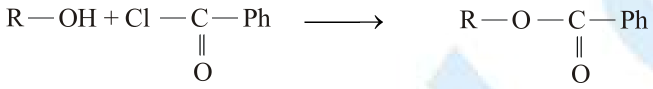
(Acetylation)



Salicylic acid

Acetoxy benzoic acid
Acetyl salicylic acid
Aspirin [Used as analgesic]

(v) Benzoylation : (Schotten Baumann's Reaction) :



$$\mathrm{R-OH + Cl-\underset{\underset{O}{\|}}{C}-Ph \longrightarrow R-O-\underset{\underset{O}{\|}}{C}-Ph}$$

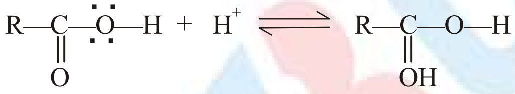
(Benzoylation)

(vi) Esterification : Conc. H_2SO_4 is used as catalyst and dehydrating agent.

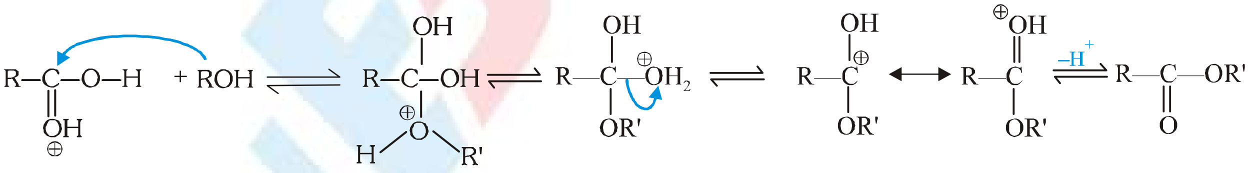
$$\mathrm{R-\underset{\underset{O}{\|}}{C}-OH + R-OH \xrightarrow{Conc.\ H_2SO_4} R-\underset{\underset{O}{\|}}{C}-OR + H_2O}$$

MECHANISM :

$$\mathrm{H_2SO_4 \longrightarrow H^+ + HSO_4^-}$$

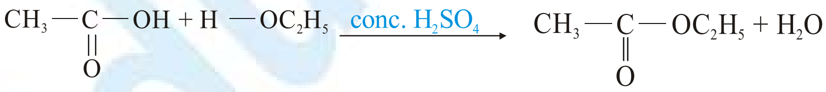


$$\mathrm{R-\underset{\underset{O}{\|}}{C}-\ddot{O}-H + H^+ \rightleftharpoons R-\underset{\underset{OH}{\|}}{C}-O-H}$$



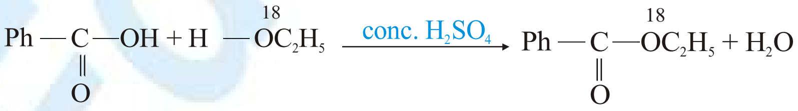
Note : This is a laboratory method to prepare ester.

Ex.



$$\mathrm{CH_3-\underset{\underset{O}{\|}}{C}-OH + H-OC_2H_5 \xrightarrow{conc.\ H_2SO_4} CH_3-\underset{\underset{O}{\|}}{C}-OC_2H_5 + H_2O}$$

Ex.



$$\mathrm{Ph-\underset{\underset{O}{\|}}{C}-OH + H-{}^{18}OC_2H_5 \xrightarrow{conc.\ H_2SO_4} Ph-\underset{\underset{O}{\|}}{C}-{}^{18}OC_2H_5 + H_2O}$$

Dry HCl can be used as dehydrating agent.

Ex.

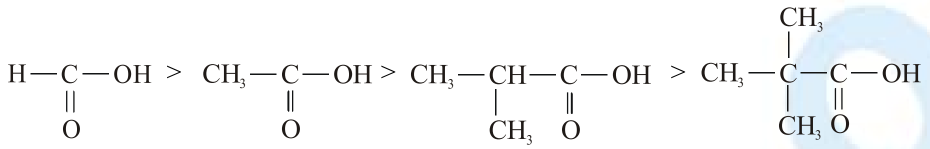
$$\mathrm{CH_3-\underset{\underset{O}{\|}}{C}-OH + H-OC_2H_5 \xrightarrow{Dry\ HCl} CH_3-\underset{\underset{O}{\|}}{C}-OC_2H_5 + H_2O}$$

EDUBULL KEY POINTS

(i) **Reactivity for esterification** $\propto \dfrac{1}{\textbf{Steric hinderence}}$.

(ii) Reactivity of R – OH [If acid is same] : $CH_3 - OH > 1° > 2° > 3°$ alcohol

(iii) Reactivity of RCOOH [If alcohol is same] :



$$H{-}\underset{\underset{O}{\|}}{C}{-}OH > CH_3{-}\underset{\underset{O}{\|}}{C}{-}OH > CH_3{-}\underset{\underset{CH_3}{|}}{CH}{-}\underset{\underset{O}{\|}}{C}{-}OH > CH_3{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}\underset{\underset{O}{\|}}{C}{-}OH$$

(vii) **Reaction with CH≡CH :**

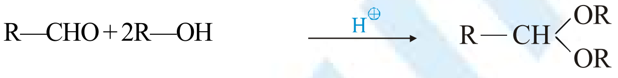
$$CH{\equiv}CH + 2CH_3{-}OH \xrightarrow[\Delta]{BF_3/HgO} CH_3CH\left\langle\begin{matrix}OCH_3\\OCH_3\end{matrix}\right.$$

Methylal

$$CH{\equiv}CH + 2CH_3CH_2{-}OH \xrightarrow[\Delta]{BF_3/HgO} CH_3CH\left\langle\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}\right.$$

Ethylal

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



$$R{-}CHO + 2R{-}OH \xrightarrow{H^{\oplus}} R{-}CH\left\langle\begin{matrix}OR\\OR\end{matrix}\right.$$

Acetal

$$R{-}\underset{\underset{O}{\|}}{C}{-}R + 2R{-}OH \xrightarrow{H^{\oplus}} \left.\begin{matrix}R\\R\end{matrix}\right\rangle C\left\langle\begin{matrix}OR\\OR\end{matrix}\right.$$

Ketal

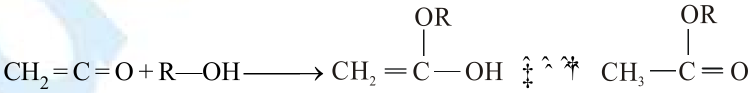
$$CH_3CHO + 2CH_3{-}OH \xrightarrow{H^{\oplus}} CH_3CH\left\langle\begin{matrix}OCH_3\\OCH_3\end{matrix}\right.$$

Methylal

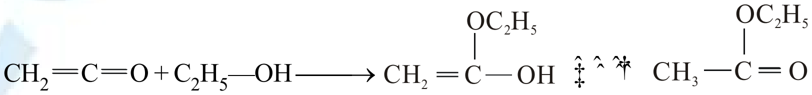
(ix) **Reaction with Grignard reagent :**

$$R{-}Mg{-}X + H{-}OR \xrightarrow{H^{\oplus}} R{-}H + Mg\left\langle\begin{matrix}X\\OR\end{matrix}\right.$$

(x) **Reaction with Ketene :** Ketene is used as acetylating agent.



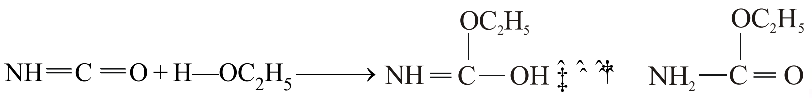
$$CH_2{=}C{=}O + R{-}OH \longrightarrow CH_2{=}\overset{\overset{OR}{|}}{C}{-}OH \rightleftharpoons CH_3{-}\overset{\overset{OR}{|}}{C}{=}O$$



$$CH_2{=}C{=}O + C_2H_5{-}OH \longrightarrow CH_2{=}\overset{\overset{OC_2H_5}{|}}{C}{-}OH \rightleftharpoons CH_3{-}\overset{\overset{OC_2H_5}{|}}{C}{=}O$$

Ethyl acetate

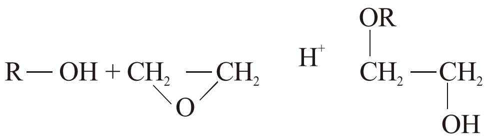
(xi) Reaction with isocyanic acid : Ethyl urethane is used in preparation of urea



$$NH=C=O+H-OC_2H_5 \longrightarrow NH=\overset{OC_2H_5}{\overset{|}{C}}-OH \rightleftharpoons NH_2-\overset{OC_2H_5}{\overset{|}{C}}=O$$

Ethyl urethane

(xii) Reaction with oxirane :



(B) Reaction involving cleavage of C $\nmid$ OH: Reactivity order or basic nature is

$$CH_3-OH < CH_3CH_2-OH < (CH_3)_2CH-OH < (CH_3)_3C-OH$$

(i) Reaction with halogen acid :

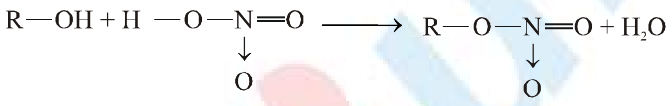
$$R-CH_2-OH + HCl \xrightarrow[\Delta]{ZnCl_2} R-CH_2-Cl + H_2O$$

$$R_2CH-OH + HCl \xrightarrow[\Delta]{ZnCl_2} R_2CH-Cl + H_2O$$

2^0 alcohol

Reactivity of the acids is HI > HBr > HCl > HF

(ii) Reaction with inorganic acids :



$$R-OH + H-O-\underset{\underset{O}{\downarrow}}{N}=O \longrightarrow R-O-\underset{\underset{O}{\downarrow}}{N}=O + H_2O$$

Nitric acid Alkyl nitrate

$$R-OH + HHSO_4 \longrightarrow R-HSO_4 + H_2O$$

Alkyl hydrogen sulphate

(iii) Reaction with phosphorous halides :

$$3R-OH + PCl_3 \longrightarrow 3RCl + H_3PO_3$$

$$R-OH + PCl_5 \longrightarrow R-Cl + POCl_3 + HCl$$

(iv) Reaction with thionyl chloride ($SOCl_2$) :

$$R-OH + SOCl_2 \xrightarrow[\text{Pyridine}]{} R-Cl + \underset{(gas)}{SO_2\uparrow} + HCl$$

(v) Reaction with NH_3 : Alumina (Al_2O_3) is used as dehydrating agent.

$$R-OH + HNH_2 \xrightarrow[250°C]{Al_2O_3} R-NH_2 + H_2O$$

(vi) Reaction with halogens : Oxidation and chlorination takes place simultaneously.

$$CH_3CH_2OH + Cl_2(dry) \longrightarrow CH_3CHO + 2HCl \text{ (Oxidation)}$$

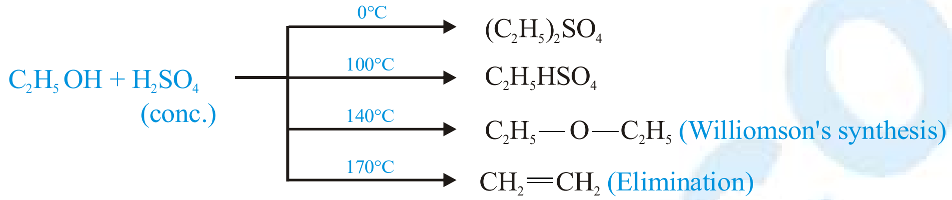
$$CH_3CHO + 3Cl_2 \longrightarrow \underset{\text{chloral}}{CCl_3CHO} + 3HCl \text{ (chlorination)}$$

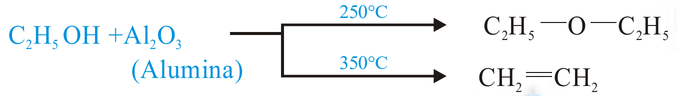
(c) Reaction involving complete molecule of alcohol :

(i) Dehydration : Removal of H_2O by two type

(a) Intermolecularly removal of H_2O [form ether]

(b) Intramolecularly removal of H_2O [form alkene]

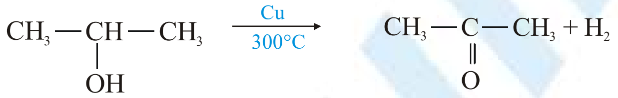




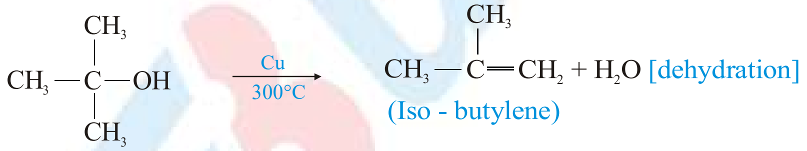
Ease of dehydration follow the order : **3° ROH > 2° ROH > 1° ROH > CH_3OH**

(ii) Catalytic Dehydrogenation : This reaction is useful in distinction of 1°, 2° and 3° alcohols.

$$\underset{\text{(p- alcohol)}}{CH_3CH_2OH} \xrightarrow[300°C]{Cu} \underset{\text{(Acetaldehyde)}}{CH_3CHO} + H_2$$



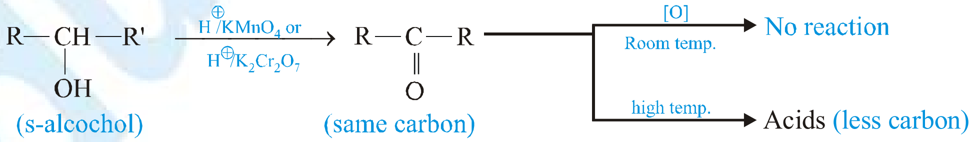
$$\underset{\text{(s- alcohol)}}{CH_3—\underset{OH}{\underset{|}{C}H}—CH_3} \xrightarrow[300°C]{Cu} \underset{\text{(acetone)}}{CH_3—\underset{O}{\underset{\|}{C}}—CH_3} + H_2$$

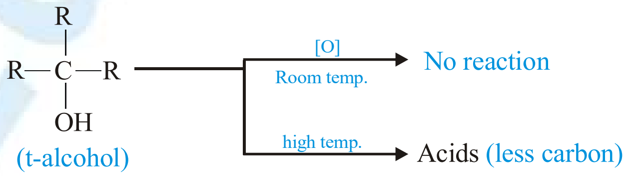


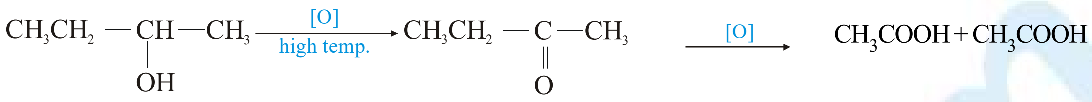
$$\underset{\text{(t. alcohol)}}{CH_3—\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}—OH} \xrightarrow[300°C]{Cu} \underset{\text{(Iso - butylene)}}{CH_3—\overset{CH_3}{\overset{|}{C}}{=}CH_2} + H_2O \text{ [dehydration]}$$

(iii) Oxidation : This reaction is useful in distinction of 1°, 2° and 3° alcohols.

$$\underset{\text{(p-alcohol)}}{R—CH_2—OH} \xrightarrow[H^{\oplus}/K_2Cr_2O_7]{H^{\oplus}/KMnO_4 or} RCHO \xrightarrow[\text{Room temp.}]{[O]} \underset{\text{(same carbon acid)}}{RCOOH}$$







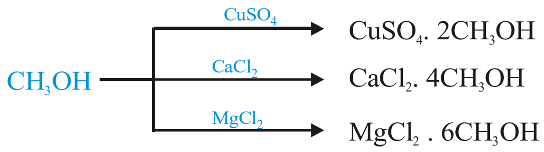
$$CH_3CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3 \xrightarrow[\text{high temp.}]{[O]} CH_3CH_2-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3 \xrightarrow{[O]} CH_3COOH + CH_3COOH$$

Carbonyl group goes with smaller alkyl group

(iv) Reaction with phosphorous pentasulphide :

$$\underset{}{R-OH + P_2S_5} \longrightarrow \underset{\text{Thio alcohol}}{R-SH} + P_2O_5$$

(v) Reaction with salts :



$$CH_3OH \xrightarrow{CuSO_4} CuSO_4.\ 2CH_3OH$$

$$CH_3OH \xrightarrow{CaCl_2} CaCl_2.\ 4CH_3OH$$

$$CH_3OH \xrightarrow{MgCl_2} MgCl_2\ .\ 6CH_3OH$$

(vi) Distinction between 1°, 2° and 3° alcohols :

(a) Lucas test : A mixture of HCl(conc.) and anhydrous $ZnCl_2$ is called Lucas reagent.

p-alcohol $\xrightarrow{ZnCl_2 + HCl}$ No turbidity at room temp. [On heating within 30 minutes.]

s-alcohol $\xrightarrow{ZnCl_2 + HCl}$ Turbidity appears within 5 minutes.

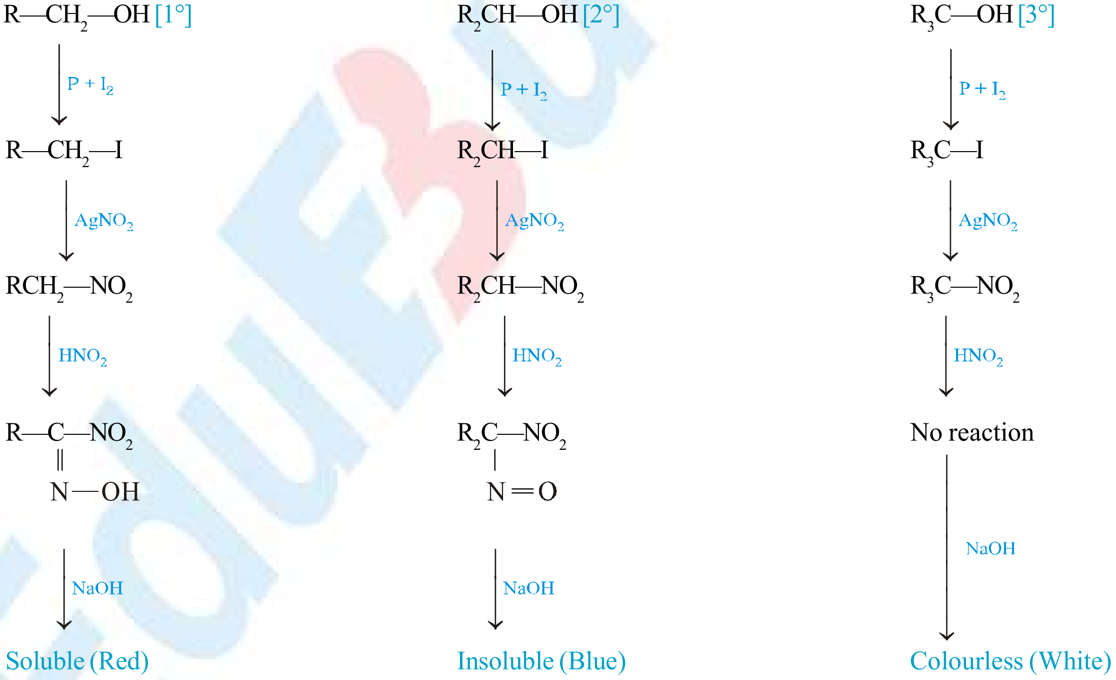
t-alcohol $\xrightarrow{ZnCl_2 + HCl}$ Turbidity appears within 1 minute.

(b) Victor - Meyer test : This is colour test for alcohol (pri. sec. & tert.) .

p-alcohol ⟶ Red colour

s-alcohol ⟶ Blue colour

t-alcohol ⟶ No colour



$$R-CH_2-OH\ [1°] \xrightarrow{P + I_2} R-CH_2-I \xrightarrow{AgNO_2} RCH_2-NO_2 \xrightarrow{HNO_2} R-\underset{\displaystyle N-OH}{\underset{\|}{C}}-NO_2 \xrightarrow{NaOH} \text{Soluble (Red)}$$

$$R_2CH-OH\ [2°] \xrightarrow{P + I_2} R_2CH-I \xrightarrow{AgNO_2} R_2CH-NO_2 \xrightarrow{HNO_2} R_2\underset{\displaystyle N=O}{\underset{|}{C}}-NO_2 \xrightarrow{NaOH} \text{Insoluble (Blue)}$$

$$R_3C-OH\ [3°] \xrightarrow{P + I_2} R_3C-I \xrightarrow{AgNO_2} R_3C-NO_2 \xrightarrow{HNO_2} \text{No reaction} \xrightarrow{NaOH} \text{Colourless (White)}$$

(vii) Dichromate test :

$$1°\ \text{Alcohol} \xrightarrow[\text{orange } [Cr^{+6}]]{H^{\oplus}/K_2Cr_2O_7} \underset{[\text{green}]}{\text{Acid} + Cr^{+3}}$$

$$2° \text{ Alcohol} \xrightarrow[\text{orange } [Cr^{+6}]]{H^{\oplus}/K_2Cr_2O_7} \text{Ketone} + Cr^{+3}$$
[green]

$$3° \text{ Alcohol} \xrightarrow[\text{orange } [Cr^{+6}]]{H^{\oplus}/K_2Cr_2O_7} \text{No oxidation, No green}$$

(viii) Test of alcoholic group :

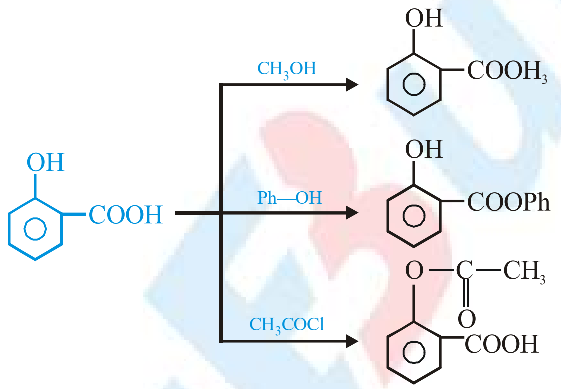
$$R—OH \xrightarrow{Na} R—ONa + \frac{1}{2} H_2$$
[effervescence of H_2]

$$R—OH \xrightarrow{PCl_5} R—Cl + POCl_3 + HCl \xrightarrow{NH_3} NH_4Cl$$
[White fumes]

$$R—OH \xrightarrow{\text{Cerric ammonium nitrate}} \text{Red colour}$$

(ix) Distinction between CH_3-OH and C_2H_5OH

	CH_3OH	CH_3CH_2OH
B.P.	65°C	78°C
I_2 + NaOH	No ppt	Yellow ppt of CHI_3
Cu/300°C	Smell of formalin [HCHO]	No smell
Salicylic acid	Smell of oil of wintergreen	No smell



Methyl salicylate
(Oil of wintergreen)

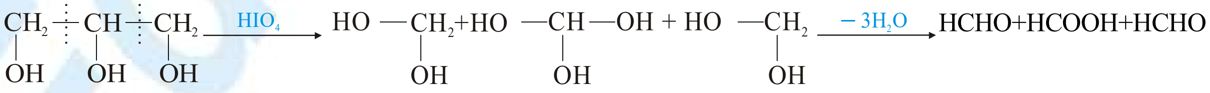
Phenyl salicylate
Salol (Internal antiseptic)

Aspirin
(Analgesic)

ADDITIONAL REACTIONS

(a) Oxidation by HIO_4 [per iodic acid] :

$$\underset{OH}{CH_2} - \underset{OH}{CH_2} \xrightarrow{HIO_4} \underset{OH}{CH_2}—OH + HO—\underset{OH}{CH_2} \xrightarrow{-2H_2O} HCHO + HCHO$$



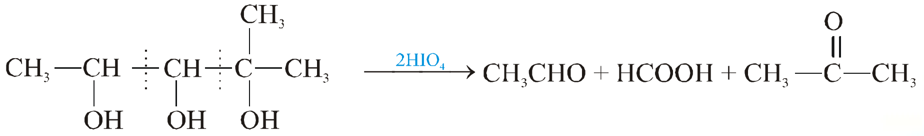
$$\underset{OH}{CH_2} - \underset{OH}{CH} - \underset{OH}{CH_2} \xrightarrow{HIO_4} HO—\underset{OH}{CH_2} + HO—\underset{OH}{CH}—OH + HO—\underset{OH}{CH_2} \xrightarrow{-3H_2O} HCHO + HCOOH + HCHO$$

(Glycerol)

Condition for oxidation by HIO_4 :

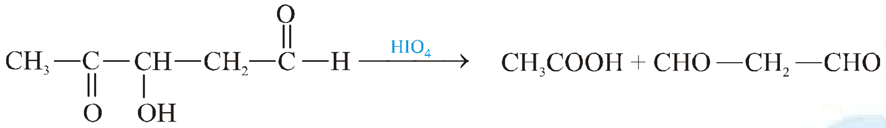
At least 2 —OH or 2 >C=O or 1 —OH and 1 >C=O should be at adjacent carbons.

Ex.



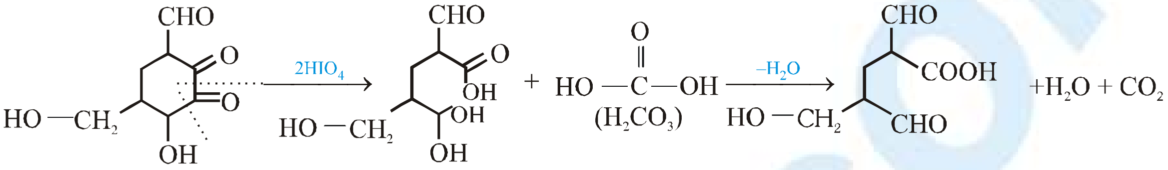
$$CH_3-\underset{OH}{CH}\vdots\underset{OH}{CH}\vdots\underset{OH}{\overset{CH_3}{C}}-CH_3 \xrightarrow{2HIO_4} CH_3CHO + HCOOH + CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

Ex.

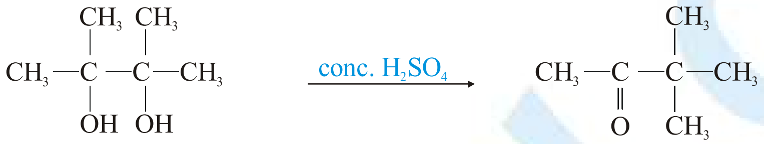


$$CH_3-\underset{O}{\underset{\|}{C}}-\underset{OH}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow{HIO_4} CH_3COOH + CHO-CH_2-CHO$$

Ex.



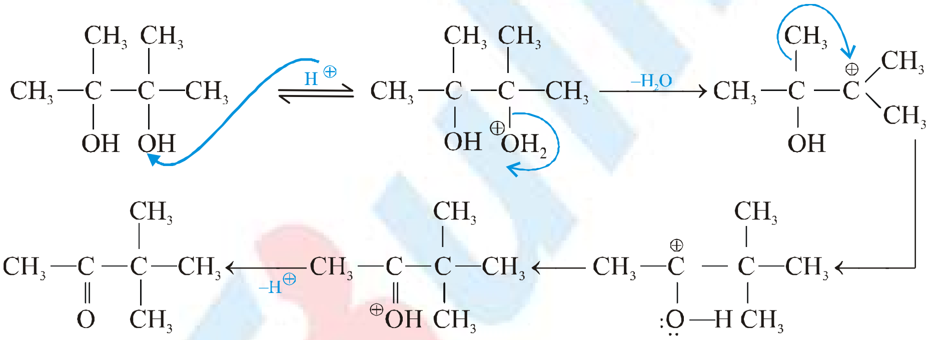
(b) Pinacole - Pinacolone Rearrangement :



$$CH_3-\underset{OH}{\overset{CH_3}{C}}-\underset{OH}{\overset{CH_3}{C}}-CH_3 \xrightarrow{\text{conc. } H_2SO_4} CH_3-\underset{O}{\underset{\|}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

Pinacole Pinacolone

MECHANISM :

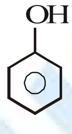


(Complete octet more stable)

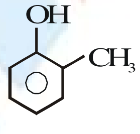
AROMATIC HYDROXY DERIVATIVES

Phenolic compounds :

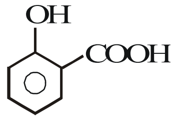
Compounds in which —OH group is directly attached to sp^2 C [Benzene ring]



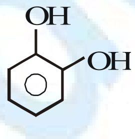
Phenol



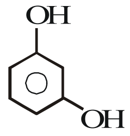
o-cresol



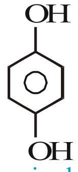
Salicylic acid



catechol



resorcinol



quinol

All phenolic compounds give characteristic colour with neutral $FeCl_3$.\

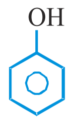
$Ph-OH \xrightarrow{\text{neutral } FeCl_3}$ Violet colour

$CH_3CH_2-OH \xrightarrow{\text{neutral } FeCl_3}$ No colour

PHENOL

Formula C_6H_5OH

Structure



Phenol is also known as carbolic acid or Benzenol or hydroxy benzene.In phenol —OH group is attached with sp^2 hybridised carbon.It was discovered by Runge in the middle oil fraction of coaltar distillation and named it carbolic acid (carbo = coal; oleum = oil) .It is also present in traces in human urine.

GENERAL METHODS OF PREPARATION

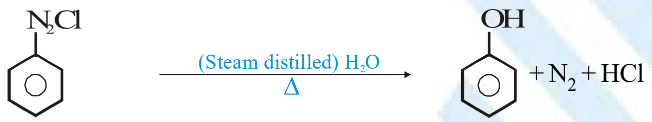
(1) From benzene sulphonic acid :

When sodium salt of benzene sulphonic acid is fused with NaOH phenol is obtained.

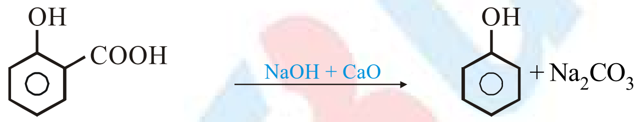
$$C_6H_5SO_3Na + NaOH \longrightarrow C_6H_5OH + Na_2SO_3$$

(2) From benzene diazonium chloride :

When benzene diazonium chloride solution is warmed, phenol is obtained with evolution of nitrogen.

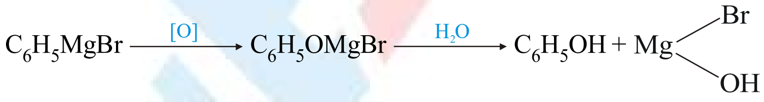


(3) By distilling a phenolic acid with sodalime (decarboxylation):



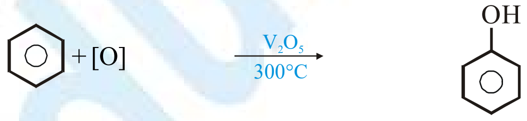
Salicylic acid

(4) From Grignard reagent : (The Grignard reagent on reaction with oxygen and subsequent hydrolysis by acid yields phenol)



$$C_6H_5MgBr \xrightarrow{[O]} C_6H_5OMgBr \xrightarrow{H_2O} C_6H_5OH + Mg\begin{smallmatrix}Br\\OH\end{smallmatrix}$$

(5) From benzene :



(6) From chloro benzene :

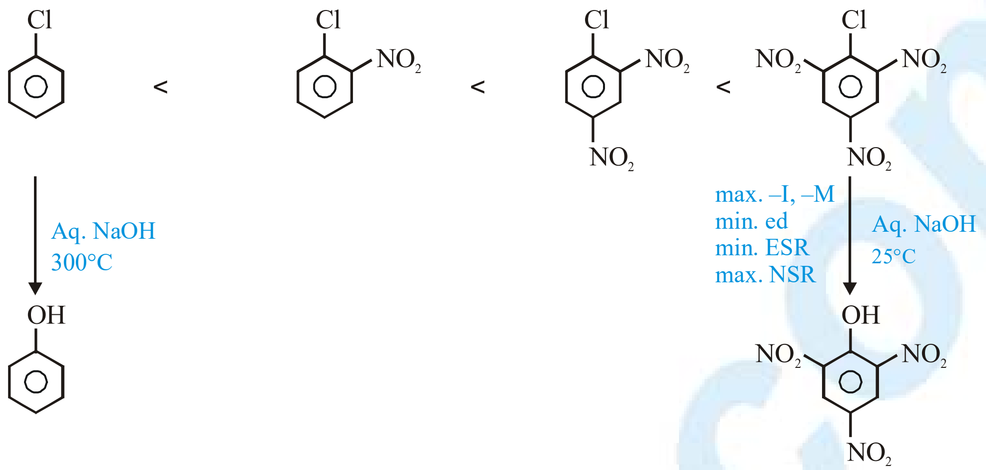
$Ph—Cl \xrightarrow{\text{Aq. NaOH}}$ No NSR at normal condition

Stable by resonance

$R—Cl \xrightarrow{\text{Aq. NaOH}} R—OH$ [NSR]

$Ph—Cl \xrightarrow[\text{300°C}]{\text{Aq. NaOH}} Ph—ONa$

Order of NSR :



2, 4, 6–Trinitrophenol (Picric acid)

(7) Industrial preparation of phenol:

Phenol can be prepared commercially by :

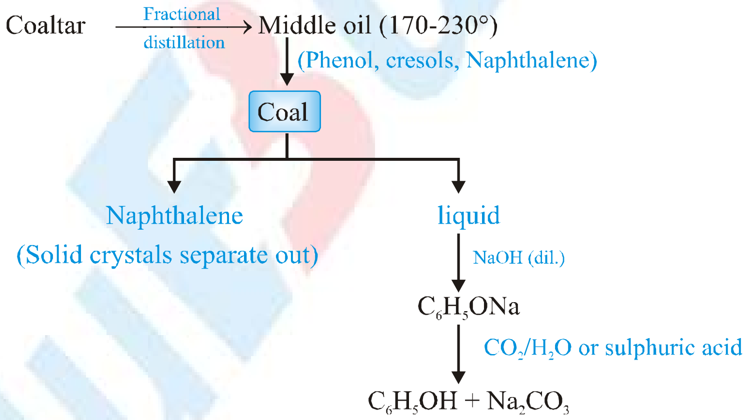
(a) Middle oil fraction of coaltar distillation

(b) Cumene

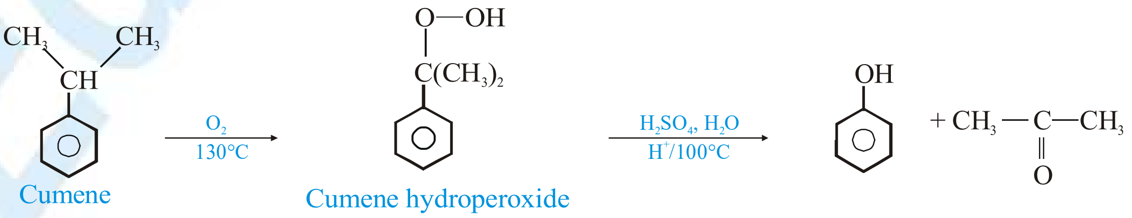
(c) Raschig process

(d) Dow's process

(a) Middle oil fraction of coaltar:



(b) From cumene (Isopropyl benzene) : Cumene is oxidised with oxygen into cumene hydroperoxide in presence of a catalyst. This is decomposed by dil. H_2SO_4 into phenol and acetone.



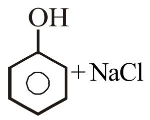
(c) **Raschig process :** Chlorobenzene is formed by the interaction of benzene, HCl and air at 300°C in presence of catalyst $CuCl_2 + FeCl_3$. It is hydrolysed by superheated steam at 425°C to form phenol and HCl.

$$C_6H_6 + HCl + \frac{1}{2}O_2 \xrightarrow[300°C]{CaCl_2/\,FeCl_3} C_6H_5Cl + H_2O$$

$$\underset{\text{(super heated steam)}}{C_6H_5Cl + H_2O} \xrightarrow{425°C} C_6H_5OH + HCl$$

(d) **Dow process :** This process involves alkaline hydrolysis of chloro benzene-(large quantities of phenol formed).

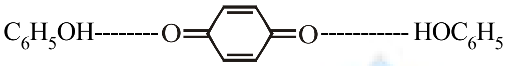
$$C_6H_5Cl + NaOH \xrightarrow[300°C]{Cu-Fe}$$



PHYSICAL PROPERTIES

(i) Phenol is a colourless, hygroscopic crystalline solid.

(ii) It attains pink colour on exposure to air and light. (slow oxidation)



Phenoquinone(pink colour)

(iii) It is poisonous in nature but acts as antiseptic and disinfectant.

(iv) Phenol is slightly soluble in water , readily soluble in organic solvents.

(v) Solublity of phenol in water is much lower than alcohols because of larger hydrocarbon part in the molecule.

(vi) Due to intermolecular H-Bonding, phenol has relatively high boiling point than the corresponding hydrocarbons, aryl halides etc. but intermolecular H-bonding in o–derivatives is used in the preparation of dyes, drugs, bakelite and it's melting point (MP) is 43° C and boiling point (BP) is 182° C .

CHEMICAL PROPERTIES

(A) REACTIONS DUE TO –OH GROUP :

Acidic Nature

Phenol is a weak acid. The acidic nature of phenol due to formation of stable phenoxide ion in solution. The phenoxide ion is stable due to resonance. The negative charge is spread through out the benzene ring which is stabilising factor in the phenoxide ion. Electron withdrawing groups ($-NO_2$, $-Cl$) increase the acidity of phenol while electron releasing groups ($-CH_3$ etc.) decrease the acidity of phenol.

$$C_6H_5OH \rightleftharpoons C_6H_5\overset{\ominus}{O} + H_3\overset{\oplus}{O}$$

Phenol is stronger acid than alcohols but weaker than the carboxylic acids and even carbonic acid.

The acidic nature of phenol is observed in the following:

(i) Phenol changes blue litmas to red.

(ii) Highly electro positive metals react with phenol.

$$2C_6H_5OH + 2Na \longrightarrow 2C_6H_5ONa + H_2$$

(iii) Phenol reacts with strong alkalies to form phenoxides.

$$C_6H_5OH + NaOH \longrightarrow C_6H_5\overset{\ominus}{O}\overset{\oplus}{Na} + H_2O$$

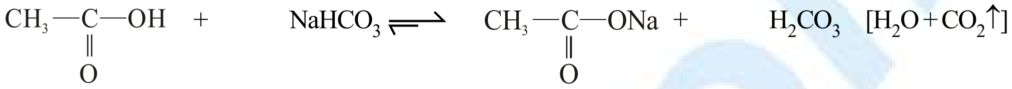
(iv) However phenol does not decompose Na_2CO_3 or $NaHCO_3$ because phenol is weaker than carbonic acid.

$$C_6H_5OH + Na_2CO_3 \text{ or } NaHCO_3 \longrightarrow \text{No reaction}$$

$$\underset{\text{Acid-I}}{Ph-OH} + \underset{\text{Base-I}}{NaHCO_3} \rightleftharpoons \underset{\text{Base-II}}{Ph-ONa} + \underset{\text{Acid-II}}{H_2CO_3}$$

$$\left.\begin{matrix}\text{Acid-I} & < & \text{Acid-II}\\ \text{Base-I} & < & \text{Base-II}\end{matrix}\right\} \text{Reaction in reverse direction.}$$

(v) Phenol does not react with $NaHCO_3$.



$$\underset{\text{Acid-I}}{CH_3-\overset{\overset{O}{\|}}{C}-OH} + \underset{\text{Base-I}}{NaHCO_3} \rightleftharpoons \underset{\text{Base-II}}{CH_3-\overset{\overset{O}{\|}}{C}-ONa} + \underset{\text{Acid-II}}{H_2CO_3}\ [H_2O + CO_2\uparrow]$$

$$\left.\begin{matrix}\text{Acid-I} & > & \text{Acid-II}\\ \text{Base-I} & > & \text{Base-II}\end{matrix}\right\} \text{Reaction in forward direction.}$$

(vi) Acetic acid reacts with $NaHCO_3$ and gives effervesence of CO_2.

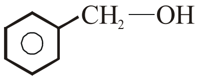
Reaction with PCl_5 : Phenol reacts with PCl_5 to form chloro benzene. The yield of chlorobenzene is poor and mainly triphenyl phosphate is formed.

$$C_6H_5OH + PCl_5 \longrightarrow C_6H_5Cl + POCl_3 + HCl$$

$$3C_6H_5OH + POCl_3 \longrightarrow (C_6H_5)_3PO_4 + 3HCl$$

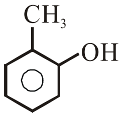
Reaction with Zn dust: When phenol is distilled with zinc dust benzene is obtained.

$$C_6H_5OH + Zn \longrightarrow C_6H_6 + ZnO$$

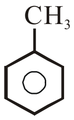
Ex. 

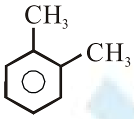
$\xrightarrow{Zn}$?

Sol. No reaction

Ex. 

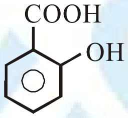
$\xrightarrow{Zn}$?

Sol. 

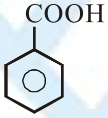
Ex. 

$\xrightarrow{Zn}$?

Sol. No reaction

Ex. 

$\xrightarrow{Zn}$?

Sol. 

Reaction with NH_3(Bucherer reaction): Phenol reacts with NH_3 in presence of anhydrous $ZnCl_2$ to form aniline.

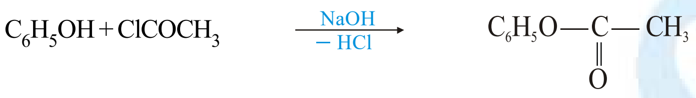
$$C_6H_5OH + NH_3 \xrightarrow[300°C]{\text{Anhydrous } ZnCl_2 \text{ or } (NH_4)_2SO_3/NH_3\ 150°C} C_6H_5NH_2 + H_2O$$

Reaction with $FeCl_3$: Phenol gives violet colouration with $FeCl_3$ solution (neutral) due to formation of a complex.

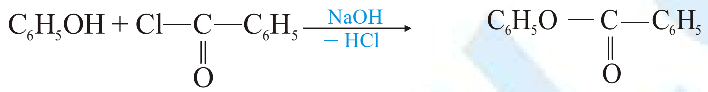
$$C_6H_5OH + FeCl_3 \longrightarrow \text{Voilet colour}$$

This reaction is used to differentiate phenol from alcohols.

Acetylation (Schotten-Baumann reaction) : Phenol reacts with acid chlorides or acid anhydrides in alkali solution to form phenyl esters.



$$C_6H_5OH + ClCOCH_3 \xrightarrow[-\,HCl]{NaOH} C_6H_5O-\underset{\underset{O}{\|}}{C}-CH_3$$



$$C_6H_5OH + Cl-\underset{\underset{O}{\|}}{C}-C_6H_5 \xrightarrow[-\,HCl]{NaOH} C_6H_5O-\underset{\underset{O}{\|}}{C}-C_6H_5$$

Ether formation (Alkylation) : Phenol reacts with alkyl halides in alkali solution to form phenyl ethers. **(Williamson's synthesis)**

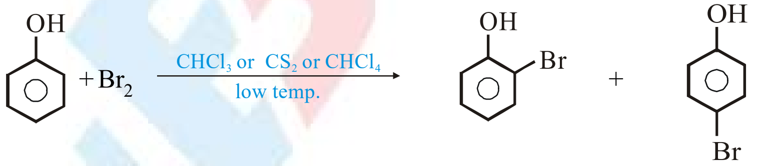
$$C_6H_5OH + NaOH \xrightarrow{\text{alkali solution}} \underset{\text{Sodium phenoxide}}{C_6H_5ONa} \xrightarrow[-NaX]{RX} C_6H_5OR$$

$$C_6H_5OH + CH_2N_2 \longrightarrow C_6H_5OCH_3 + N_2\uparrow$$

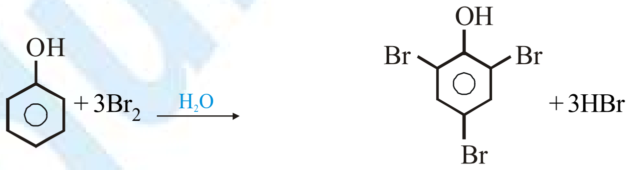
Reaction with P_2S_5 : $5C_6H_5OH + P_2S_5 \xrightarrow{\Delta} 5C_6H_5SH + P_2O_5$

(B) REACTION OF BENZENE RING : The —OH group is ortho and para directing. It activates the benzene nucleus.

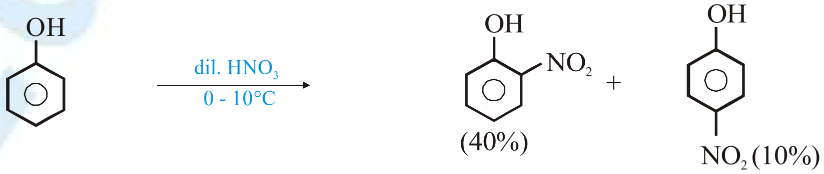
Halogenation : Phenol reacts with bromine in CCl_4 to form mixture of o–and p–bromo phenol.



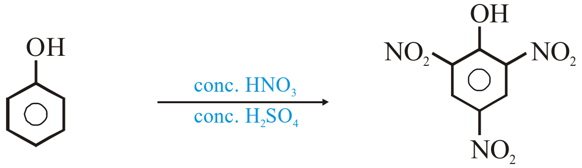
Phenol reacts with bromine water to form a white ppt. of 2,4,6 tribromo phenol.



Nitration : Phenol reacts with dil. HNO_3 at 0°–10° C to form o- and p- nitro phenols.

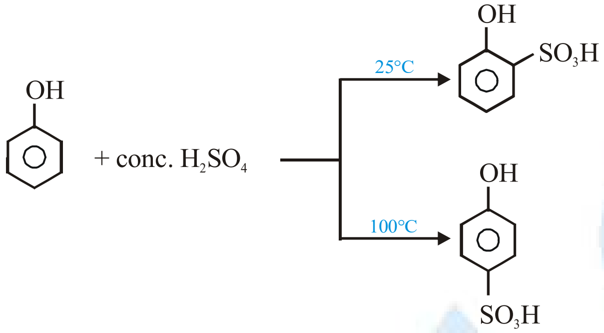


When phenol is treated with nitrating mixture to form 2,4,6- trinitro phenol (picric acid)



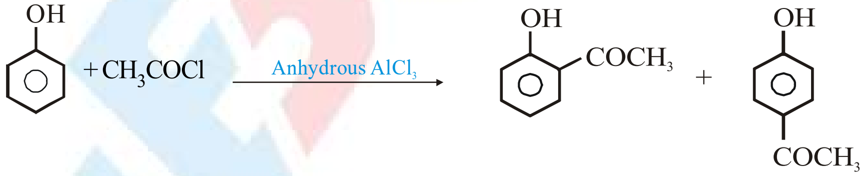
[2, 4, 6–Trinitrophenol (Picric acid)]

Sulphonation: Phenol reacts with fuming H_2SO_4 to form o–and p–hydydroxy benzene sulphonic acid at different temperatures.



Friedel-Craft's reaction : Phenol when treated with methyl chloride in presence of anhydrous $AlCl_3$ p-cresol is main product.

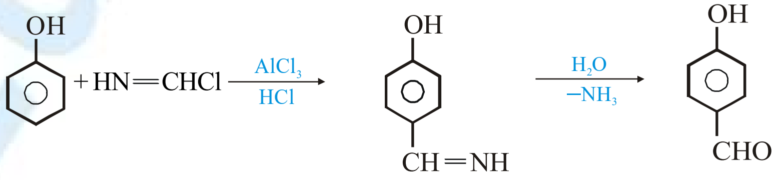
o-cresol p-cresol



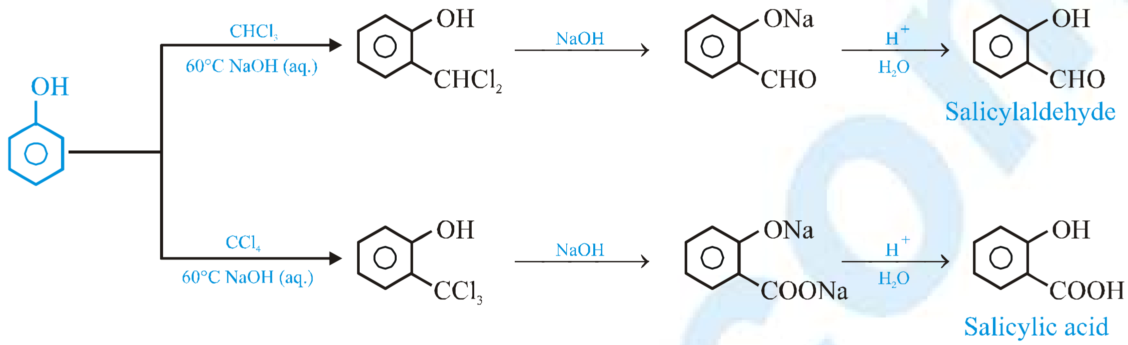
o – and p – hydroxy acetophenone

Gattermann aldehyde synthesis : When phenol is treated with liquid HCN and HCl gas in presence of anhydrous $AlCl_3$ yields mainly p- hydroxy benzaldehyde (formylation)

$$HCl + HCN \xrightarrow{AlCl_3} HN{=}CHCl$$



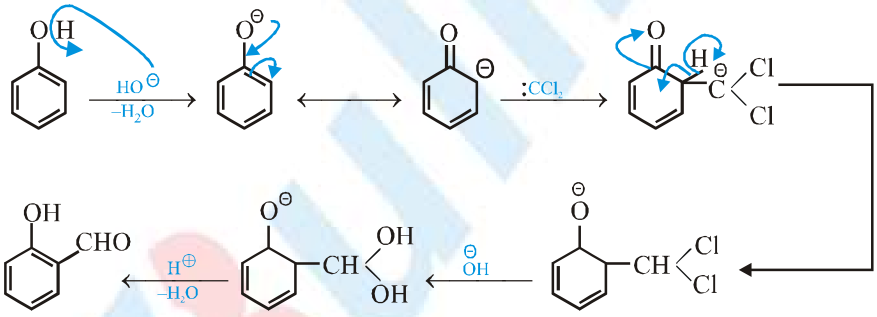
Riemer-Tiemann reaction : Phenol on refluxing with chloroform and NaOH (aqueous) followed by acid hydrolysis yields o–hydroxy benzaldehyde. When CCl_4 is used salicylic acid is formed.



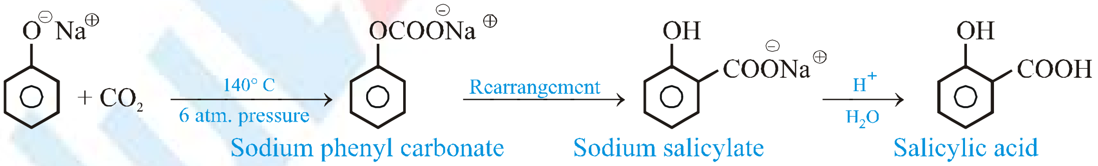
MECHANISM :

CCl_2 is neutral attacking electrophile (formed by α,α– elimination reaction)

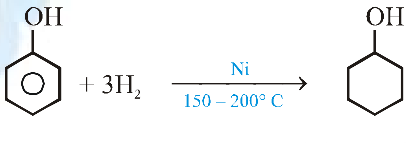
$$CHCl_3 \xrightarrow{KOH} :CCl_2$$



Kolbe 's Schmidt reaction : This involves the reaction of C_6H_5ONa with CO_2 at 140^0 C followed by acid hydrolysis salicylic acid is formed followed.



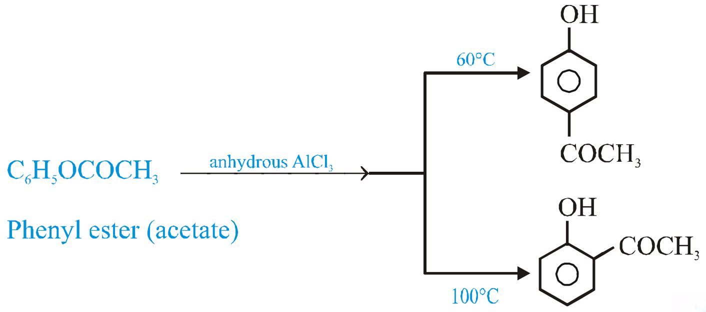
Hydrogenation: Phenol when hydrogenated in presence of Ni at $150\text{-}200^0C$ forms cyclohexanol.



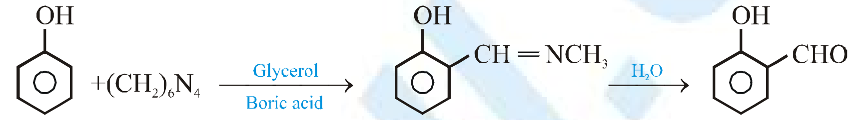
Cyclohexanol. ($C_6H_{11}OH$)
(used as a good solvent)

Fries rearrangement reaction :

$$C_6H_5OH + CH_3COCl \xrightarrow{\text{Anhydrous AlCl}_3} C_6H_5OCOCH_3$$



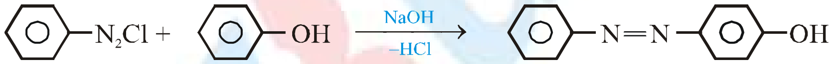
Duff 's reaction: This method gives only the o-compound which is hindered by the presence of a –I group in the ring.



Hexamethylene tetramine

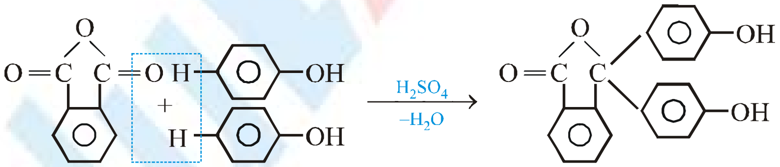
acidified with H_2SO_4
and steam distilled (15–20°C)

Coupling reactions: Phenol couples with benzene diazonium chloride in presence of an alkaline solution to form a dye (p- hydroxy azobenzene) red only.



p–hydroxy azobenzene (Orange dye or Red dye)

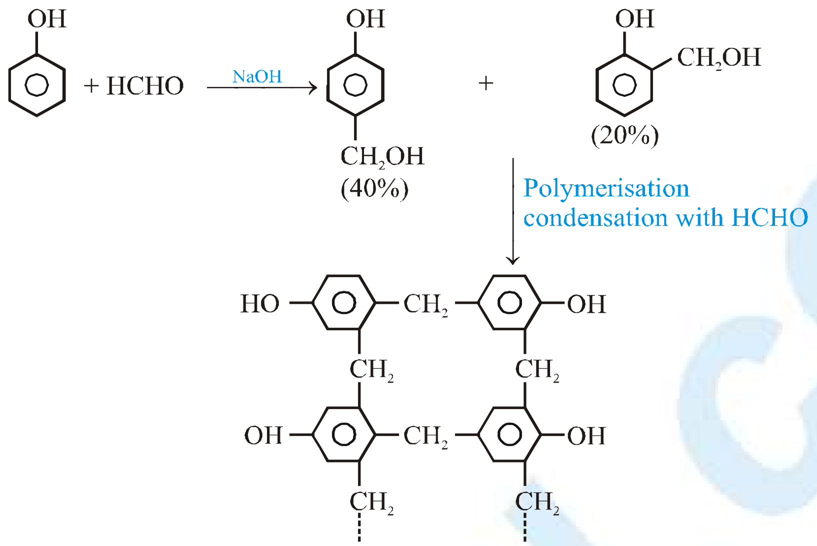
Phenol couples with phthalic anhydride in presence of conc. H_2SO_4 to form a dye (phenolphthalien) used as an indicator.



Phenol (2 molecules)

Phenolphthalien (Colourless in acidic
medium and pink in alkaline medium)

Lederer Manasse (Condensation with formaldehyde) : Phenol condenses with HCHO (excess) in presence of NaOH or weak acid (H^+) to form a polymer known as bakelite (aresin).

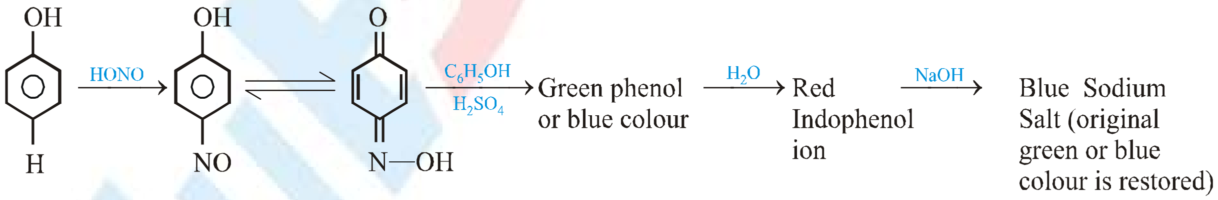


Polymer bakelite (Phenol formaldehyde resin)

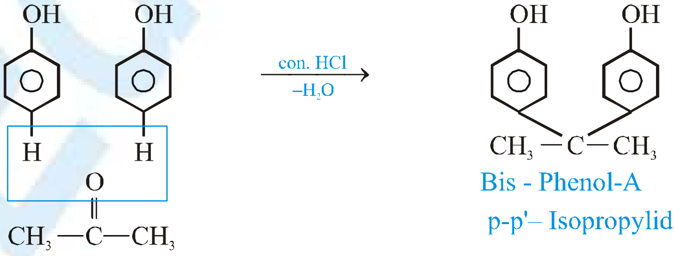
Leibermann's nitroso reaction : When phenol is reacted with $NaNO_2$ and conc. H_2SO_4 it gives a deep green or blue colour which changes to red on dilution with water. When made alkaline with NaOH original green or blue colour is restrored.

This reaction is used as a test of phenol.

$$2NaNO_2 + H_2SO_4 \longrightarrow 2HNO_2 + Na_2SO_4$$



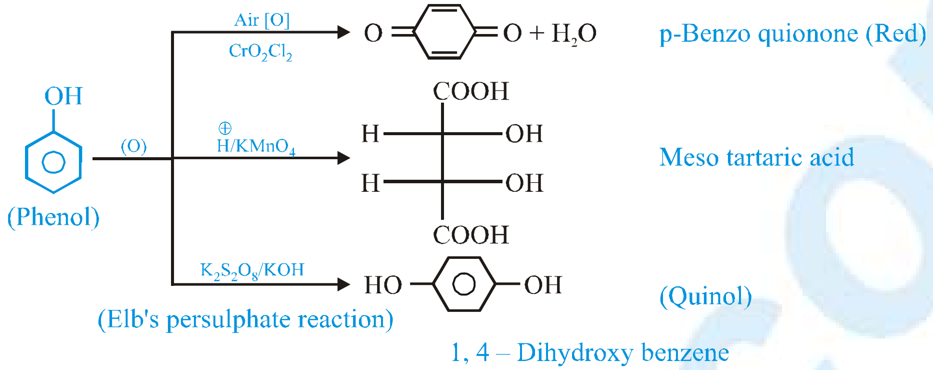
Reaction with acetone: (Condensation with acetone)



Bis - Phenol-A

p-p'– Isopropylidene diphenol

Oxidation:



TESTS OF PHENOL

(i) Phenol turns blue litmus to red.

(ii) Aqeous solution of phenol gives a violet colour with a drop of ferric chloride.

(iii) Phenol gives Lieber mann 's nitroso test.

Phenol in conc. $H_2SO_4 \xrightarrow[\text{excess of water}]{NaNO_2}$ Red colour $\xrightarrow{\text{NaOH excess}}$ Blue colour

(iv) Aqeous solution of phenol gives a white ppt. of 2,4,6 tribromophenol with bromine water.

(v) Phenol combines with phthalic anhydride in presence of conc. H_2SO_4 to form phenolphthalein which gives pink colour with alkali.

(vi) With ammonia and sodium hypochlorite , phenol gives blue colour.

Differences between phenol and alcohol (C_2H_5OH) :

(i) Phenol is more acidic than aliphatic alcohol due to resonance in phenoxide ion.

(ii) Phenol gives violet colour with $FeCl_3$ while aliphatic alcohol does not give.

(iii) Phenol gives triphenyl phosphate with PCl_5 while aliphatic alcohol gives alkyl chloride.

(iv) Phenol has phenolic odour whereas alcohol has pleasent odour.

(v) Phenol on oxidation gives quinone while alcohol gives aldehyde or ketone and acids.

Uses of Phenol : Phenol is used :

(a) As an antiseptic in soaps and lotions. "Dettol" (2,4-Dichloro-3,5-dimethyl phenol)

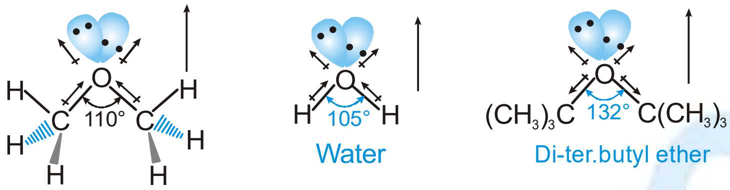
(b) In manufacture of azodyes, phenolphthalein , picric acid (explosive), cyclohexanol (Solvent for rubber), plastics (bakelite) etc.

(c) In manufacture of drugs like aspirin salol, phenacetin etc.

(d) As preservative for ink.

ETHER

Like water, ethers have a bent structure, with an sp^3 hybrid oxygen atom giving a nearly tetrahedral bond angle.



dimethyl ether   Water   Di-ter.butyl ether

Bonding in ethers is readily understood by comparing ethers with water and alcohol. Van der Waals strain involving alkyl groups causes the bond angle at oxygen to the larger in ethers than in alcohol, and larger in alcohols than in water. An extreme example is di-tert-butyl ether, where steric hindrance between the tert-butyl groups is responsible for a dramatic increase in the C – O – C bond angle.

R—O—R (Dialkyl ether), alkoxy alkane. It's General formula is $C_nH_{2n+2}O$.

$CH_3—O—CH_2CH_3$ (Methoxy ethane) or ethyl methyl ether or 2–oxa butane

Ether is monoalkyl derivative of R–OH and dialkyl derivative of H_2O

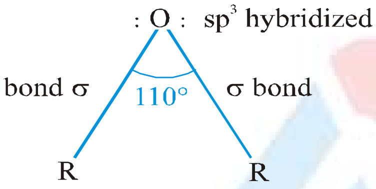
$$R-OH \xrightarrow[+R]{-H} R-O-R \xleftarrow[+2R]{-2H} H-O-H$$

Classification : They may be classified as :

(a) Simple or symmetrical ether. e.g. R–O–R

(b) Mixed or unsymmetrical ether e.g. R–O–R'

Structure :



The molecule of ether is bent due to lone pair of electron on oxygen atom- bond electron repulsion. The bond angle is 110^0. It is greater than that of water 105^0 due to the repulsion between bulky alkyl groups.

Due to bent structure, it posses dipole moment and hence are polar molecules.

GENERAL METHODS OF PREPARATION

(A) From alkyl halides :

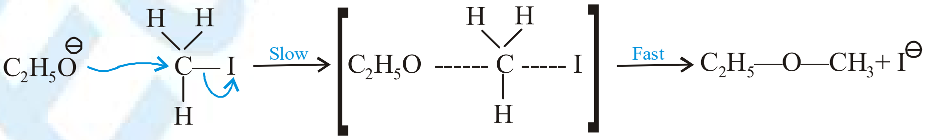
(i) By Williamson's synthesis :

$$R-X + Na-O-R \longrightarrow R-O-R + NaX \ [\,S_N2 \text{ Reaction}]$$

Ex. $CH_3-I + C_2H_5\,O^-\,Na^+ \longrightarrow CH_3-CH_2O-CH_3 + NaI$

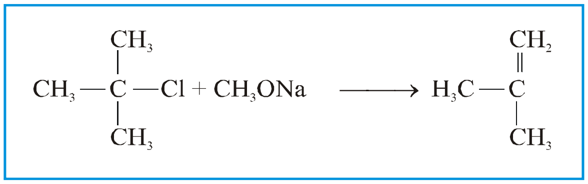
MECHANISM : [S_N2 Reaction]

$$C_2H_5\overset{\ominus}{O}\,Na^{\oplus} \rightleftharpoons C_2H_5O^{\ominus} + Na^{\oplus}$$



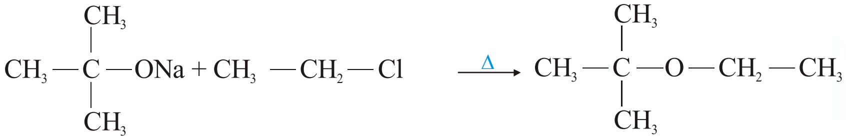
$$Na^{\oplus} + I^{\ominus} \longrightarrow NaI$$

Ex.



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Cl + CH_3ONa \longrightarrow H_3C-\overset{\overset{CH_2}{\|}}{\underset{\underset{CH_3}{|}}{C}}$$

Ex.



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-ONa + CH_3-CH_2-Cl \xrightarrow{\Delta} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-O-CH_2-CH_3$$

Ex. $CH_2{=}CH{-}Cl + CH_3CH_2{-}ONa \longrightarrow$ No reaction

[Stable by Resonance]

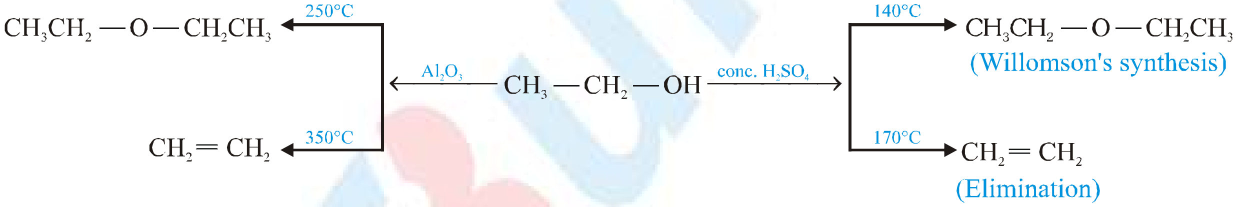
(ii) Reaction with Dry Ag2O :

$$2RX + Ag_2O \xrightarrow{\Delta} R{-}O{-}R + 2AgX$$

Ex. $2CH_3{-}CH_2{-}Cl + Ag_2O \xrightarrow{\Delta} CH_3CH_2OCH_2CH_3 + 2AgCl$

(B) From R–OH:

(i) By dehydration : $R - OH \xrightarrow[\Delta]{conc.\ H_2SO_4} ?$



(ii) Reaction with CH_2N_2 (diazomethane) :

$$R - OH + CH_2 - N_2 \xrightarrow[BF_3]{\Delta} R - O - CH_2 - H + N_2$$

PHYSICAL PROPERTIES

- **(i)** CH_3OCH_3 , $CH_3OCH_2CH_3$ are gases and higher are volatile liquids.
- **(ii)** Ether are less polar **[μ=1.18D]**.
- **(iii)** Ethers are less soluble in H_2O.
- **(iv)** Ethers have less BP then corresponding alcohol.

Ex. Ethers are less soluble in H_2O . Why ?

Sol. **Reason :** Due to less polar, it forms weaker H–Bonding with H_2O.

Ex. Ethers have less BP then corresponding alcohol. Why ?

Sol. **Reason :** No H–Bonding in ether molecules.

CHEMICAL PROPERTIES

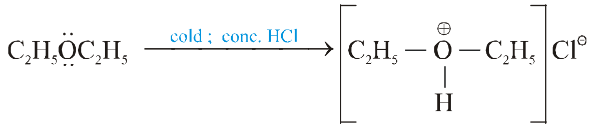
Ethers are less polar so less reactive and do not react with active metals [Na,K], cold dil. acid, oxidising and reducing agent.

Reason : They do not have any active functional group.

1. **Basic nature :** Due to presence of ●.p on oxygen atom ether behave as lewis base

Ethers react with cold conc. acid and form oxonium ion

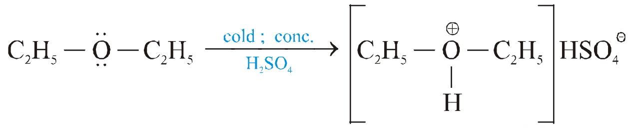
Ex.



$$C_2H_5\ddot{O}C_2H_5 \xrightarrow{\text{cold ; conc. HCl}} \left[C_2H_5-\underset{\underset{H}{|}}{\overset{\oplus}{O}}-C_2H_5\right]Cl^{\ominus}$$

(diethyl oxonium chloride)

Ex.

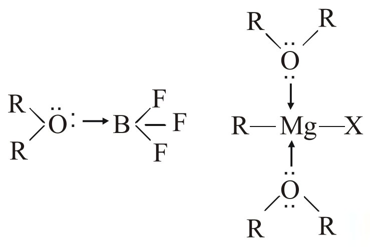


$$C_2H_5-\ddot{O}-C_2H_5 \xrightarrow[H_2SO_4]{\text{cold ; conc.}} \left[C_2H_5-\underset{\underset{H}{|}}{\overset{\oplus}{O}}-C_2H_5\right]HSO_4^{\ominus}$$

(diethyl oxonium hydrogen sulphate)

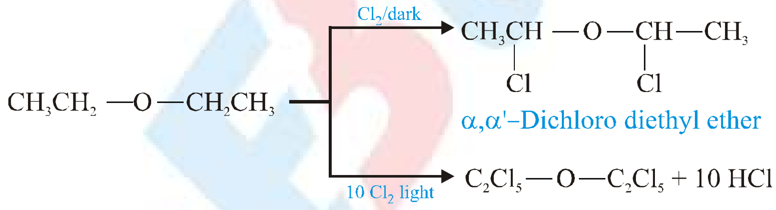
Ether form dative bond with Lewis acids like BF_3, $AlCl_3$, RMgX etc.

Ex.



[Ether is used as solvent] for Grignard reagent.

2. **Halogenation :**



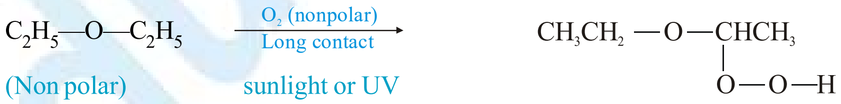
$$CH_3CH_2-O-CH_2CH_3 \xrightarrow{Cl_2/\text{dark}} CH_3\underset{\underset{Cl}{|}}{CH}-O-\underset{\underset{Cl}{|}}{CH}-CH_3$$

α,α'-Dichloro diethyl ether

$$CH_3CH_2-O-CH_2CH_3 \xrightarrow[10\ Cl_2\ \text{light}]{} C_2Cl_5-O-C_2Cl_5 + 10\ HCl$$

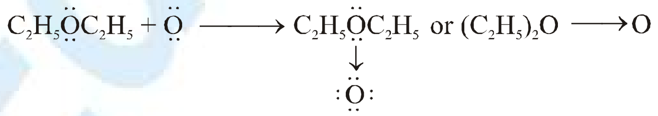
Perchlorodiethyl ether

3. **Formation of peroxides :** Ether add up atmospheric oxygen or ozonised oxygen. It is explained by Free radical mechanism as intermediates is free radical.

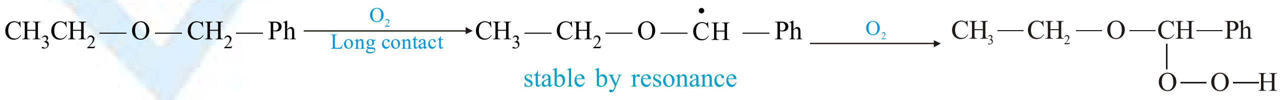


$$C_2H_5-O-C_2H_5 \xrightarrow[\text{Long contact}]{O_2\ \text{(nonpolar)}} CH_3CH_2-O-\underset{\underset{O-O-H}{|}}{CH}CH_3$$

(Non polar) sunlight or UV



$$C_2H_5\ddot{O}C_2H_5 + \ddot{O} \longrightarrow \underset{\underset{:\ddot{O}:}{\downarrow}}{C_2H_5\ddot{O}C_2H_5} \text{ or } (C_2H_5)_2O \longrightarrow O$$



$$CH_3CH_2-O-CH_2-Ph \xrightarrow[\text{Long contact}]{O_2} CH_3-CH_2-O-\dot{C}H-Ph \xrightarrow{O_2} CH_3-CH_2-O-\underset{\underset{O-O-H}{|}}{CH}-Ph$$

stable by resonance

Peroxides are unstable and explosives.

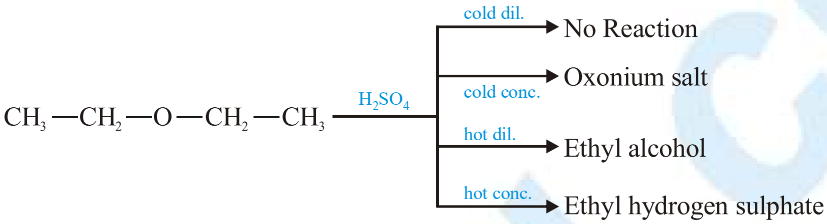
Test for peroxides

ether (peroxide) $\xrightarrow{FeSO_4/KCNS}$ Red colour

ether (Peroxides) + $Fe^{+2} \longrightarrow Fe^{+3} \xrightarrow{CNS} Fe(CNS)_3$ (Red)

4. **Reaction with hot dil. H_2SO_4 :** $R{-}O{-}R \xrightarrow[H_2SO_4]{\text{hot dil.}} 2R{-}OH$

5. **Reaction with hot conc. H_2SO_4 :** $R{-}O{-}R \xrightarrow{\text{hot conc. } H_2SO_4} 2RHSO_4$



6. **Reaction with PCl_5 :** $ROR + PCl_5 \xrightarrow{\text{heat}} 2RCl + POCl_3$

7. **Reaction with BCl_3 :** $3ROR + BCl_3 \longrightarrow 3RCl + (RO)_3B$

8. **Reaction with RCOCl :** $ROR + RCOCl \xrightarrow[ZnCl_2 \text{ heat}]{AlCl_3} RCOOR + RCl$

9. **Reaction with CO :** $ROR + CO \xrightarrow[150° C]{BF_3/HgO \text{ 500 atm}} RCOOR$

10. **Reaction with C_2H_5Na :**

$$\underset{\substack{| \\ H}}{CH_2}CH_2{-}O{-}CH_2\underset{\substack{| \\ H}}{CH_2} + \underset{\text{Stronger base}}{\overset{\ominus}{C}_2H_5} \longrightarrow CH_3CH_2OH + CH_2{=}CH_2 + C_2H_6$$

11. **Dehydration :** $CH_3CH_2{-}O{-}CH_2CH_3 \xrightarrow{Al_2O_3} 2CH_2{=}CH_2 + H_2O$

12. **Reduction :** $CH_3CH_2OCH_2CH_3 \xrightarrow[\text{heat}]{\text{Red P + HI}} 2CH_3CH_3$

13. **Oxidation :**

$$CH_3CH_2{-}O{-}CH_2CH_3 \xrightarrow{H^+/K_2Cr_2O_7} 2CH_3CH_2OH \xrightarrow{[O]} 2CH_3CHO \xrightarrow{[O]} 2CH_3COOH$$

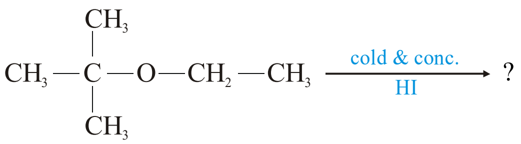
14. **Combustion :** $C_2H_5OC_2H_5 + 6O_2 \longrightarrow 4CO_2 + 5H_2O$
(explosive mixture)

15. **Reaction with HX :** Reactivity of HX $\boxed{\textbf{HI > HBr > HCl}}$

(A) **REACTION WITH COLD CONC. HX :**

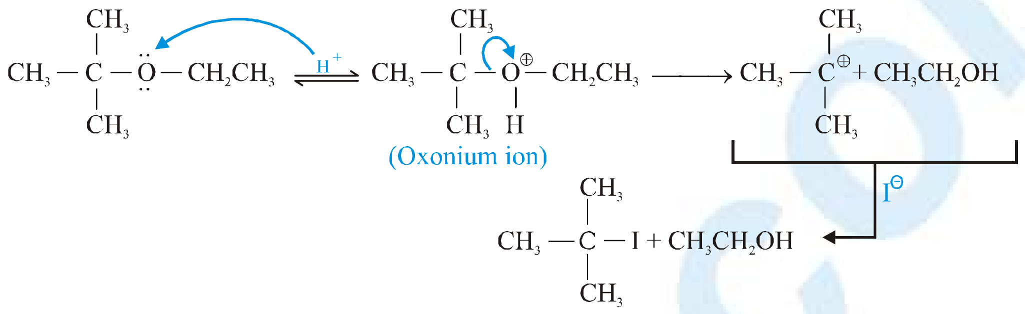
Ethers forms oxonium salt with cold and conc. HCl (less reactive)
Cold conc. HI and HBr (more reactive) break C–O bond.

Ex.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-CH_2-CH_3 \xrightarrow[HI]{\text{cold \& conc.}} ?$$

Sol. Mechanism



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\ddot{\underset{..}{O}}-CH_2CH_3 \overset{H^+}{\rightleftharpoons} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{H}{\overset{\oplus}{O}}-CH_2CH_3 \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C^{\oplus}}}+CH_3CH_2OH$$

(Oxonium ion)

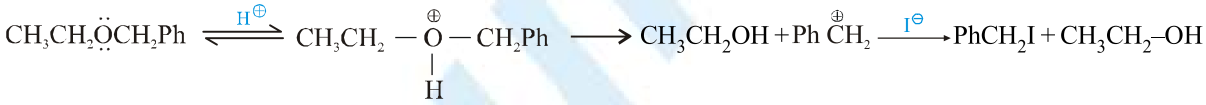
$$\xrightarrow{I^{\ominus}} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-I+CH_3CH_2OH$$

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 [$P\overset{\oplus}{h}$, $CH_2=\overset{\oplus}{C}H$, $CH_3\overset{\oplus}{C}H_2$] then SN^2 reaction occurs, and $X^{\ominus}$ attacks at less hindered carbon.

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

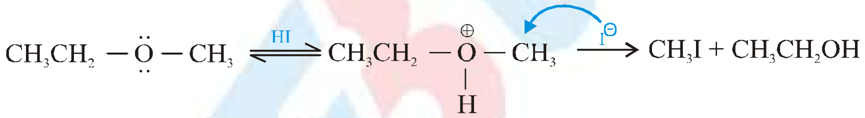
Sol. Mechanism :



$$CH_3CH_2\ddot{\underset{..}{O}}CH_2Ph \overset{H^{\oplus}}{\rightleftharpoons} CH_3CH_2-\underset{H}{\overset{\oplus}{O}}-CH_2Ph \longrightarrow CH_3CH_2OH+Ph\overset{\oplus}{C}H_2 \xrightarrow{I^{\ominus}} PhCH_2I+CH_3CH_2{-}OH$$

Ex. $CH_3CH_2 - O - CH_3 \xrightarrow{\text{anhy. HI}} ?$

Sol.

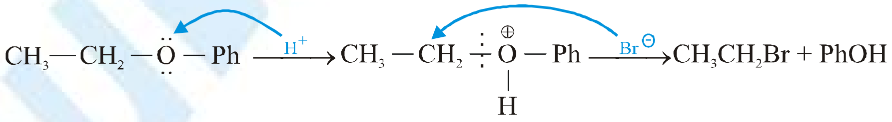


$$CH_3CH_2-\ddot{\underset{..}{O}}-CH_3 \overset{HI}{\rightleftharpoons} CH_3CH_2-\underset{H}{\overset{\oplus}{O}}-CH_3 \xrightarrow{I^{\ominus}} CH_3I+CH_3CH_2OH$$

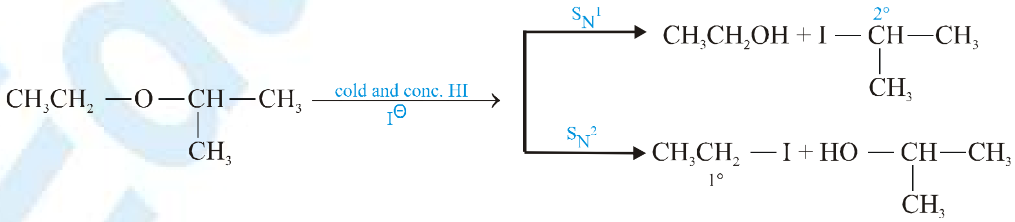
Oxonium ion gives less stable carbocation
SN^2 reaction $I^{\ominus}$ attacks at less hinderd carbon.

Ex. $CH_3 - CH_2 - O - Ph \xrightarrow{\text{aq. HBr}} ?$

Sol. Mechanism :



$$CH_3-CH_2-\ddot{\underset{..}{O}}-Ph \xrightarrow{H^+} CH_3-CH_2 \vdots \underset{H}{\overset{\oplus}{O}}-Ph \xrightarrow{Br^{\ominus}} CH_3CH_2Br+PhOH$$



$$CH_3CH_2-O-\underset{CH_3}{CH}-CH_3 \xrightarrow[I^{\ominus}]{\text{cold and conc. HI}} \begin{cases} \xrightarrow{S_N^1} CH_3CH_2OH + I-\underset{CH_3}{\overset{2^\circ}{CH}}-CH_3 \\ \xrightarrow{S_N^2} \underset{1^\circ}{CH_3CH_2}-I+HO-\underset{CH_3}{CH}-CH_3 \end{cases}$$

If excess of HI is used then two moles of alkyl hallides are formed.

$$CH_3CH_2 - O - CH_2Ph \xrightarrow{HI} CH_3CH_2OH + PhCH_2I \xrightarrow{HI} CH_3CH_2-I+PhCH_2-I$$

(B) REACTION WITH HOT AND CONC. HX :

$$CH_3CH_2 — O — CH_3 \xrightarrow{\text{hot \& conc. HI}} CH_3CH_2 — I + CH_3 — I$$

Ex. $C_2H_5 — O — C_2H_5 \xrightarrow{\text{hot \& conc. HBr}}$? + ?

Sol. $C_2H_5 — Br + C_2H_5 — Br$

Uses of ether :

(i) General anaesthetics agent.

(ii) Refrigerant a mixture of ether and dry ice gives temperature as low 110°C.

(iii) Solvent for oil, fats, resins, Grignard reagent.

(iv) For providing inert & moist free medium to organic reaction example : Wurtz reactions.

(v) In perfumery.

(vi) Di-isopropyl ether ⟶ Petrol as an antiknock comp.

(vii) Mixture of alcohol and ether is used as a substitute of petrol. Trade name **"Natalite"**

(viii) Halothane ($CF_3CHClBr$) used as an anaesthetic because it produces unconsciousness without affecting lung and heat.

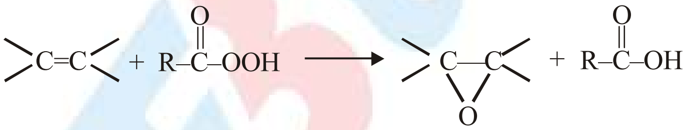
PREPARATION OF EPOXIDES :

(i) Epoxidation of alkenes by reaction with peroxy acids

(ii) Base-promoted ring closure of vicinal halohydrins

(iii) Epoxidation of alkenes by reaction with peroxy acids

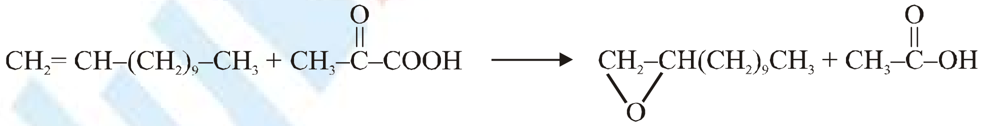
Epoxidation of alkenes by reaction with peroxy acids :



Peroxy acid   Epoxide

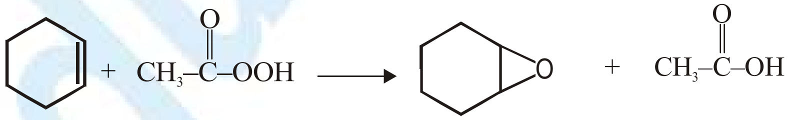
Ex. :

(a)

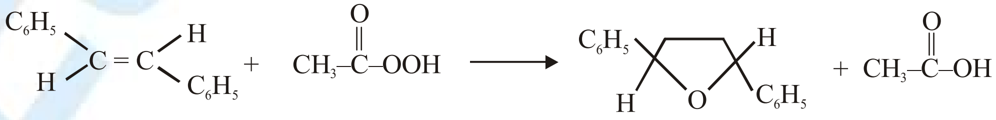


$$CH_2{=}CH{-}(CH_2)_9{-}CH_3 + CH_3{-}\overset{\overset{O}{\|}}{C}{-}COOH \longrightarrow CH_2{-}CH(CH_2)_9CH_3 + CH_3{-}\overset{\overset{O}{\|}}{C}{-}OH$$

(b)

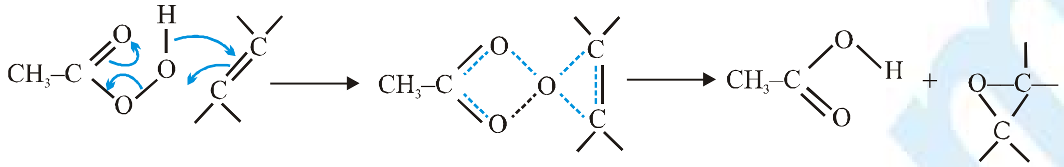


(c) Epoxidation is a stereospecific syn addition :

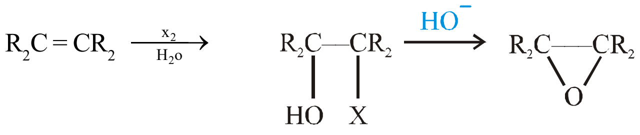


(E) -1,2-diphenyl ethene   trans -2,3-diphenyl oxirane

MECHANISM :

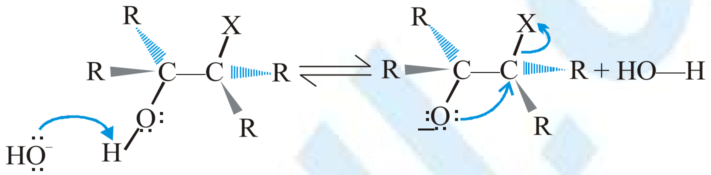


Base-promoted ring closure of vicinal halohydrins :

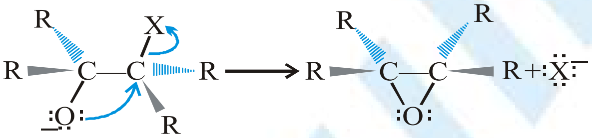


Mechanism :

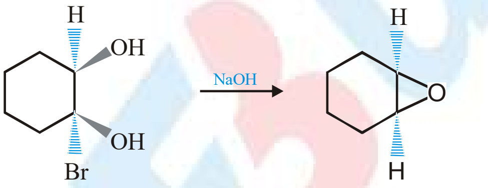
Step I



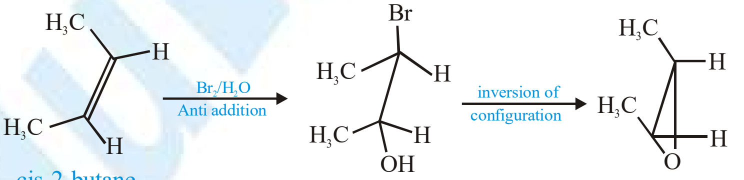
Step II



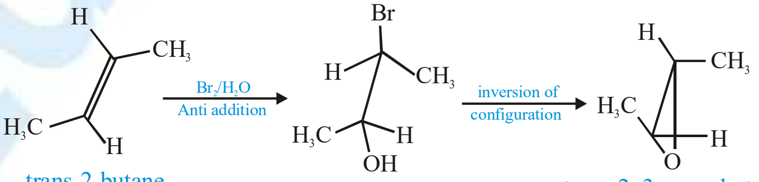
Ex. **(i)**


trans-2-bromocyclohexanol
1, 2-epoxycyclohexane

(ii)

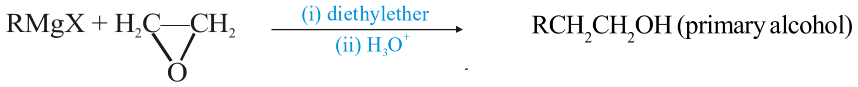

cis-2-butane
cis-2, 3-epoxybutane

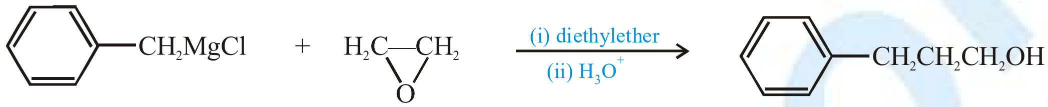
(iii)


trans-2-butane
trans-2, 3-epoxybutane

Reaction of Epoxides :

With Grignard reagent :



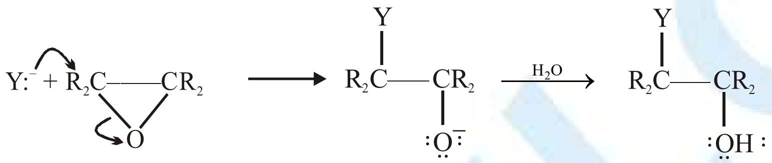


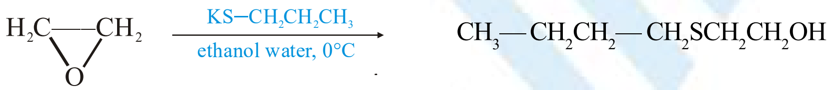
Benzyl magnesium chloride

Ethylene oxide

3-phenyl-1-propanol

Nucleophilic ring opening reactions of epoxides :

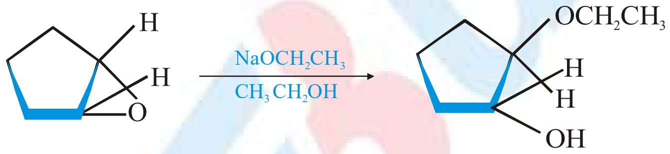


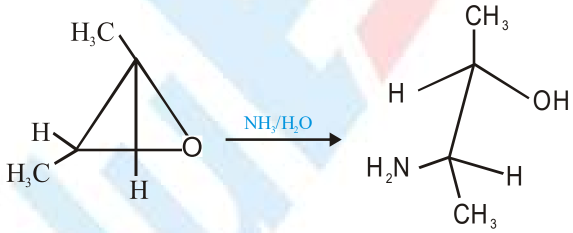


2-(butylthio) ethanol

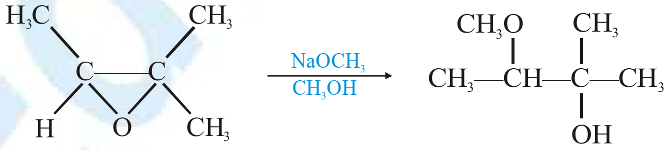
Note : Nucleophilic ring opening reactions of epoxides is the characteristic feature of S_{N^2} reaction.

(i)

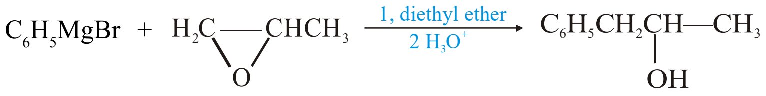


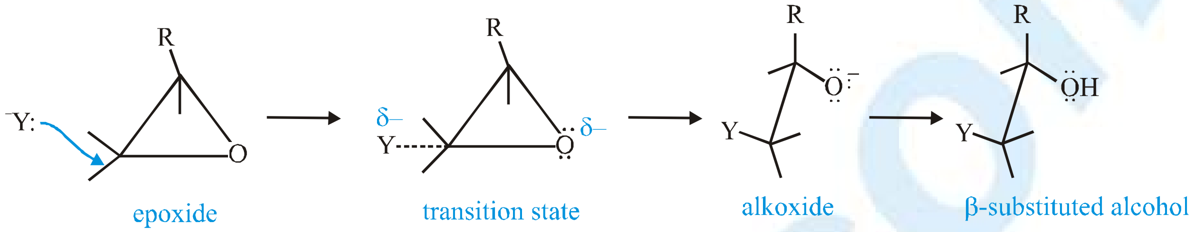


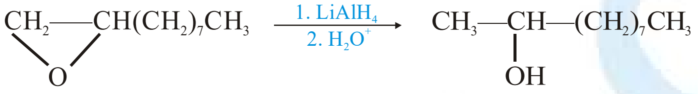
(ii)



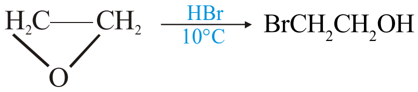
Nucleophilic ring opening of epoxides :



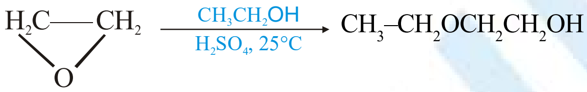


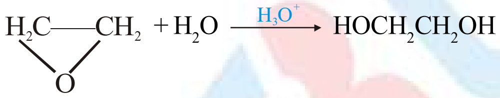


(i)



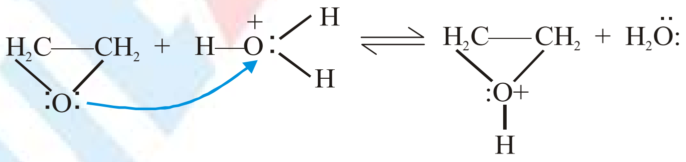
(ii)



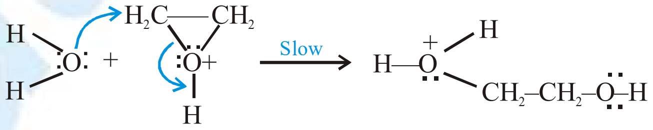


MECHANISM

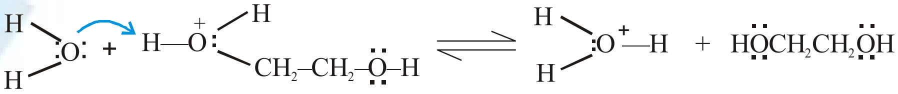
Step-1 :



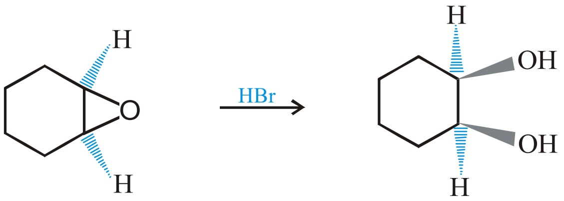
Step-2 :



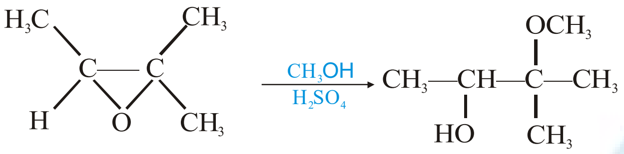
Step-3 :



Ex.:

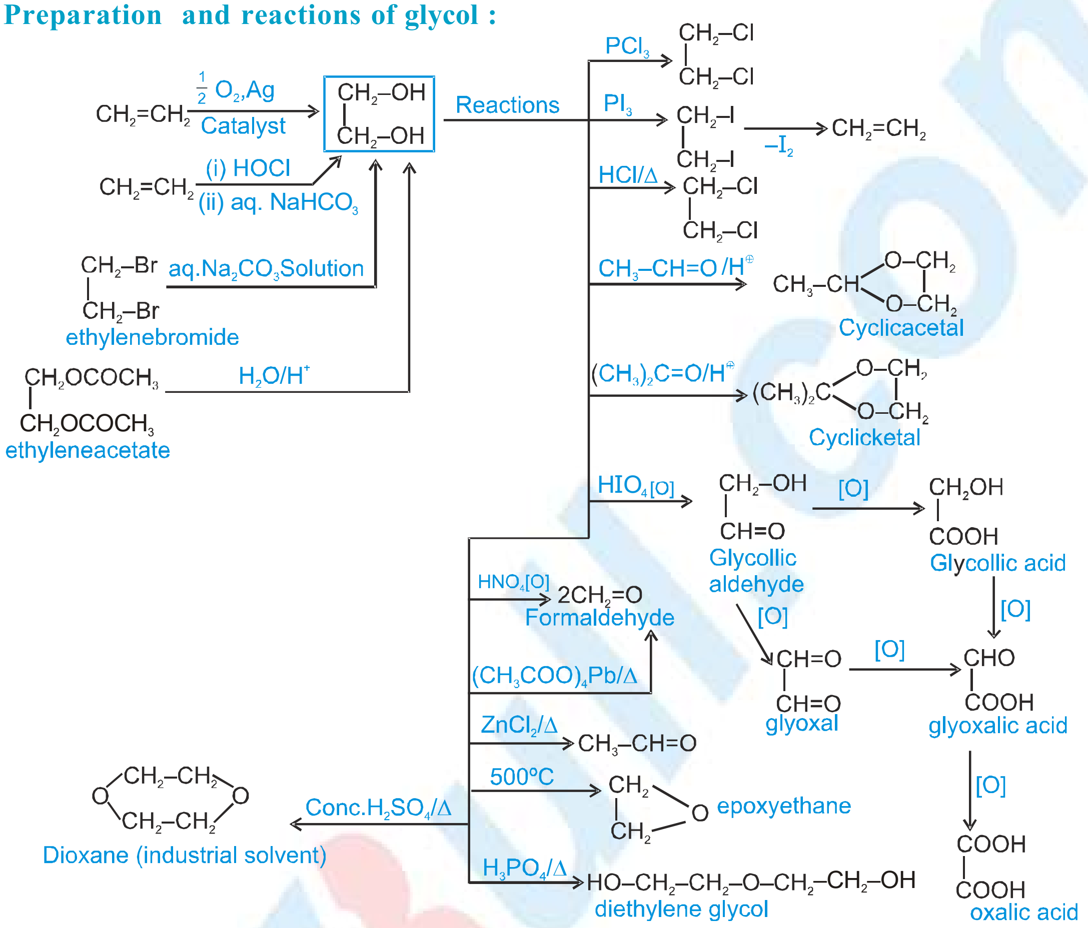


1,2-Epoxycyclohexane trans -2-bromo cyclohexanol



2,2,3-trimethyl oxirane 3-methoxy-3-methyl-2-butanol

1. Preparation and reactions of glycol :



2. General Reactions of Glycerol :