Unit - XI

Alcohols, Phenols and Ethers

Alcohol → $CH_4 \xrightarrow{-H/OH} CH_3OH$ (alcohol)
is the hydroxy derivative of alkanes (HC).
Represent by general formula ROH. where R is alkyl group.
eg ⇒ CH_3OH, C_2H_5OH
Depending upon the no. of OH group there are following types of alcohol ⇒

1) Monohydric eg ⇒ CH_3OH, C_2H_5OH
2) Dihydric eg ⇒ $CH_2(OH)-CH_2(OH)$ (glycol)
3) Trihydric eg ⇒ $CH_2(OH)-CH(OH)-CH_2(OH)$ (glycerol)

Depending upon the nature of carbon to which OH group is attached there are three types of alcohol

1) 1° alcohol eg. CH_3-CH_2-OH
2) 2° alcohol eg ⇒ $CH_3-CH(OH)-CH_3$
   iso propyl alcohol (C_3H_7OH)
3) 3° alcohol → eg ⇒ $(CH_3)_3C-OH$

Methods of preparation →

1) From alkyl halide → when alkyl halide react with aqueous KOH and moist AgOH alcohol is formed as a product.
   $R-X + KOH(aq) \longrightarrow R-OH + KX$
   (alcohol)

Eg:- $CH_3CH_2Cl + KOH \rightarrow CH_3CH_2OH + KCl$
(ethyl alcohol)

2) From carbonyl compounds ($>C=O$) → Alcohol can be prepared from carbonyl compound by following method :-

→ By reduction → Carbonyl compounds on reduction with reducing agents such as H_2 Ni/Pt, $LiAlH_4$ and $NaBH_4$ forms alcohol as a product.

Aldehyde on reduction gives 1° alcohol.
Ketone on reduction gives 2° alcohol.

$CH_3CHO + H_2 \xrightarrow{Ni/Pt} CH_3CH_2OH$
(Acetaldehyde) (ethyl alcohol) (1° alcohol)

$CH_3COCH_3 + 2[H] \xrightarrow{LiAlH_4} CH_3-\underset{OH}{CH}-CH_3$
(Acetone) (2° alcohol)

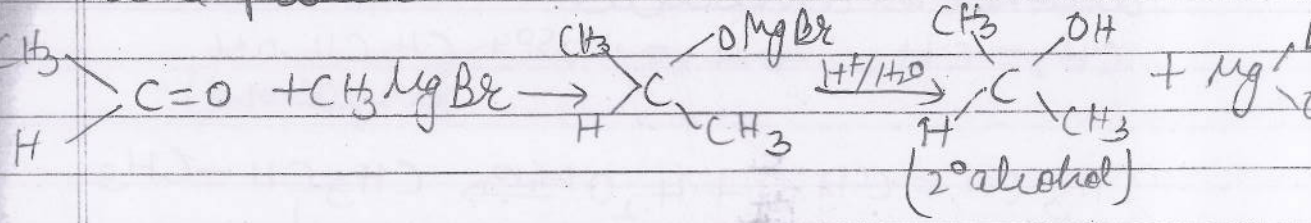
→ By reduction with grignard reagent → Carbonyl compounds on addition with grignard reagent forms an additional compound which on hydrolysis in presence of acid forms alcohol as a product.

$>C=O + RMgX \longrightarrow >C(OMgX)R \xrightarrow{H^+/H_2O} >C(OH)R + Mg(X)(OH)$
(Additional compound)

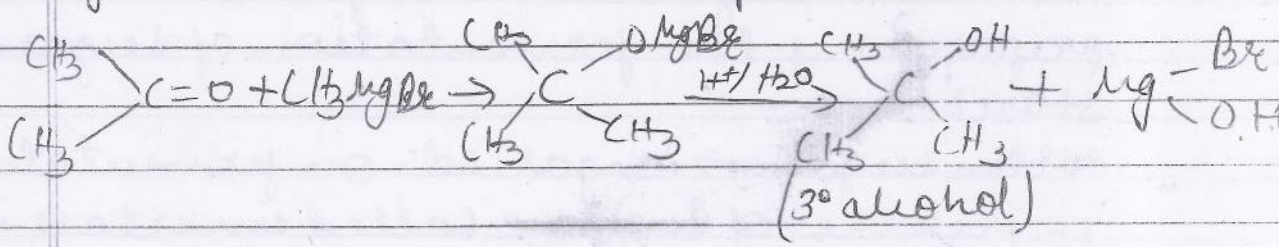
formeldehyde when react with grignard reagent forms 1° alcohol

$H_2C=O + CH_3MgBr \longrightarrow H_2C(OMgBr)CH_3 \xrightarrow{H^+/H_2O} H_2C(OH)CH_3$ (1° alcohol)
(formeldehyde)
$+ Mg(Br)(OH)$

Aldehydes other than formaldehyde when react with grignard reagent forms 2° alcohol as a product.



Ketone when react with grignard reagent forms 3° alcohol as a product.



3) From acid → carboxylic acid on reduction with strong reducing agent forms alcohol as a product.

$$RCOOH + 4[H] \xrightarrow{LiAlH_4} RCH_2OH + H_2O$$

eg → $CH_3COOH + 4[H] \xrightarrow{LiAlH_4} CH_3CH_2OH + H_2O$ (ethyl alcohol)

4) From ester ($RCOOR$) ($R-\overset{O}{\overset{\|}{C}}-OR$) → Ester on reduction with different reducing agents forms mixture of alcohols as a product.

$$R-\overset{O}{\overset{\|}{C}}-OR + 4[H] \xrightarrow{LiAlH_4} RCH_2OH + ROH$$

eg → $CH_3-\overset{O}{\overset{\|}{C}}-OCH_3 + 4[H] \xrightarrow{LiAlH_4} CH_3CH_2OH + CH_3OH$ (ethyl alcohol) (methyl al

5) From aliphatic primary amine (RNH_2) → 1° amines when react with nitrous acid (HNO_2, $HONO$, $NaNO_2 + HCl$) gives alcohol as a product.

$$RNH_2 + HONO \longrightarrow ROH + H_2O + N_2$$

(alcohol)

eg → $CH_3NH_2 + HONO \longrightarrow \underset{\text{(alcohol)}}{CH_3OH} + N_2 + H_2O$

Industrial method of preparation →

1) From alkene (by hydration) → Alkene on hydration in presence of a H_2SO_4 forms alcohol as a product.

$CH_2=CH_2 + H_2O \xrightarrow{H_2SO_4} \underset{\text{(ethyl alcohol)}}{CH_3CH_2OH}$

$CH_3CH=CH_2 + H_2O \xrightarrow{H_2SO_4} CH_3\underset{OH}{\underset{|}{C}}H-CH_3$

2) From carbohydrates → Ethyl alcohol is prepared by the fermentation of sugar and starch.

From sugar → Sugar sol. on fermentation in presence of enzyme called invertase is converted into glucose and fructose which in presence of another enzyme called zymase is converted into ethyl alcohol.

$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{invertase}} \underset{\text{(glucose)}}{C_6H_{12}O_6} + \underset{\text{(fructose)}}{C_6H_{12}O_6}$

$C_6H_{12}O_6 \xrightarrow{\text{zymase}} \underset{\text{(ethyl alcohol)}}{2C_2H_5OH} + CO_2$

From starch → Starch solution on fermentation in presence of enzyme called diastase convert into maltose.

$(C_6H_{10}O_5)_n + nH_2O \longrightarrow \underset{\text{(Maltose)}}{nC_{12}H_{22}O_{11}}$

Maltose in presence of enzyme called maltase is converted into glucose which further converted into ethyl alcohol

in presence of enzyme called zymase.

$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Maltase}} C_6H_{12}O_6 + C_6H_{12}O_6$
(Maltose)

$C_6H_{12}O_6 \xrightarrow{\text{zymase}} 2C_2H_5OH + CO_2$
(alcohol)

* Chemical rxns (properties) of alcohol → Alcohol gives following type of a rxn
A) Reactions involving cleavage of O-H bond
B) Reactions involving cleavage of R-OH bon
C) Reactions due to both R and OH group.

Reactions involving cleavage of O-H bon
→ • Reaction with metals → Alcohol react with metal and liberate hydrogen gas

$2ROH + 2Na \longrightarrow 2RONa + H_2$
(Na alkoxide)

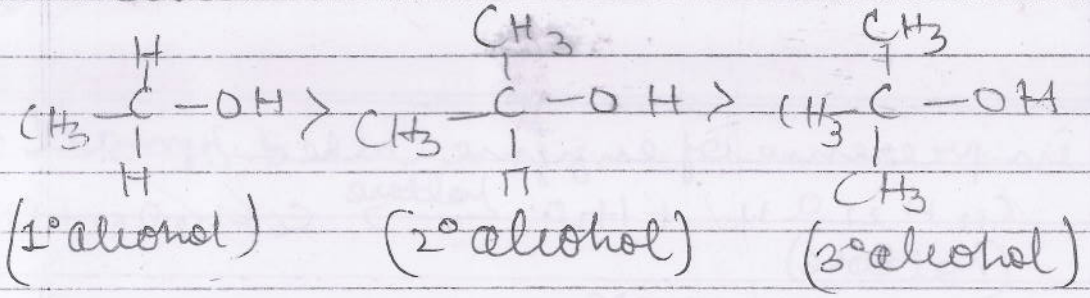
It is clear from the above rxn that alcoh is acidic in nature.
Alcohols are weakly acidic in nature and are weaker acid than water.

$R \xrightarrow{+I\text{ effect}} O-H$ (alcohol) $H-O-H$ (water)

In alcohol there is a presence of alkyl group due to +I effect of alkyl group it releases the e^- to oxygen and compen sate its electro-ve nature. Thus alcohol cannot easily release H^+ ion. This expl less acidic nature of alcohol than water

- Comparision of acidic strength of 1°, 2° and

alcohols →



(1° alcohol) (2° alcohol) (3° alcohol)

This order can be explained in terms of e⁻ releasing inductive effect of alkyl group. The acidic characters of alcohols is due to the cleavage of O–H bond and giving H⁺.

The alkyl group increases the e⁻ density around the oxygen. As a result the e⁻ of O–H bond can't be break and O–H remains strong. Therefore, greater is the no of alkyl group present smaller will be its tendency to release H⁺ ion. ∴ acidic character decreases.

• Reaction with carboxylic acid ⇒ (esterification)

→ Alcohols react with carboxylic acid in presence of a H_2SO_4 and forms esters as a product. This rxn is known as esterification.

$$ROH + RCOOH \xrightleftharpoons{H_2SO_4} \underset{\text{ester}}{RCOOR} + H_2O$$

eg: $CH_3OH + CH_3COOH \xrightleftharpoons{H_2SO_4} \underset{\text{(Ester)}}{CH_3COOCH_3} + H_2O$

• Reaction with grignard reagent → alcohol when react with grignard reagent forms alkane as a product.

$$ROH + RMgX \longrightarrow \underset{\text{(alkane)}}{RH} + Mg\begin{matrix}\nearrow OR \\ \searrow X\end{matrix}$$

eg: $C_2H_5OH + CH_3MgBr \longrightarrow \underset{\text{(alkane)}}{CH_4} + Mg\begin{matrix}\nearrow OC_2H_5 \\ \searrow Br\end{matrix}$

Reactions involving cleavage of R–OH bon

→ • Reaction with halogen acid

$$R-OH + HX \longrightarrow \underset{\text{(haloalkane)}}{R-X} + H_2O$$

eg → $CH_3CH_2OH + HCl \xrightarrow{\text{anhy. } ZnCl_2} \underset{\text{(Chloroethane)}}{CH_3CH_2Cl} + H_2O$

$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-OH + HCl \longrightarrow CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}-H + H_2O$$

• Reaction with phosphorous ~~acid~~ halide → Alcohol when react with P halide and forms haloalkane as a product.

$$R-OH + PX_5 \longrightarrow R-X + HX + POX_3$$

eg → $CH_3OH + PCl_5 \longrightarrow CH_3Cl + HCl + POCl_3$

$$3R-OH + PX_3 \longrightarrow 3R-X + H_3PO_3$$

eg → $3C_2H_5OH + PBr_3 \longrightarrow 3C_2H_5Br + H_3PO_3$
(phosphorous acid)

• Reaction with thionyl chloride ($SOCl_2$)
→ Alcohol when react with thionyl chlorid forms chloroalkane as a product.

$$R-OH + SOCl_2 \xrightarrow{Py} R-Cl + SO_2 + HCl$$

eg → $C_2H_5OH + SOCl_2 \xrightarrow{Py} C_2H_5Cl + SO_2 + HC$
(Chloroethane)

Reaction due to both R and OH group →

1) Dehydration → when alcohols are heated wit protonic acid (H_2SO_4 etc.) at 443 K, alcohol undergo dehydration and forms alkene as a

product -

$$CH_3CH_2OH \xrightarrow[\Delta]{H^+/Al_2SO_4\ 443K} CH_2=CH_2 + H_2O$$

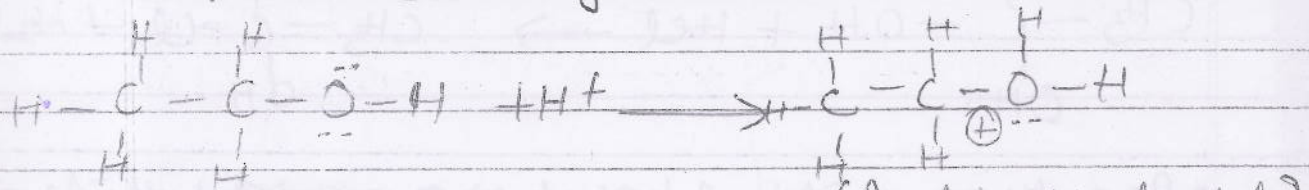
(alkene)

$$CH_3-CH_2-\underset{OH}{CH}-CH_3 \xrightarrow[\Delta]{H^+/H_2SO_4\ 443K} CH_3-CH=CH-CH_3 + H_2O$$

[Prop 1ene]

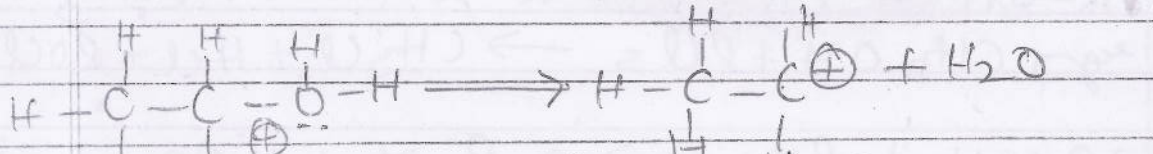
Mechanism of dehydration of alcohol → Dehydration of alcohol involves three step mechanism:

1) Protonation of alcohol →



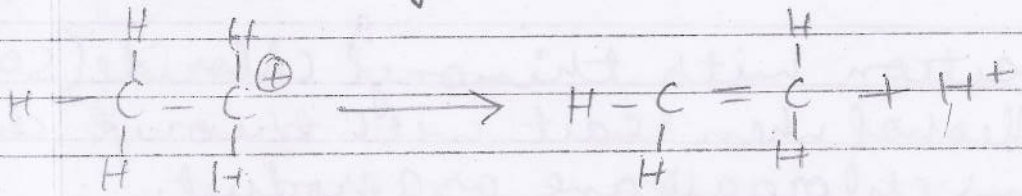
(Protonated alcohol)

2) Loss of water molecule →



(Carbocation)

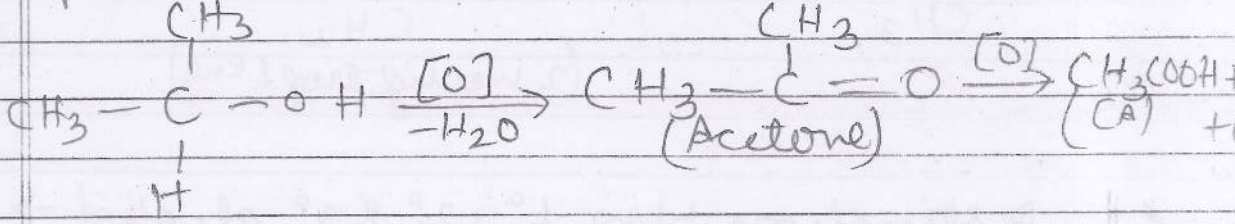
3) Removal of H^+ ion →



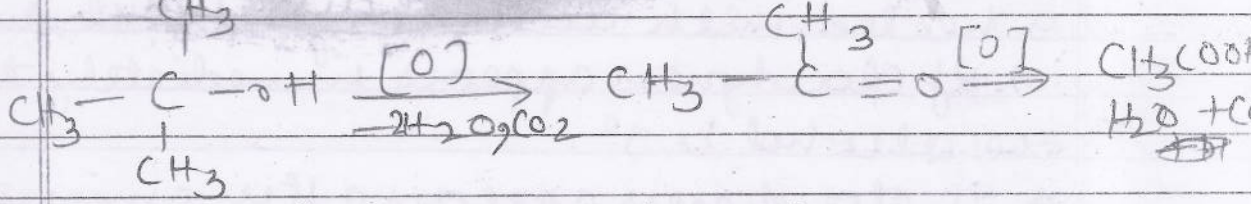
2) Oxidation → Alcohol undergo oxidation with number of oxidising agent such as alkalin or acidic $KMnO_4$, $K_2Cr_2O_7$, HNO_3, CrO_3 etc - Alcohol on oxidation gives carbonyl compounds which further on oxidation gives carboxylic acid,

$CH_3CH_2OH \xrightarrow[-H_2O]{[O]} CH_3CHO \xrightarrow{[O]} CH_3COOH$
(Acetaldehyde) (CA)

1° alcohols on oxidation gives carboxylic acid as a final product which contains same no. of carbon atoms as present in parent alcohol.

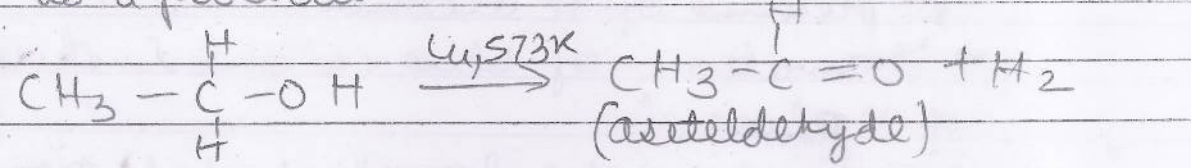


2° alcohols on oxidation gives carboxylic acid as a final product which contains one carbon less than its parent alcohol.

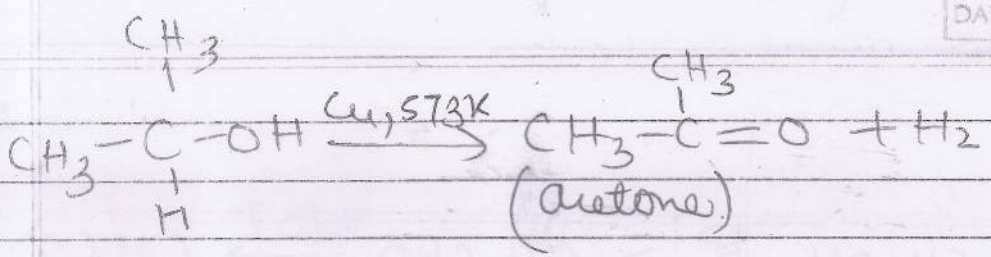


3° alcohol on oxidation gives CA as a final product which contains two carbon less than its parent alcohol.

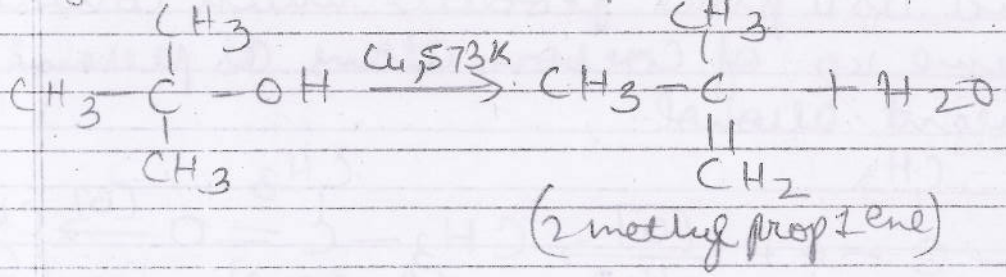
3) Dehydrogenation → Alcohol when heated with Cu at 573K undergo dehydrogenation and gives different products. 1° alcohol on heating with Cu at 573K forms aldehyde as a product.



2° alcohol on heating with Cu at 573K forms a ketone as a product.



3° alcohol on heating with Cu at 573K forms Alkene as a product.



* Distinction b/w 1°, 2° & 3° alcohol → 1°, 2° & 3° alcohol can be distinguish from following test →

1) Lucas test → In this test the alcohol is heated with lucas reagent (HCl + anhy. $ZnCl_2$)
⇒ If cloudyness appears immediately then the alcohol is 3°
⇒ If cloudyness appears after 5 minutes then the alcohol is 2°
⇒ If cloudyness appears only on heating then the alcohol is 1°.

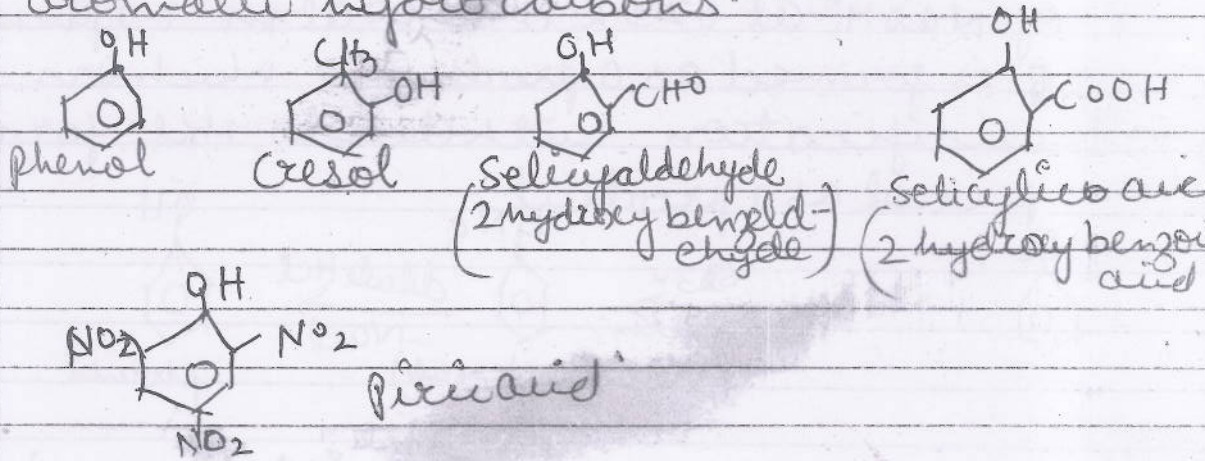
2) Victor meyer's test → In this test iodine is passed through alcohol in presence of a Red P followed by addition of silver nitrite and nitrous acid.
⇒ Formation of blood red colour indicates presence of 1° alcohol
⇒ Formation of blue colour indicates presence of 2° alcohol.
⇒ Formation of colourless solution indicates

the presence of 3° alcohol.

3) oxidation

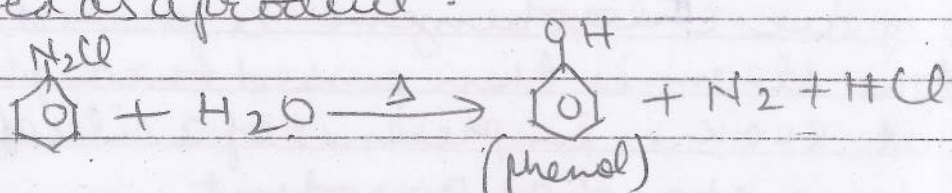
4) Dehydrogenation

Phenol → are the hydroxy derivatives of aromatic hydrocarbons.

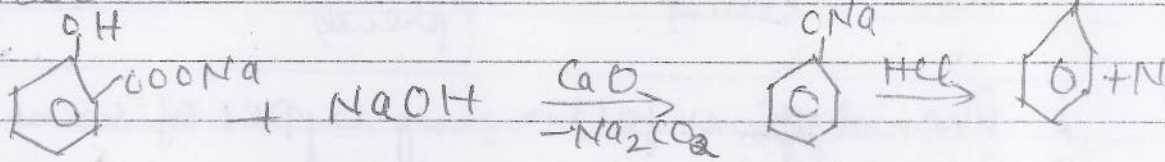


Method of preparation →

1) From diazonium salt → when aqueous sol. diazonium salt is heated with phenol is formed as a product.



2) From salt of salicylic acid → Na salt of salicylic acid when fused with sodalime ($NaOH + CaO$) forms Na phenoxide which on acidification with HCl forms phenol as product.



3) From grignard reagent → when O_2 gas is passed through grignard reagent in presence of ether additional to product

formed which on acidic hydrolysis gives phenol as a product.

$$C_6H_5MgBr + \frac{1}{2}O_2 \xrightarrow{\text{ether}} \text{(O-MgBr)} \xrightarrow{H^+/H_2O} \text{(O-H)} + Mg(Br)(OH)$$

(phenol)

Commerical method of preparation →

1) From chlorobenzene (dow's process)

→ Haloarenes when react with aqueous soln of NaOH at 623 K and 300 atm - Na phenoxide is formed as a product which on acidification with dilute HCl forms phenol as a product.

$$\text{(O-Cl)} + NaOH \xrightarrow[300\,atm]{623\,K} \text{(O-Na)} \xrightarrow{\text{dilute HCl}} \text{(O-H)} + NaCl$$

(Na phenoxide) phenol

2) From benzene → (Raschig's process)

when vapours of HCl are passed through benzene at 500K in presence of a cuperic chloride or ferric chloride and excess of air chlorobenzene is formed as a product. The steam is then passed through chlorobenzene at 800K in presence of a silica (SiO_2) to form phenol as a product.

$$2\,\text{(O)} + O_2 + 2HCl \xrightarrow{CuCl/FeCl_2} 2\,\text{(O-Cl)} + 2H_2O$$

$$\text{(O-Cl)} + H_2O \xrightarrow[800K]{SiO_2} \text{(O-H)} + HCl$$

(steam) (phenol)

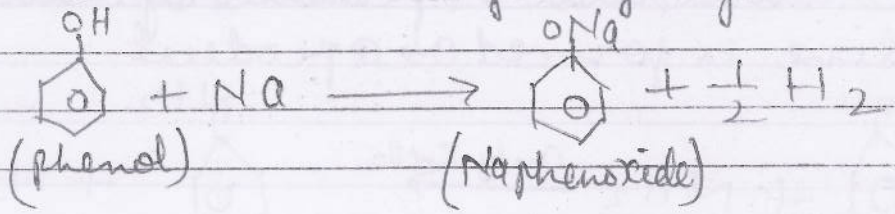
* Phenol gives following types of rxns →

1) Rxn due to OH group

2) Rxn due to ring
3) Special rxn

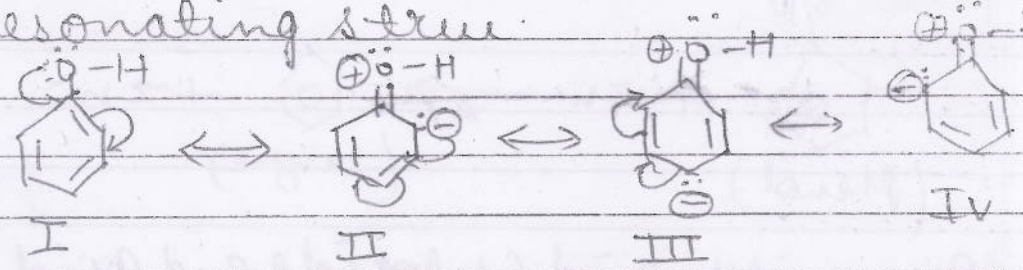
Rxn due to OH group →

1) Acidic character → Phenol when react with metals liberate hydrogen gas.



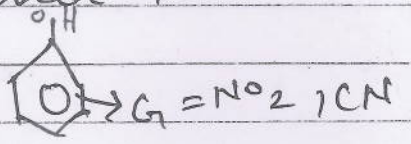
This rxn shows the acidic character of phenol. Phenol is weakly acidic in natu

- Phenols are more acidic than alcohol → This can be explain with the help of resonating struc



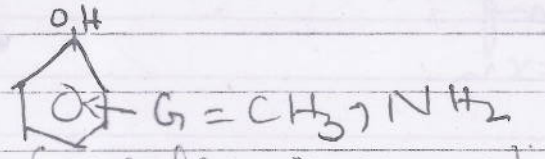
It is clear from the resonating structures II, III & IV that oxygen acquire a +ve charge. In order to neutralise this +ve charge oxygen will attract the e⁻ of O-H and thus releases H^+ ion easily. This shows more acidic character of phenol than alcohol.

Effect of substituent on the acidic chara of phenol →



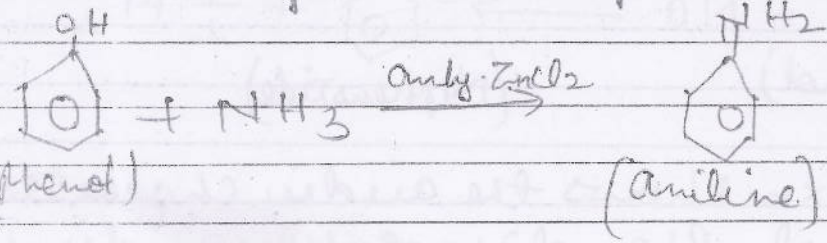
Acidic character increases

When e^- withdrawing group such as NO_2, CN is attached to the ring the acidic character of the substituted phenol increases

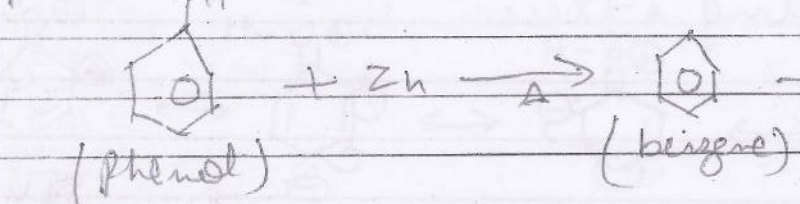


Acidic character decreases

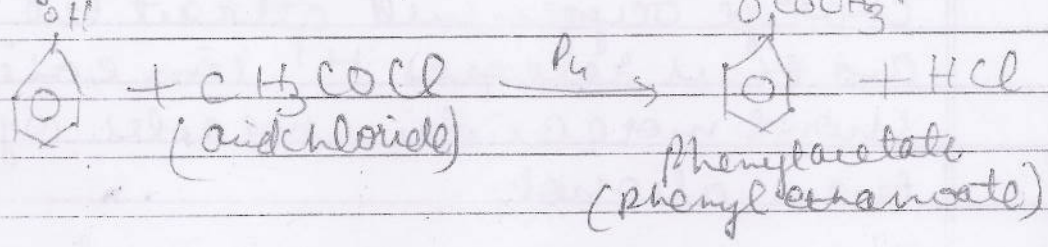
2) Rxn with ammonia → Phenol when react with ammonia in presence of anhy. $ZnCl_2$ aniline is formed as a product.

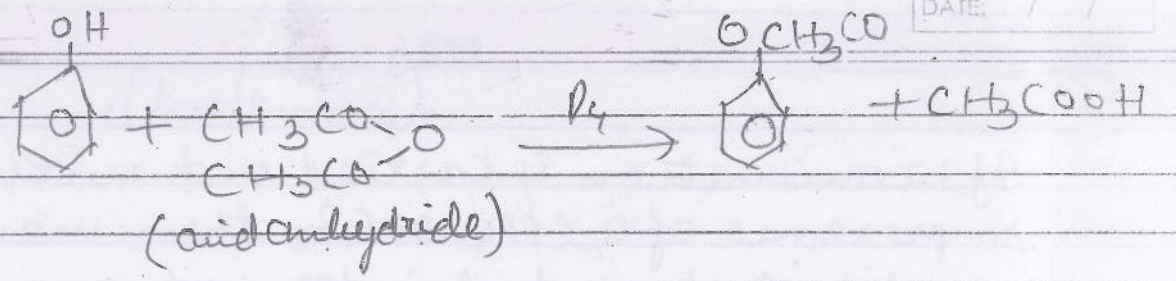


3) Rxn with zinc dust → Phenol when ~~reac~~ heated with Zn dust forms benzene as a product -

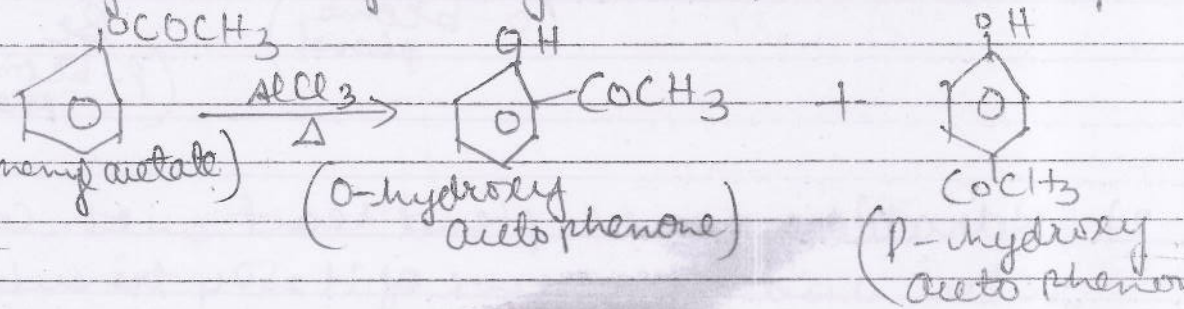


4) Rxn with acid chloride and acid anhydride → Phenol when react with acid chloride and acid anhydride in presence of pyridine and forms ester as a product.

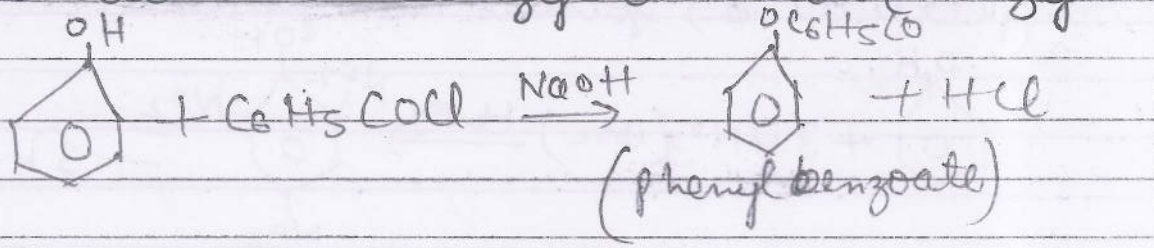




Fries rearrangement → when phenyl acetat is heated with $AlCl_3$ it undergo rearrang and forms hydroxy aceto phenone as a prod



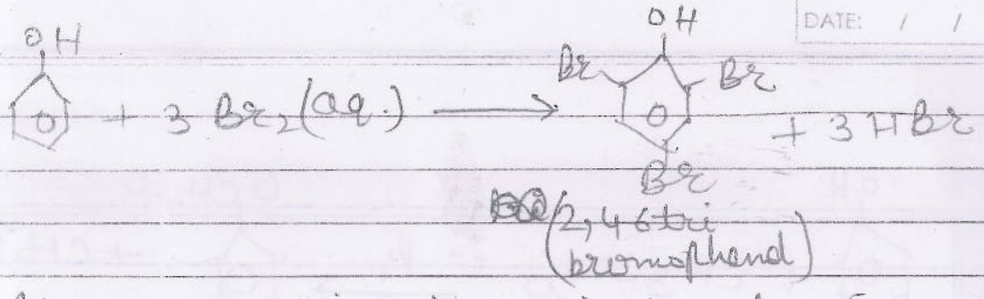
5) Reaction with benzyl chloride (benzoylati



when phenol react with benzoyl chloride in presence of a NaOH forms phenol benzoat as a product - This rxn is K/a Schotten Baumann's rxn.

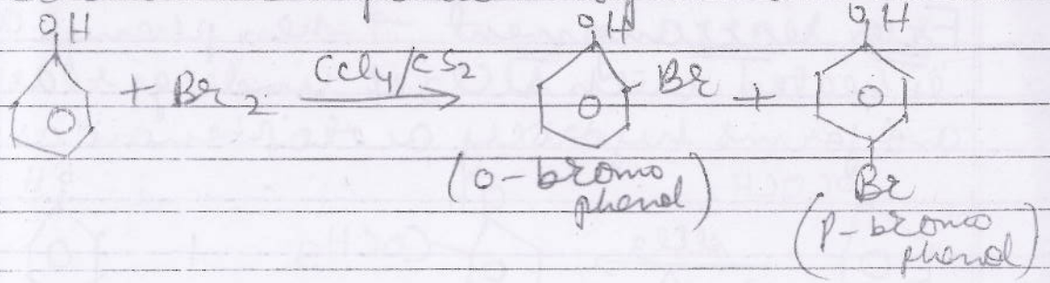
Rexn due to ring :→ is electrophilic Sub- stitution rxn. In phenol the OH group on benzene ring is ortho & para direct

1) Bromination → when phenol react wi aqueous sol. of bromine or bromine water tri substitution occurs and 2,4, tri bromo phenol is formed as a product

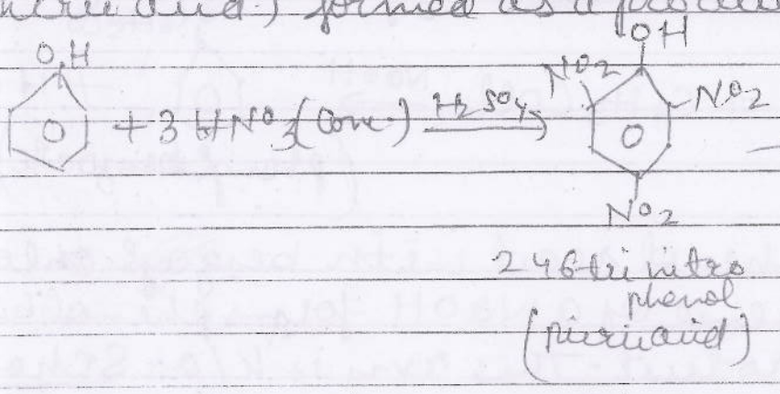


2,4,6 tri bromophenol

If bromination is carried out with Br_2 in presence of a CCl_4 or CS_2 then mono substituted product is formed.

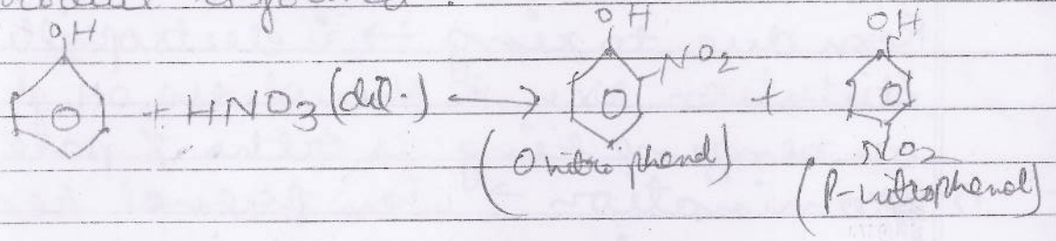


2) **Nitration** → when phenol react with conc. nitric acid in presence of H_2SO_4 tri substitution occurs and 2,4,6 tri nitro phenol (picric acid) formed as a product.



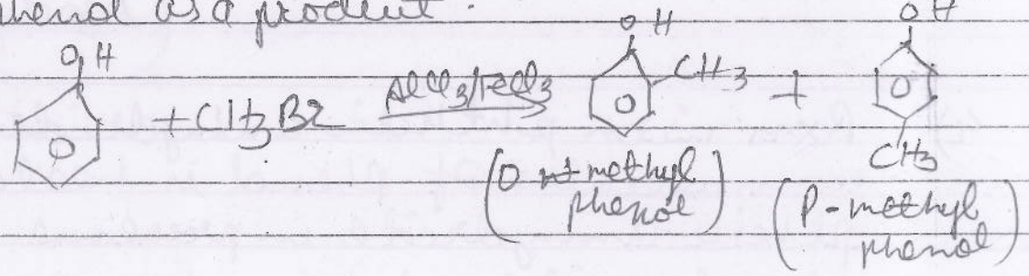
2,4,6 tri nitro phenol (picric acid)

If the nitration is carried out in presence of a dilute HNO_3 then mono substituted product is formed.



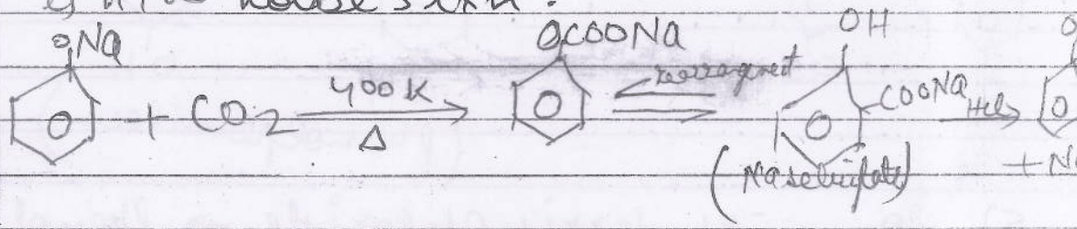
(o-nitro phenol) (p-nitrophenol)

3) Alkylation → Phenol when react with alkyl halide in presence of halogen carriers such as $AlCl_3$ / $FeCl_3$ forms mono substituted alkyl phenol as a product.

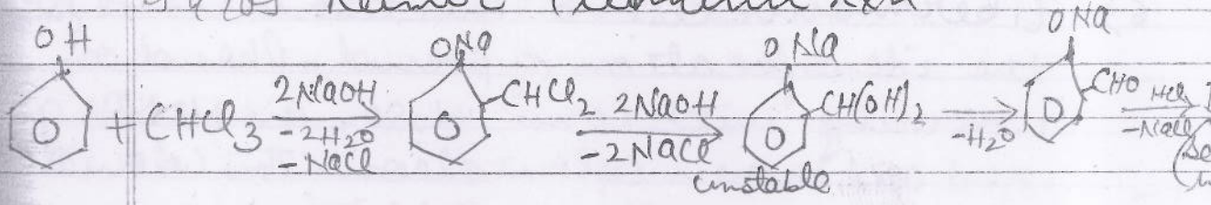


Special rxns →

1) Kolbe's rxn → when Na phenoxide is heated with CO_2 at 400K additional product is formed which on rearrangement gives Na salicylate which further on acidification gives salicylic acid as a product. This rxn is also kolbe's rxn.

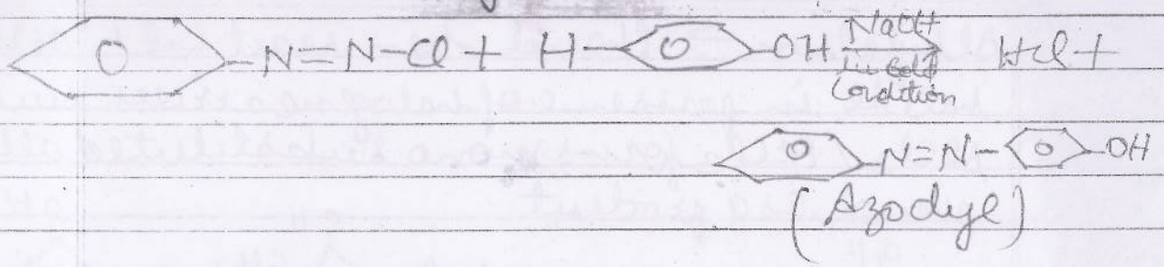


2) Reimer Tiemann rxn → when phenol react with chloroform ($CHCl_3$) in presence of NaOH followed by hydrolysis & acidification salicylaldehyde is formed as a product. This rxn is also Reimer Tiemann rxn.



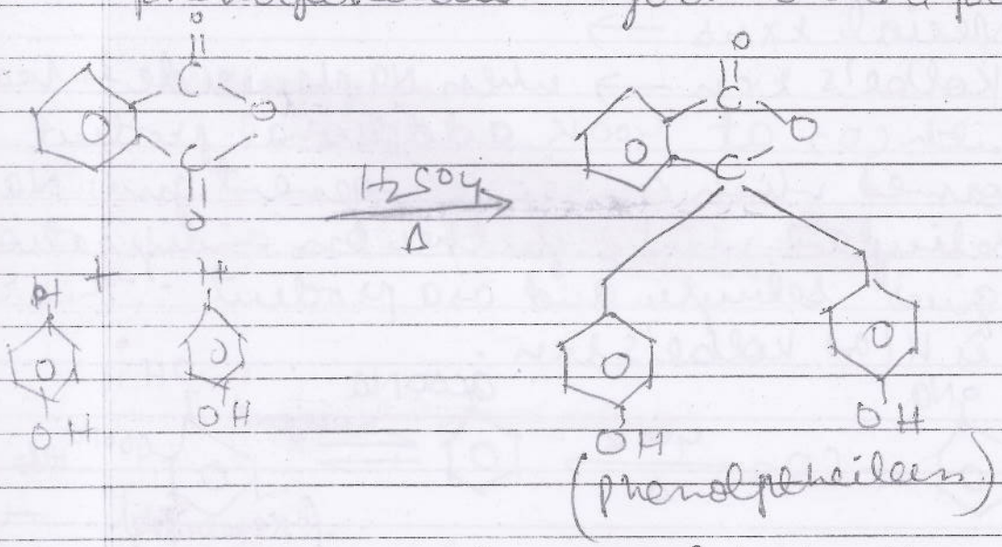
3) Coupling rxn → when phenol react with benzene diazonium salt chloride in presence of alkali (NaOH) under ice cold condition.

Azodye is formed as a product - This rxn is known as coupling rxn.



(Azodye)

4) Rxn with phthalic anhydride → When two molecules of phenol is heated with phthalic anhydride in presence of H_2SO_4 phenolpthalein is formed as a product.



(phenolphthalein)

5) Rxn with ferric Chloride → Phenol react with ferric chloride & forms coloured complex.

$$3C_6H_5OH + FeCl_3 \longrightarrow Fe(OC_6H_5)_3 + 3HCl$$

(violet colour)

6) Libermann test → This test is used for the identification of phenol - Phenol on warming with Conc. H_2SO_4 and $NaNO_3$ gives red and brown colouration. This colouration changes to blue & green on addition of aqueous NaOH.

Ethers →

Method of preparations →

1) From alkyl halide

(i) By williamson synthesis →

$$R-X + NaOR \rightarrow \underset{\text{(ether)}}{ROR} + NaX$$
(Na alkoxide)

eg. $CH_3Cl + NaOCH_3 \rightarrow CH_3OCH_3 + NaCl$

Limitations → This rxn can't be used to prepare aromatic ether.

(ii) Two molecules of alkyl halide when heated with silver oxide forms ethers as a product.

$$\begin{matrix} R-X \\ R-X \end{matrix} + Ag_2O \xrightarrow{\Delta} \underset{\text{(ether)}}{ROR} + 2AgX$$

eg. $2CH_3Br + Ag_2O \xrightarrow{\Delta} CH_3OCH_3 + 2AgBr$

2) From alcohol → 1° alcohol when heated to a temperature of 413K forms ether as a product.

$$R-OH + R-OH \xrightarrow[\Delta]{413K} ROR + H_2O$$

eg. $CH_3OH + CH_3OH \xrightarrow[\Delta]{413K} CH_3OCH_3 + H_2O$

Ether gives following types of rxns →

(1) Rxn due to ethereal oxygen
(2) Rxn due to cleavage of C–O bond
(3) Rxn due to alkyl group
(4) Rxn due to ring

⇒ Rxn due to etheral oxygen →
Rxn with concentrated H_2SO_4 → ether react with conc. acid & forms oxonium salt.

$$R-\ddot{O}-R + H_2SO_4 \longrightarrow \left[R-\overset{\oplus}{\underset{H}{O}}-R\right] HSO_4^{\ominus}$$

eg ⇒ $CH_3-\ddot{O}-CH_3 + H_2SO_4 \longrightarrow \left[CH_3-\overset{\oplus}{\underset{H}{O}}-CH_3\right] HSO_4^{\ominus}$

⇒ Rxn due to cleavage of C-O bond
Rxn with halogen acids → ether react with halogen acids & forms alcohol and alkyl halide as a product.

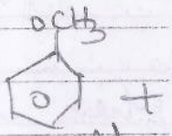
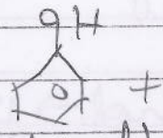
$$R-OR + HX \longrightarrow \underset{\text{(alcohol}}{ROH} + \underset{\text{(alkyl halide)}}{RX}$$

If the halogen acids is in excess then only alkyl halide is formed as a product.

$$R-OR + \underset{\text{(excess)}}{HX} \longrightarrow ROH + RX$$

$$R-OH + HX \longrightarrow R-X + H_2O$$

eg ⇒ $CH_3CH_2O\boxed{O}CH_3 + HI \longrightarrow CH_3CH_2OH + CH_3I$

*  + HI $\xrightarrow{373K}$  + CH_3I

(Anisol) (phenol)

⇒ Rxn due to alkyl group →
Halogenation → ether react with halogen in dark & forms a halogens substituted product.

$$CH_3CH_2OCH_2CH_3 + Cl_2 \xrightarrow{\text{dark}} CH_3-\underset{Cl}{CH}OCH_2CH_3 + HCl$$

$CH_3CH_2OCH_2CH_3 + Cl_2$ (excess) $\rightarrow CCl_3CCl_2OCCl_2CCl_3 + 10HCl$

Rxn with air → Ether react with oxygen in presence of air & forms peroxide as a product

$CH_3CH_2OCH_2CH_3 + O_2 \rightarrow CH_3CH(O-O-H)OCH_2CH_3$ (peroxide)

⇒ Rxn due to ring →