CHAPTER

11

ALCOHOL, PHENOL AND ETHER

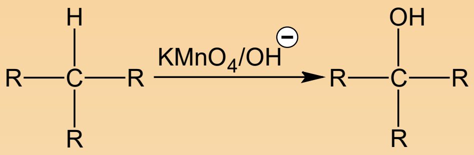
INTRODUCTION

Alcohols and phenols arise through the replacement of a hydrogen atom in hydrocarbons (specifically aliphatic for alcohols and aromatic for phenols) by a hydroxyl (-OH) group. When naming alcohols, the procedure involves substituting the 'e' at the end of the parent alkane's name with the suffix 'ol'.

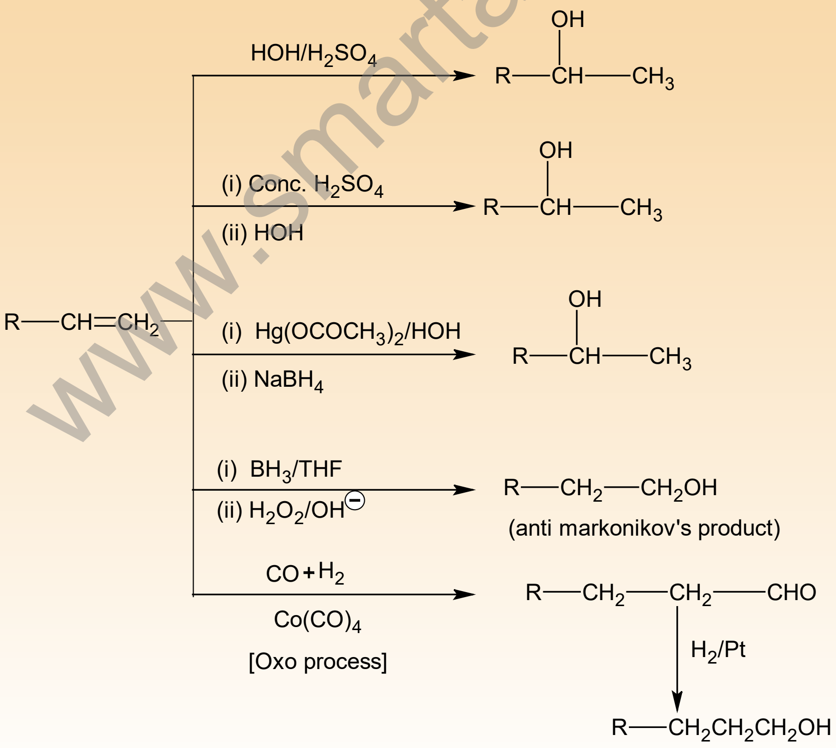
PREPARATION OF ALCOHOLS

1. From Alkanes

Alkanes having tertiary carbon on oxidation with cold alkaline KMnO4 give tertiary alcohol.

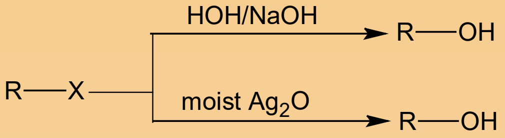


2. **From Alkenes :** Alkenes can be converted into alcohol by the following reactions:



3. From alkyl halides

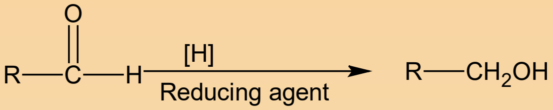
Alkyl halides give alcohol with KOH/NaOH or with moist Ag_2O.



4. Reduction of aldehydes and ketones

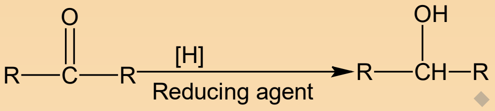
(a) Reduction by reducing agents

(i) Aldehyde gives primary alcohol



$$R-\overset{O}{\overset{\|}{C}}-H \xrightarrow[\text{Reducing agent}]{[H]} R-CH_2OH$$

(ii) Ketone gives secondary alcohol



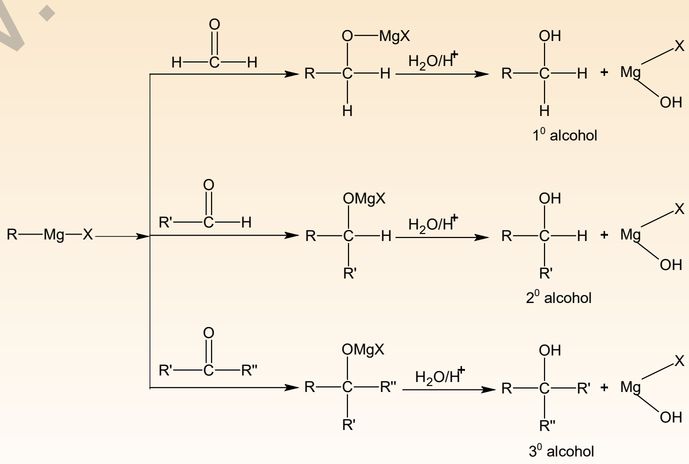
$$R-\overset{O}{\overset{\|}{C}}-R \xrightarrow[\text{Reducing agent}]{[H]} R-\overset{OH}{\overset{|}{C}H}-R$$

Reducing agents

- $LiAlH_4$
- $NaBH_4$
- Na/C_2H_5OH
- Metal (Zn, Fe or Sn)/Acid (HCl, dil H_2SO_4 or CH_3COOH)
- (a) Aluminium isopropoxide/isopropylalcohol (b) H_2O
- H_2/Ni

(b) Reduction by Grignard reagents

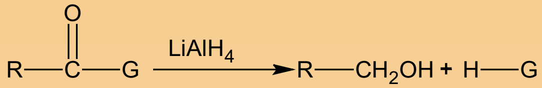
Addition followed by hydrolysis



Methanol can not be prepared by this method.

5. Reduction of carboxylic acid, Acid chlorides and esters:

(a) Reduction by $LiAlH_4$



$$R-\overset{O}{\overset{\|}{C}}-G \xrightarrow{LiAlH_4} R-CH_2OH + H-G$$

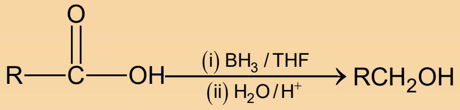
G = OH (acid)

G = Cl (acid chloride)

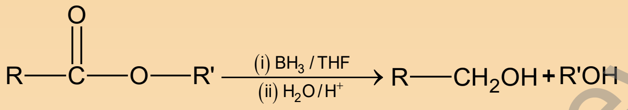
G = OR′ (ester)

(b) Reduction by BH_3

Carboxylic acids and esters are reduced in to primary alcohol by BH_3.

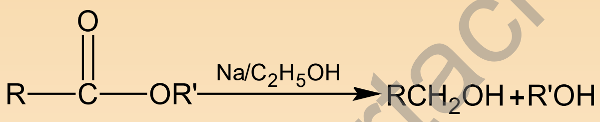


$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\text{(ii) } H_2O/H^+]{\text{(i) } BH_3/THF} RCH_2OH$$



$$R-\overset{O}{\overset{\|}{C}}-O-R' \xrightarrow[\text{(ii) } H_2O/H^+]{\text{(i) } BH_3/THF} R-CH_2OH + R'OH$$

(c) Bouveault – Blanc reaction

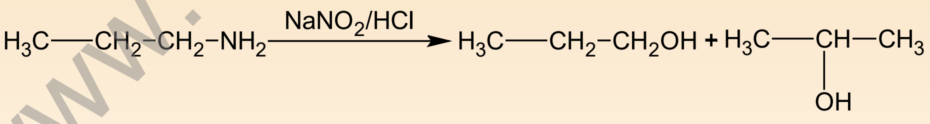


$$R-\overset{O}{\overset{\|}{C}}-OR' \xrightarrow{Na/C_2H_5OH} RCH_2OH + R'OH$$

6. From aliphatic primary amines

It react with nitrous acid to give alcohol.

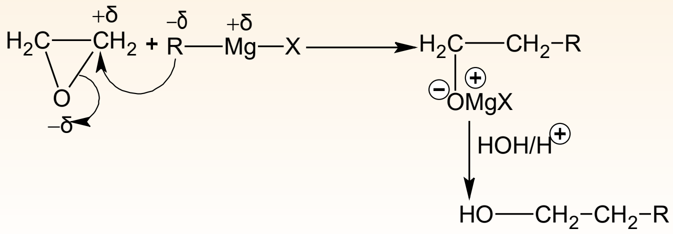
- ➢ Nature of alcohol depends on the nature of carbon having —NH_2 group.
- ➢ Reaction proceeds through carbocation hence rearranged alcohol is obtained.



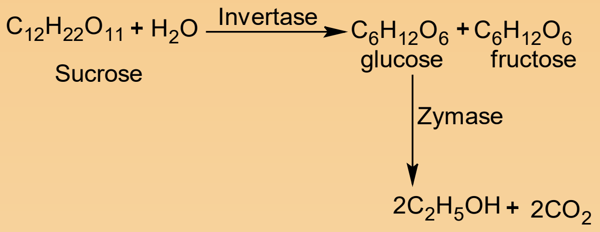
$$H_3C-CH_2-CH_2-NH_2 \xrightarrow{NaNO_2/HCl} H_3C-CH_2-CH_2OH + H_3C-\underset{OH}{\underset{|}{CH}}-CH_3$$

7. From Oxiranes

Oxiranes react with Grignard reagent to give mono hydric alcohol. Nature of G.R is basic hence it attack on less hindered carbon of oxirane ring.



8. Fermentation of carbohydrates



$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

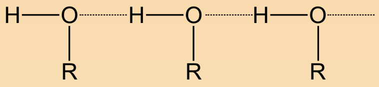
PHYSICAL PROPERTIES

Solubility

Alcohols are soluble in water due to formation of H – bonding between water & them. As the molecular mass increases, the alkyl group become larger which resists the formation of H – bonds with water molecules and hence the solubility goes an decreasing.

Boiling Point

Intermolecular H – bonding is present between alcohol molecules. This makes high boiling point.



Amongst the isomeric alcohols, the order of boiling point is 1° > 2° > 3° alcohol.

CHEMICAL PROPERTIES

Chemical properties of alcohols can be discussed under following categories:

(A) Reaction involving breaking of carbon – oxygen bond.

(B) Reaction involving breaking of oxygen – hydrogen bond.

(C) Oxidation of alcohols.

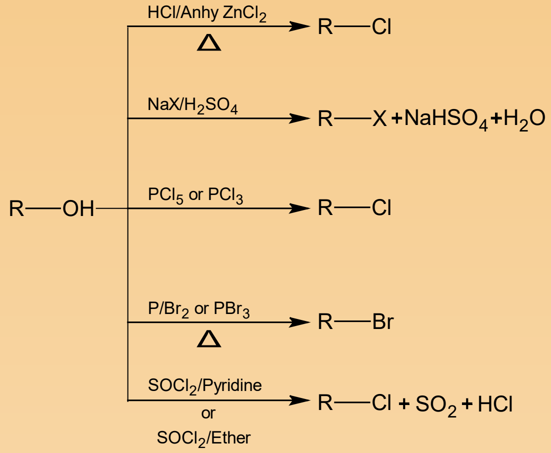
(D) Dehydrogenation of alcohols.

(E) Some miscellaneous reactions of monohydric alcohol.

(A) **Reaction involving breaking of carbon – oxygen bond**

Order of reactivity of alcohol. 3° > 2° > 1°

(i) **SN reaction**



(ii) **Dehydration of alcohol**

Dehydration of alcohol to give alkene.

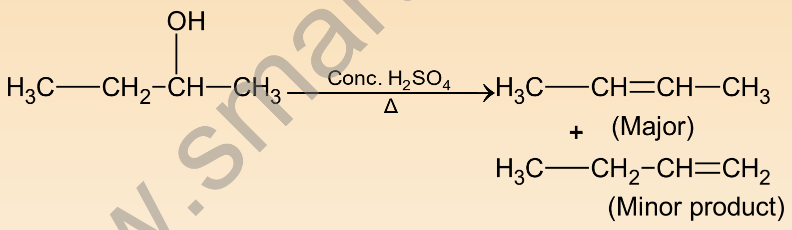
(a) Dehydrating agents are

Conc H_2SO_4/Δ, $KHSO_4$/Δ, H_3PO_4/Δ, Anhyd Al_2O_3/Δ, Anhyd PCl_5/Δ, Anhyd $ZnCl_2$/Δ, BF_3/Δ, P_2O_5/Δ.

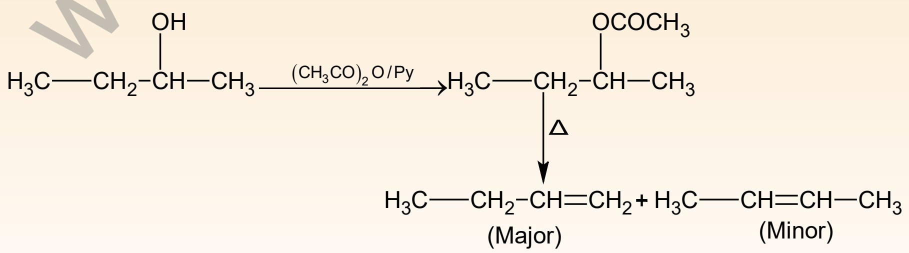
(b) Reactivity of alcohols. (Ease of dehydration)

3° > 2° > 1°

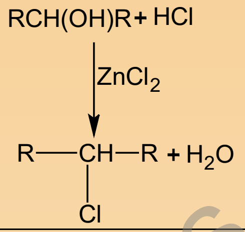
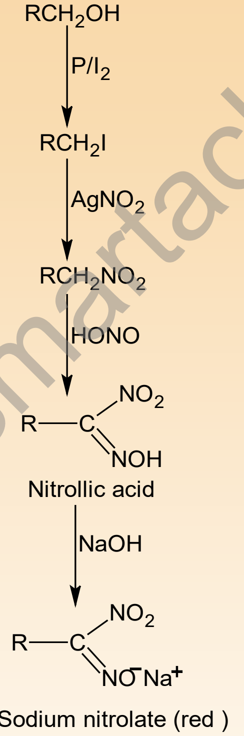
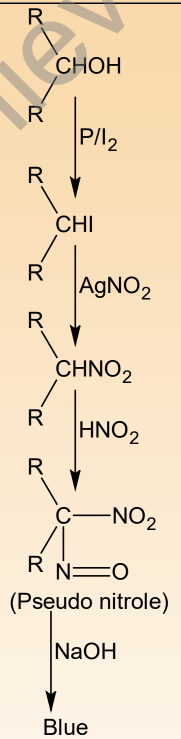
(c) Product formation always takes place by saytzeff rule.



Note: Alcohols on acetylation gives acetyl derivative which on pyrolytic elimination always gives Hofmann product.

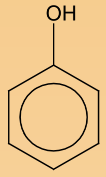


Distinguishing 1°, 2°, 3° alcohol

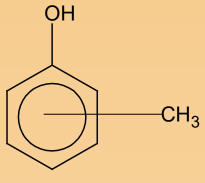
Test	**1° alc**	**2° alc**	**3° alc**
(I) Lucas test [$ZnCl_2$ + HCl]	No reaction at room temperature	White turbidity after 5 – 10 min.  $RCH(OH)R + HCl \xrightarrow{ZnCl_2} R{-}\underset{Cl}{\underset{\mid}{CH}}{-}R + H_2O$	White turbidity instantaneously $R_3C{-}OH + HCl \xrightarrow{ZnCl_2} R_3C{-}Cl$
(II) Victor Meyer test (P/I_2, $AgNO_2$, HNO_2, NaOH)	Red colour	Blue colour	Colourless
	 Nitrollic acid Sodium nitrolate (red)	 (Pseudo nitrole) Blue	$R_3C{-}OH \xrightarrow{P/I_2} R_3C{-}I \xrightarrow{AgNO_2} R_3C{-}NO_2 \xrightarrow{HNO_2}$ No reaction (colourless)

PHENOL

These are organic compounds a hydroxyl group attached directly to a benzene ring.



Phenol or carbolic acid



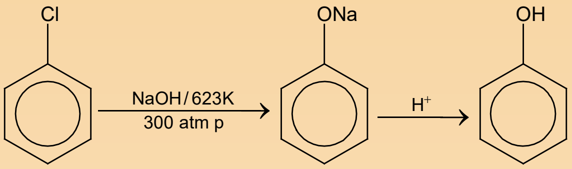
(o , p , m)
Cresol

Preparation

Industrial Method

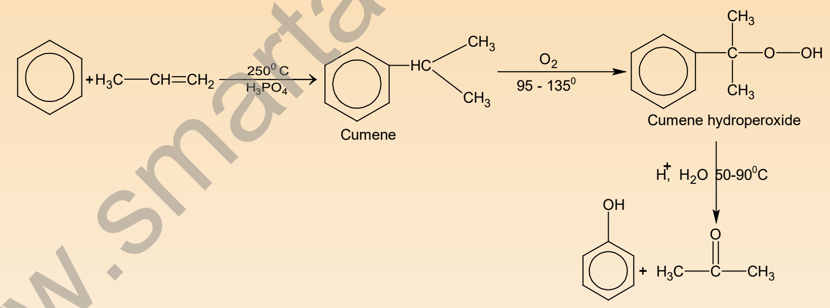
(i) From chloro benzene (Dow's process)

Chlorobenzene is heated with NaOH at 673 K and under pressure of 300 atm to produced sodium phenoxide which on acidification yields phenol.



(ii) Cumene Process

Cumene obtained from propene & benzene cumene on air oxidation followed by acidification with H_2SO_4 gives phenol & acetone.



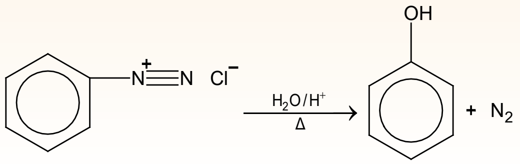
(iii)From benzene sulphonic acid

It is fused with NaOH gives sodium salt of phenol.

$$C_6H_5SO_3H \xrightarrow[\text{Fusion}]{\text{NaOH}} C_6H_5SO_3Na \longrightarrow C_6H_5ONa \xrightarrow{H_2O^+/H^+} C_6H_5OH$$

(iv)From benzene diazonium chloride

This gives Ar SN1 reaction with H_2O to form phenol.



PHYSICAL PROPERTIES

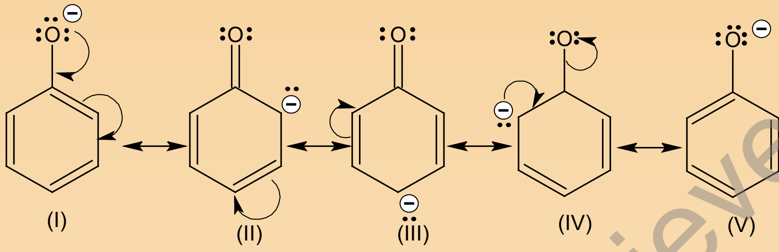
Phenol is needle shaped solid, soon liquefies due to high hygroscopic nature. It is less soluble in water, but readily soluble in organic solvents.

Phenol has high boiling point due to presence of hydrogen bonding.

Acidity of phenol

Phenol is weak acid. It reacts with aqueous NaOH to form sodium phenoxide, but does not react with sodium bicarbonate.

The acidity of phenol is due to the stability of the phenoxide ion, which is resonance stabilized as shown below:



In substituted phenols, the presence of electron withdrawing groups at ortho and para positions such as nitro group, stabilizes the phenoxide ion resulting in an increase in acid strength. It is due to this reason that ortho and para nitro phenols are more acidic than phenol.

On the other hand, electron releasing groups such as alkyl group, do not favour the formation of phenoxide ion – resulting in decrease in acid strength.

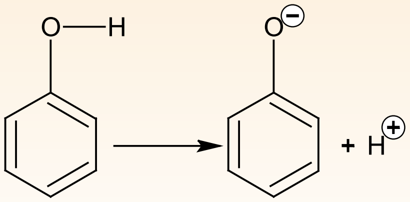
For example: (cresol are less acidic then phenol)

CHEMICAL REACTIONS

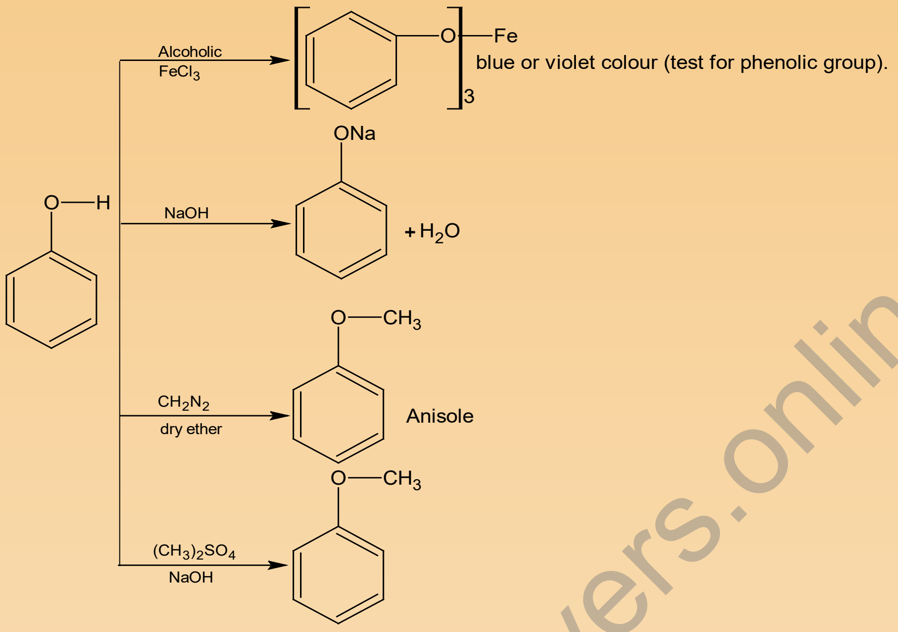
(A) Reaction due to breaking of O – H bond

Phenol is more reactive than alcohol for this reaction because phenoxide ion is more stable than the alkoxide ion.

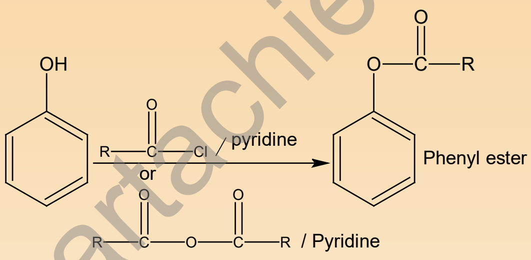
$$R-O-H \longrightarrow R-\overset{\ominus}{O} + H^{\oplus}$$



Reactions of phenol due to breaking of —O — H bond are given below:

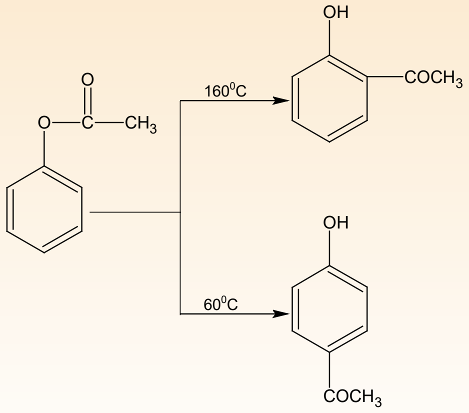


Acylation



Fries rearrangement

Phenolic esters are converted in to o — and p — hydroxy ketones in the presence of anhydrous $AlCl_3$. Generally low temperature favours the formation of p – isomer and higher temperature favour the o - isomer.



(B) **Reactions due to breaking of carbon- Oxygen bond**

Nucleophilic substitution reaction

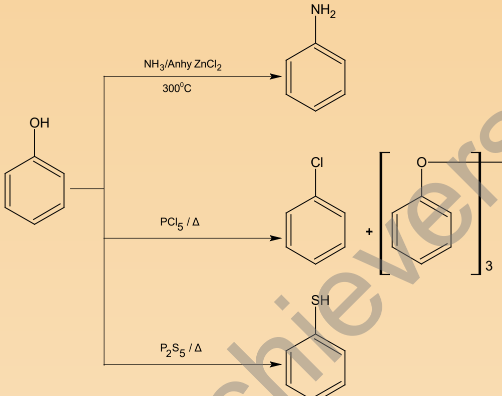
Phenols are less reactive than aliphatic compound because:

(i) —OH group is present on sp^2 hybridised carbon. This makes C — O bond stronger.

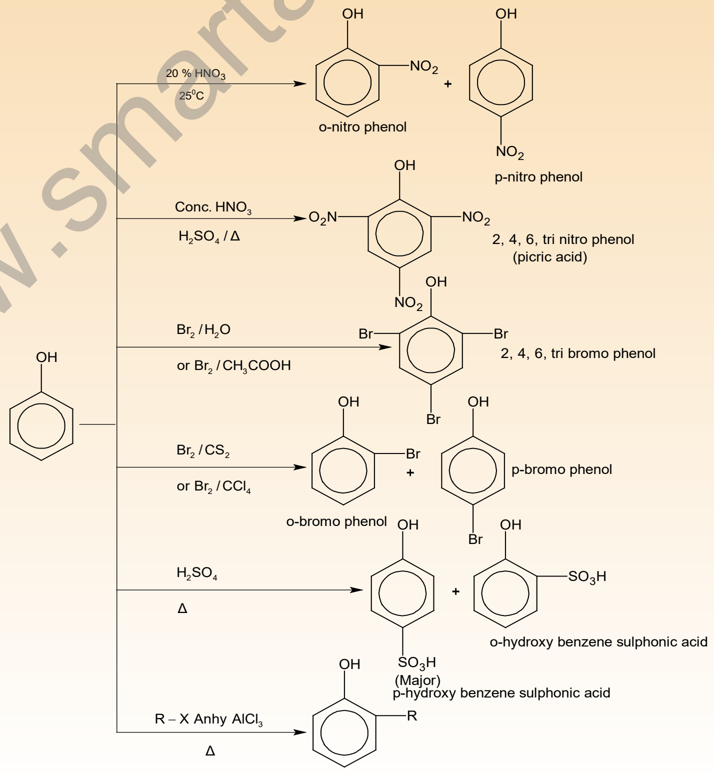
(ii) 'O' is more electronegative than halogens. This also makes C — O bond stronger than C — X.

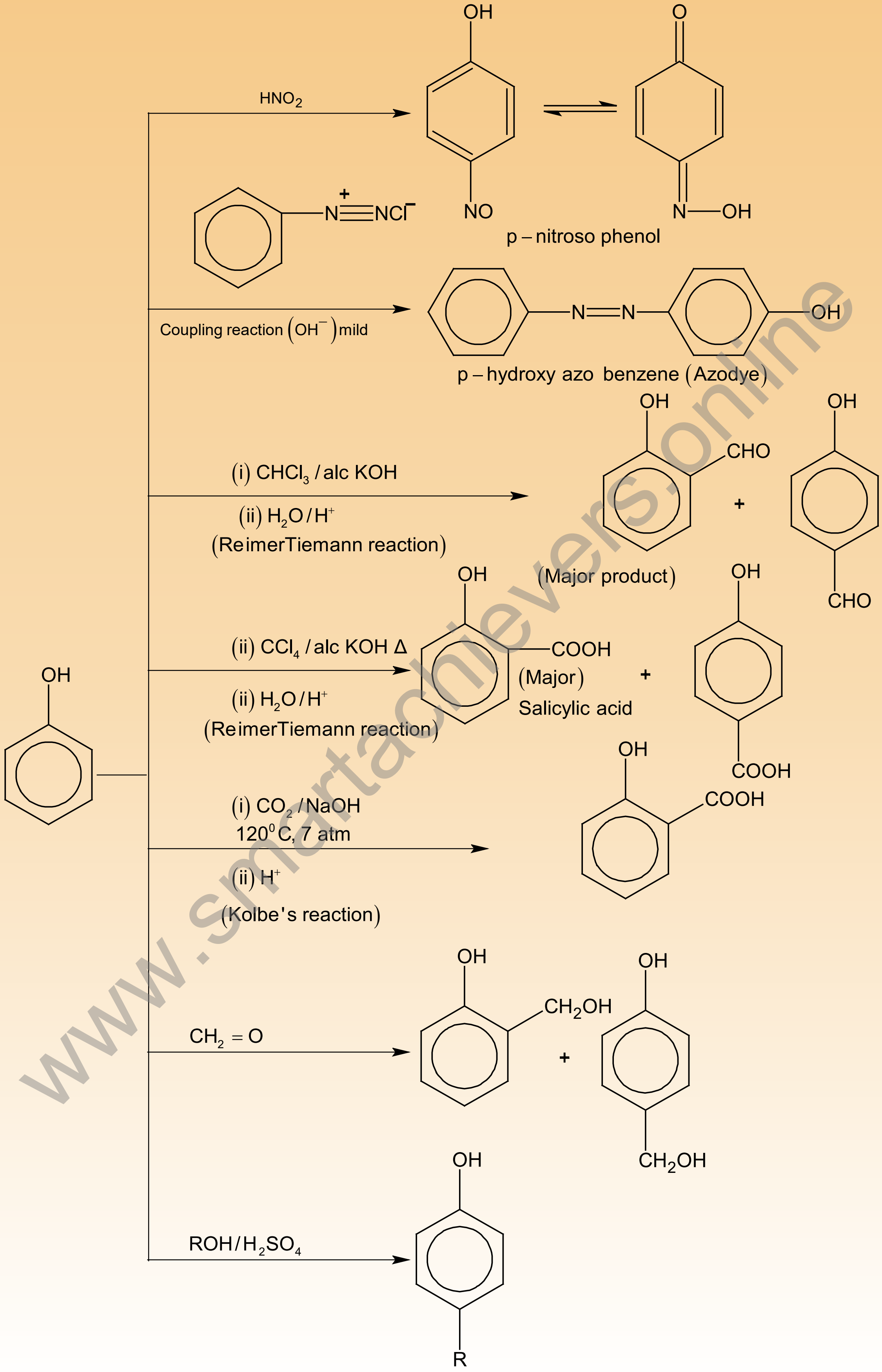
(iii) There is some double bond character between carbon and oxygen due to the resonance. This also makes C — O bond stronger.

However it give SN under drastic condition.



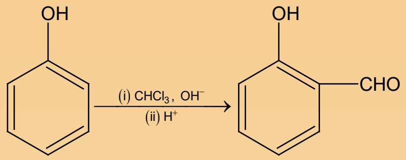
(C) **EAS in Phenol:** It is strong activating group.




OH
HNO$_2$
OH
NO
O
N—OH
p – nitroso phenol
N≡NCl$^-$
Coupling reaction (OH$^-$) mild
N=N
OH
p – hydroxy azo benzene (Azodye)
(i) CHCl$_3$ / alc KOH
(ii) H$_2$O / H$^+$
(ReimerTiemann reaction)
OH
CHO
(Major product)
+
OH
CHO
(ii) CCl$_4$ / alc KOH Δ
(ii) H$_2$O / H$^+$
(ReimerTiemann reaction)
OH
COOH
(Major)
Salicylic acid
+
OH
COOH
(i) CO$_2$ / NaOH
120^{0}C, 7 atm
(ii) H$^+$
(Kolbe's reaction)
OH
COOH
CH$_2$ = O
OH
CH$_2$OH
+
OH
CH$_2$OH
ROH / H$_2$SO$_4$
OH
R

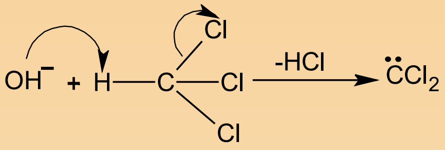
Mechanism of some important reactions

1. Reimer Tieman reaction

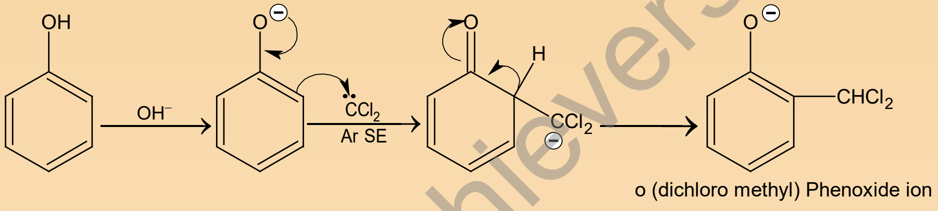


The electrophile is the dichloro carbene, :CCl$_2$, formation of carbene is an example of α - elimination.

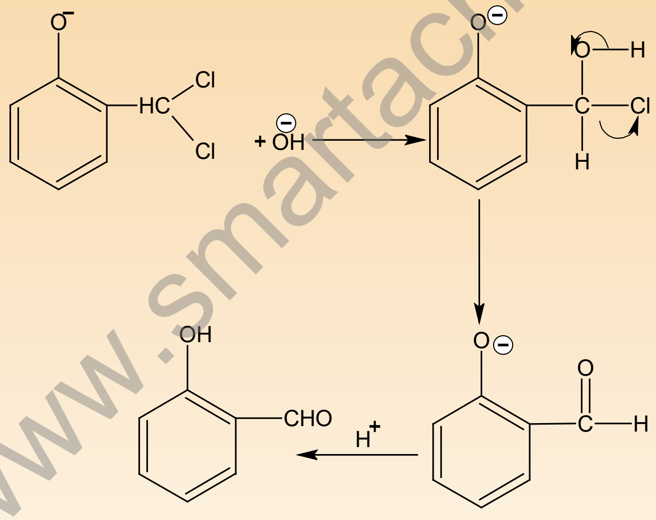
(i)



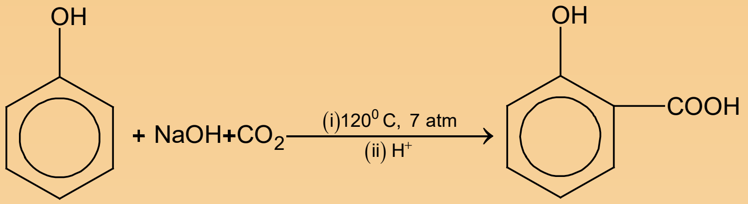
(ii)



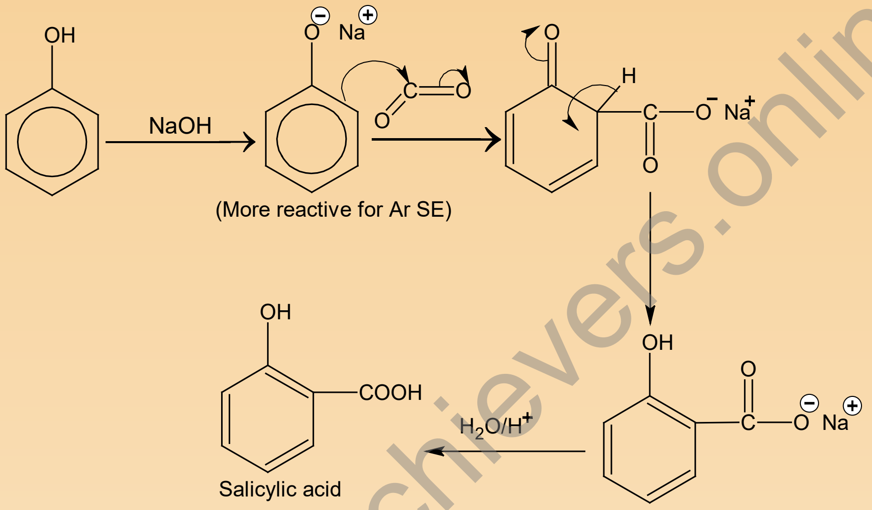
(iii)



2. Kolbe's reaction



Mechanism



Some Commercially Important Alcohols And Phenols

(i) **Methanol:** Methanol is also called wood spirit since originally it was obtained by destructive distillation of wood. Now a days it is prepared by catalytic hydrogenation of water gas.

$$CO + 2H_2 \xrightarrow[573-673K,\ 200-300K]{CuO-ZnO-CrO_3} CH_3OH$$

Uses: It is largely used as:

(a) a solvent for paints, varnishes and celluloids.

(b) for manufacturing of formaldehyde.

(c) for denaturing ethyl alcohol, i.e. to make it unfit for drinking purpose. Denatured alcohols is called methylated spirit.

(d) in manufacture of perfumes and drugs.

Ethanol: Ethanol is mainly prepared by hydration of ethene formation of carbohydrates gives only 95% alcohol the rest being water. This is called rectified spirit.

Uses: It is largely used as an

(a) antiseptic.

(b) solvent for paints, lacquers, varnishes, dyes, cosmetics, perfumes, tinctures, cough syrups etc.

(c) As an important starting material for manufacture of ether, chloroform, Iodoform etc.

(d) As an important beverage.

(e) As power alcohol a mixture of 20% absolute alcohol and 80% petrol (gasoline) with benzene or tetralin as a co-solvent.

(f) As an antifreeze in automobile radiators.

Absolute alcohol: Absolute alcohol is 100% ethanol prepared from rectified spirit 95.5% alcohol as follows:

In laboratory absolute alcohol is prepared by keeping the rectified spirit in contact with calculated amount of quick lime for few hours and then refluxing and distilling it.

Phenol or Carbolic Acid

Uses

(i) As an antiseptic and disinfectant in soaps and lotions.

(ii) In manufacture of drugs like, aspirin, salol, salicylic acid, phenacetin.

(iii) In the manufacture of bakelite.

(iv) In the manufacture of picric acid, phenolphthalein, azo dyes.

(v) As a preservative for ink.

ETHER

* R — O — R′ Alkoxy alkane (Di alkyl ether)

* R = R′ Symmetrical ether.

R ≠ R′ Unsymmetrical or mixed ether.

‘O’ is to be counted with least number of C atom.

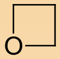
Example:

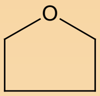
$CH_3—O—C_2H_5$ Methoxy ethane

$CH_3—O—C_6H_5$ Methoxy benzene

There are various types of cyclic ethers also.


Oxirane
(Epoxide)


Oxetane
(Oxacyclo butane)


Tetra hydro furan
(Oxacyclo pentane)

PREPARATION OF ETHERS

(i) From 1° alcohol

(a) With H_2SO_4

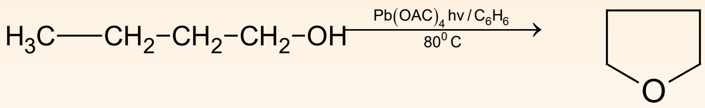
$$R-O-H+R-O-H\xrightarrow[140^0\text{ C or }Al_2O_3/525K]{H_2SO_4}R-O-R(\text{symmetrical ether})$$

Order of dehydration 1° > 2° > 3° alcohol

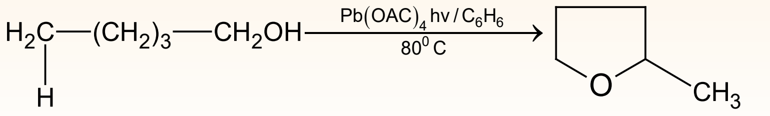
(b) With diazomethane

$$R-O-H\xrightarrow[(C_2H_5O)_3Al]{CH_2N_2}R-O-CH_3+N_2$$

(c) Alcohol having at least one hydrogen at fourth carbon gives five membered cyclic ether with $Pb(OAC)_4$. The reaction is free radical reaction which is initiated by heat or light.



Tetrahydro furan



2 methyl tetra hydro furan

Williamson's synthesis

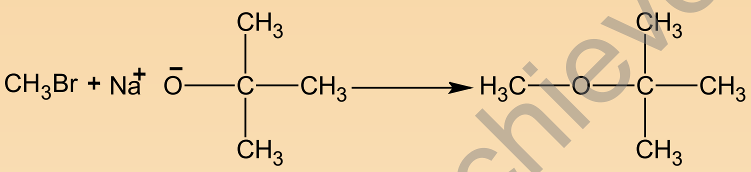
S_N2 reaction of a sodium alkoxide with alkyl halide, alkyl sulphonate or alkyl sulphate is known as Williamson synthesis of ethers.

$$R-ONa + R'L \xrightarrow{SN_2} R-O-R' + NaL$$

$$[L = X,\ SO_2R'',\ \ -O-SO_2-OR']$$

- In this reaction alkoxide may be alkoxide of primary, secondary as well as tertiary alcohol.
- Alkyl halide must be primary.
- In case of tertiary alkyl halide, elimination occurs giving alkenes
- With a secondary alkyl halide, both elimination and substitution products are obtained.

$$R—X + \overset{+}{Na}\ .\ \overset{\ominus}{O}—R \longrightarrow R—O—R' + Na^{+}X^{-}$$

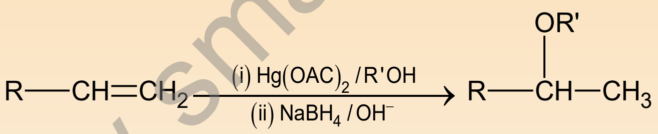


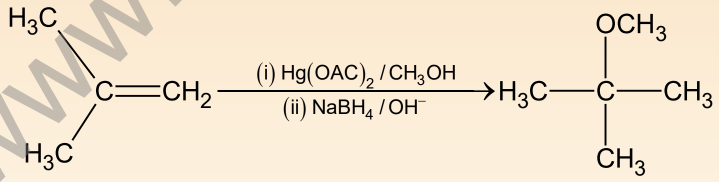
Sodium ter. butoxide

ter. butyl methyl ether

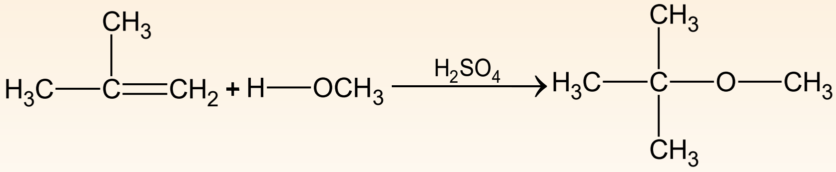
(3) From Alkane

(a)



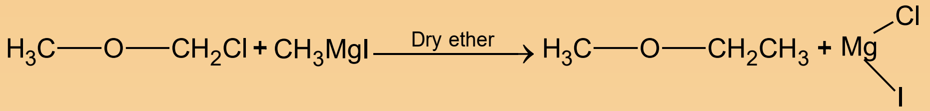


(b)



(4) From Grignard reagent

Higher ethers can be prepared by treating α - halo ethers with suitable reagents.



$$H_3C-O-CH_2Cl + CH_3MgI \xrightarrow{\text{Dry ether}} H_3C-O-CH_2CH_3 + Mg\begin{matrix} Cl \\ I \end{matrix}$$

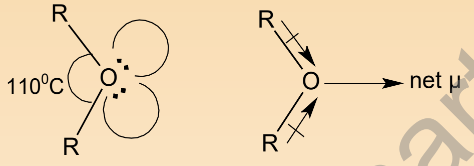
(5) From Alkyl halide

$$2RI + \underset{dry}{Ag_2O} \longrightarrow R-O-R + 2AgI$$

PROPERTIES OF ETHERS

Dipole nature of ether

Ethers have a tetrahedral geometry i.e. oxygen is sp^3 hybridized. The C — O — C bond angle in ether is 110°. Because of the greater electronegativity of oxygen than carbon, the C — O bonds are slightly polar and are inclined to each other at an angle of 110°C, resulting in a net dipole moment.



The bond angle is slightly greater than the tetrahedral angle due to repulsive interaction between the two bulky groups.

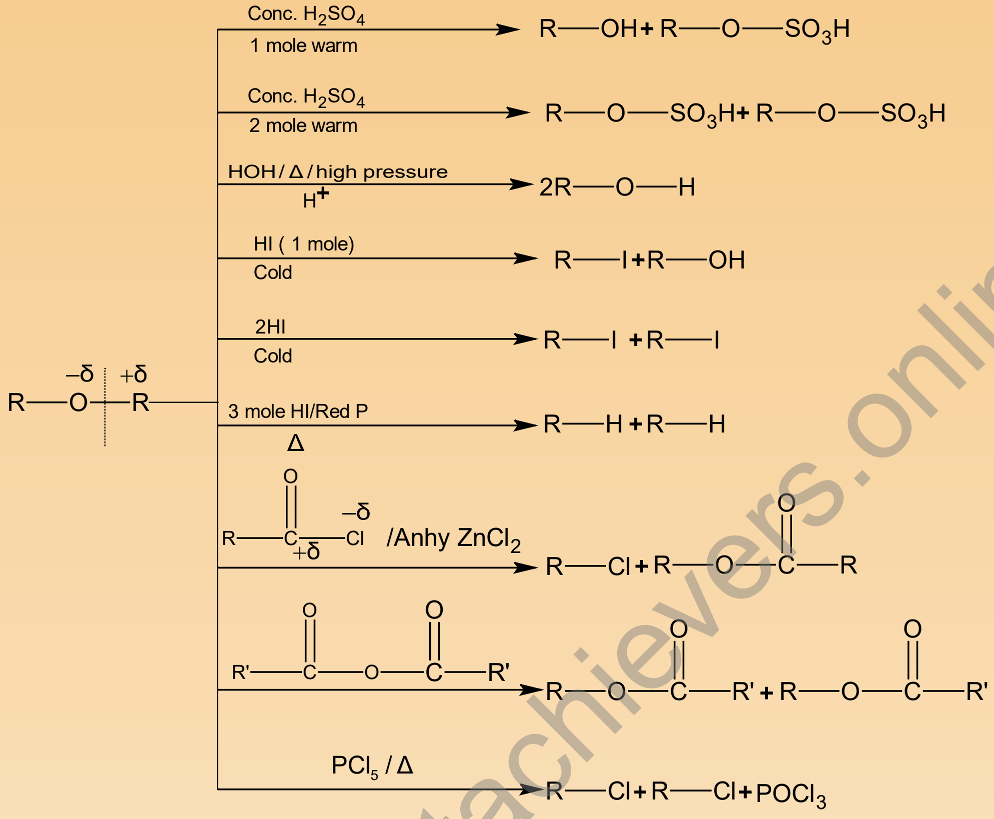
Chemical Reaction

Dialkyl ethers reacts with very few reagents other than acids. The only active site for other reagents are the C — H bonds of the alkyls. Ethers has ability to solvate cations (electrophile) by donating an electron pair from their oxygen atom. These properties make ether as solvents for many reactions.

On standing in contact with air, most aliphatic ethers are converted slowly into unstable peroxides.

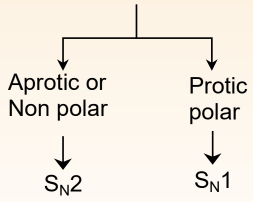
Ether gives following reactions:

1. Nucleophilic substitution reactions



Note:

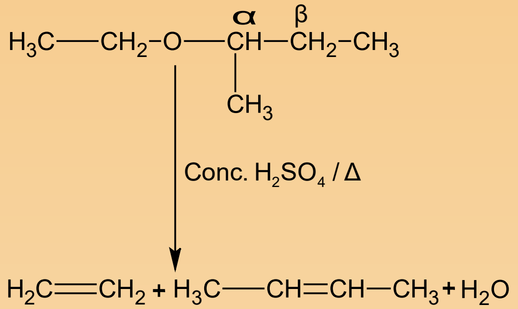
Type of ethers also make a difference in the mechanism followed during the cleavage of C—O by HI/HBr.

Combinations	**Mechanism follows**
1°R + 2°R	Less sterically hindered ⇒ S_N2
2°R + 3°R	More sterically hindered ⇒ S_N1
1°R + 3°R	Nature of mechanism decoded by nature of solvent. 

Methyl cation is stabler than phenyl cations

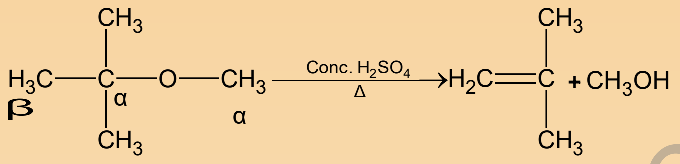
(B) Dehydration with H_2SO_4/Δ and Anhy Al_2O_3/Δ

(i) When both alkyl groups has β - hydrogen.



$$H_3C{-}CH_2{-}O{-}\overset{\alpha}{CH}(CH_3){-}\overset{\beta}{CH_2}{-}CH_3 \xrightarrow{\text{Conc. } H_2SO_4/\Delta} H_2C{=}CH_2 + H_3C{-}CH{=}CH{-}CH_3 + H_2O$$

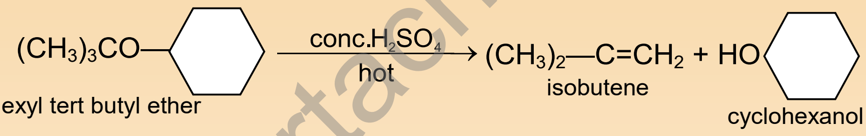
(ii) When only alkyl group has β - hydrogen.



$$H_3C{-}\underset{\alpha}{C}(CH_3)_2{-}O{-}\underset{\alpha}{CH_3} \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} H_2C{=}C(CH_3)_2 + CH_3OH$$

- Hot conc. H_2SO_4 react with secondary and tertiary ethers to give a mixture of alcohols and alkenes.

$(CH_3)_3CO{-}CH_3 \xrightarrow[\text{hot}]{\text{Conc.}H_2SO_4} (CH_3)_2{-}C{=}CH_2 + CH_3OH$

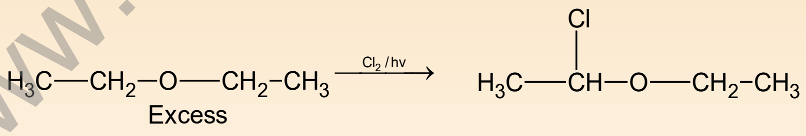


(C) Miscellaneous reactions

(1) **Halogenation:**

Monohalogenation takes place at α carbon (with small amount)

(a)



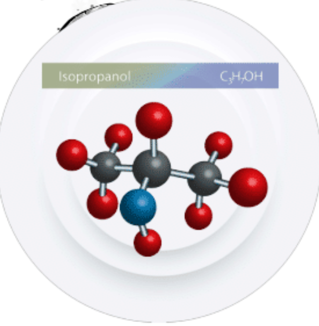
$$\underset{\text{Excess}}{H_3C{-}CH_2{-}O{-}CH_2{-}CH_3} \xrightarrow{Cl_2/hv} H_3C{-}\overset{Cl}{CH}{-}O{-}CH_2{-}CH_3$$

(b) $\underset{\text{Small}}{H_3C{-}CH_2{-}O{-}CH_2{-}CH_3} \xrightarrow{Cl_2(\text{excess})/hv} Cl_5C_2{-}O{-}C_2Cl_5$

(2) **Reaction with CO:** give ester

$R-O-R+CO \xrightarrow[200\text{ atm, }BF_3]{125-180^0C} RCOOR$

Alcohols, Phenols And Ethers

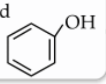


Trace the Mind Map
- First Level
- Second Level
- Third Level

Classification

Mono, Di, Tri, or polyhydric :

(i) Containing C_{sp^3} – OH bond
$-CH_2OH$ (1°) $>CHOH$ (2°) $\geqslant COH$ (3°)
(ii) Containing C_{sp^2} -OH bond
Vinylic alcohol :
$CH_2 = CH - OH$ Phenols



Ethers

(i) Simple/symmetrical : Alkyl or aryl attached to oxygen atom same.
(ii) Mixed/unsymmetrical : Two groups are different.

Nomenclature

Alcohols

Common name : Alkyl group + ol; IUPAC name : substituting 'e' of alkane with suffix 'ol'

Phenols

Common name : Terms ortho, meta and para are used. IUPAC name : Dihydroxy derivatives as 1,2–, 1,3– and 1,4 –benzenediol

Ethers

Common name : Alkyl/aryl groups in alphabetical order followed by ether. IUPAC name : In alkyl /aryl group 'e' replaced by oxy followed by parent hydrocarbon.

Structures of functional groups

- Oxygen of –OH group is attached to C by a σ bond formed by the overlap of sp^3 orbital of C with a sp^3 orbital of oxygen.
- In ethers, tetrahedral arrangement for four electron pairs.

Preparation

Alcohols

1. From alkenes :- (i) By acid catalysed hydration

$$>C=C< + H_2O \underset{}{\overset{H^+}{\rightleftharpoons}} >\underset{H}{C}-\underset{OH}{C}<$$

(ii) By hydroboration – oxidation

$$CH_3-CH=CH_2+(H-BH_2)_2 \longrightarrow CH_3-\underset{H}{CH}-\underset{BH_2}{CH_2} \xrightarrow{CH_3-CH=CH_2} (CH_3-CH_2-CH_2)_2BH$$

$$3CH_3-CH_2-CH_2-OH+B(OH)_3 \xleftarrow[3H_2O_2,OH]{H_2O} CH_3-CH_2-CH_2)_3BH\ (CH_3-CH=CH_2)$$

2. From carbonyl compounds :

(i) By reduction of aldehydes and ketones

$$RCHO + H_2 \xrightarrow{Pd} RCH_2OH,\ RCOR' \xrightarrow{NaBH_4} R-\underset{OH}{CH}-R'$$

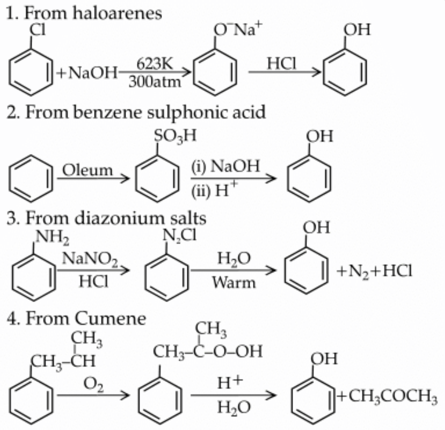
(ii) By reduction of carboxylic acids and esters

$$RCOOH \xrightarrow[H^+]{R'OH} RCOOR' \xrightarrow[catalyst]{H_2} RCH_2OH + R'OH$$

3. From Grignard reagent

$$>C=O+R \longrightarrow MgX \longrightarrow \left[>\underset{R}{C}-OMg-X\right] \xrightarrow{H_2O} >\underset{R}{C}-OH+Mg(OH)X$$

Phenols



1. From haloarenes

2. From benzene sulphonic acid

3. From diazonium salts

4. From Cumene

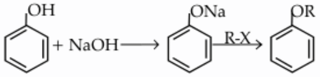
Ethers

1. By dehydration of alcohols

$$CH_3CH_2OH \xrightarrow[413\ K]{H_2SO_4} C_2H_5OC_2H_5$$

2. Williamson synthesis

$$RX + R'ONa \longrightarrow R-O-R' + NaX$$



Properties

Alcohols

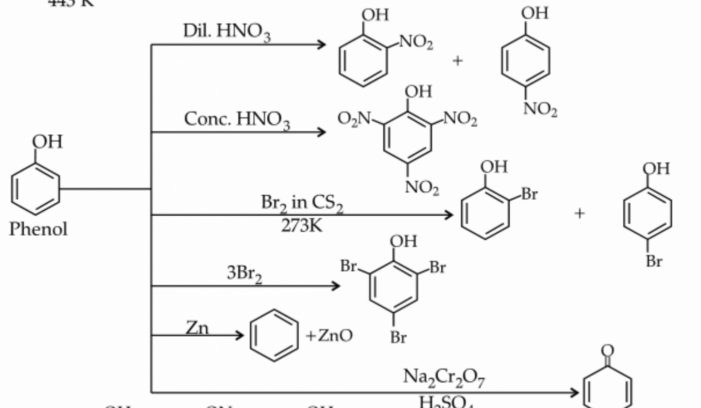
(i) Physical :
- Boiling point increases with increase in the number of C atoms.
- Solubility decreases with increase in size of alky/aryl groups.

(ii) Chemical : $2-R-O-H + 2Na \longrightarrow 2R-O-Na + H_2$;Acidity – primary > secondary > tertiary

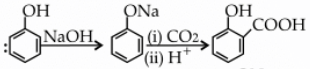
$$Ar/R-O-H + R'-COOH \overset{H^+}{\rightleftharpoons} Ar/R\text{-}COOR' + H_2O;\ ROH + HX \longrightarrow R-X + H_2O$$

$$C_2H_5OH \xrightarrow[443\ K]{H_2SO_4} CH_2 = CH_2 + H_2O;\ RCH_2OH \xrightarrow{Oxidation} R\text{-}\overset{H}{C}=O \longrightarrow R\text{-}\overset{OH}{C}=O$$

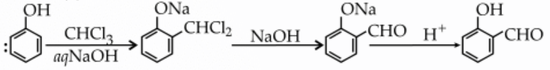
Phenol



Kolbe's reaction :



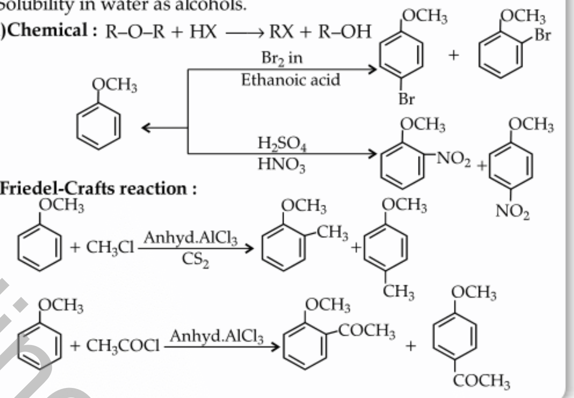
Reimer Tiemann reaction :



Ethers

(i)Physical :
- C–O bonds are polar.
- Boiling points comparable to those of alkanes.
- Solubility in water as alcohols.

(ii)Chemical : $R-O-R + HX \longrightarrow RX + R-OH$



Friedel-Crafts reaction :

Commercially important alcohols

- **Methanol (Wood spirit) :**
Used as solvent in paint, varnishes and making formaldehyde.
- **Ethanol :**
Used as solvent in paint industry and preparation of a number of carbon compounds.

PRACTICE QUESTIONS

1. An organic compound '*X*' on treatment with pyridinium chloro chromate in dichloromethane gives compound '*Y*'. Compound '*Y*,reacts with I_2 and alkali to form triiodomethane. The compound '*X*' is
   a) C_2H_5OH
   b) CH_3CHO
   c) CH_3COCH_3
   d) CH_3COOH

2. Ethyl alcohol is industrially prepared from the ethylene by:
   a) Permanganate oxidation
   b) Catalytic reduction
   c) Absorbing in sulphuric acid followed by hydrolysis
   d) Fermentation

3. Lucas reagent is used to distinguish among primary, secondary and tertiary:
   a) Alkyl halides
   b) Alcohols
   c) Aliphatic amines
   d) Aromatic amines

4. Ketone upon treatment with Grignard reagent gives
   a) Primary alcohol
   b) Secondary alcohol
   c) Tertiary alcohol
   d) Aldehyde

5. The starting material for the preparation of CH_3I in one step reaction is:
   a) CH_3OH
   b) C_2H_5OH
   c) CH_3CHO
   d) CH_3COCH_3

6. From methyl alcohol we get:
   a) Neoprene rubber
   b) Perspex rubber
   c) Bakelite a hard plastic
   d) Sponge rubber

7. *Tert*-butyl methyl ether on heating with anhydrous HI in ether gives
   a) $CH_3OH + (CH_3)_3CI$
   b) $CH_3I + (CH_3)_3COH$
   c) $CH_3I + (CH_3)_3Cl$
   d) None of the above

8. Diethyl ether is decomposed on heating with:
   a) NaOH
   b) Water
   c) $KMnO_4$
   d) HI

9. Most viscous among the following is:
   a) Propan-1-ol
   b) Propan-2-ol
   c) Propane-1, 2-diol
   d) Propane-1,2,3-triol

10. In the fermentation of sugar molasses, the percentage of ethanol formed is:
    a) 10 %
    b) 40 %
    c) 95 %
    d) 70 %

11. A liquid was mixed with ethanol and a drop of concentrated H_2SO_4 was added. A compound with a fruity smell was formed. The liquid was:
    a) HCHO
    b) CH_3COCH_3
    c) CH_3COOH
    d) CH_3OH

12. Ethyl alcohol reacts with following to form a compound of fruity smell:
a) PCl_5 b) $K_2Cr_2O_7 + H_2SO_4$ c) CH_3COOH d) CH_3COCH_3

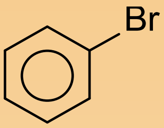
13. Carbolic acid is
a) HCOOH b) CH_3COOH c) C_6H_5COOH d) C_6H_5OH

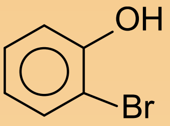
14. Lucas reagent is
a) Conc. HCI and anhydrous $ZnCI_2$ b) Conc. $HNO_3$and hydrous $ZnCI_2$
c) Conc. HCI and hydrous $ZnCI_2$ d) Conc. HNO_3 and anhydrous $ZnCI_2$

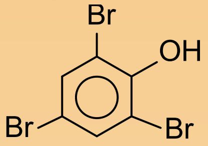
15. An aldehyde on treatment with Zn/HCl yields:
a) 1° alcohol b) 2 ° alcohol c) 3 ° alcohol d) None of these

16. In the reaction,
$A \xrightarrow[H_2SO_4]{K_2Cr_2O_7}$ acetone $\xrightarrow{\text{Oxidation}}$ acetic acid, A is
a) 1-propanol b) 2-butanol c) 2-propanol d) Ethanol

17. The product obtained by the reaction of HBr with phenol is

a) 

b) 

c) 

d) There is no reaction

18. An ether is more volatile than an alcohol having the same molecular formula. This is due to

a) Dipolar character of ethers
b) Alcohols having resonance structures
c) Intermolecular hydrogen bonding in ethers
d) Intermolecular hydrogen bonding in alcohols

19. Glycol condenses with ketones to give:

a) Cyclic acetals
b) Cyclic ketals
c) Acetaldehyde
d) Oxalic acid

20. The explosive nitroglycerine is:

a) A soap
b) A salt
c) An ester
d) A complex compound

21. The compound $CH_3CH_2CH_2Br$ is converted into $CH_3CH_2CH_2OH$ by:

a) Dehydration
b) Hydrogenation
c) Elimination
d) Substitution

22. Consider the following reaction,

$$\text{ethanol} \xrightarrow{PBr_3} X \xrightarrow{\text{alc. KOH}} Y \xrightarrow[\text{(ii) } H_2O\text{, heat}]{\text{(i) } H_2SO_4 \text{ at room temperature}} Z;$$

The product Z is:

a) CH_3CH_2OH
b) $CH_2{=}CH_2$
c) $CH_3CH_2{-}O{-}CH_2{-}CH_3$
d) $CH_3{-}CH_2{-}O{-}SO_3H$

23. In which of the following reactions the product is an ether?

a) $C_6H_6 + CH_3COCl$/anhydrous $AlCl_3$
b) C_2H_5Cl + aq. KOH
c) $C_6H_6 + C_6H_5COCl$/anhydrous $AlCl_3$
d) $C_2H_5Cl + C_2H_5ONa$

24. The b.p. of alcohols are....than corresponding thiols.

a) More
b) Less
c) Same
d) Either of these

25. Enzymes are:
   a) Living organisms
   b) Dead organisms
   c) Complex nitrogenous substances produced from living cells
   d) None of the above

26. Which of the following is used as anaesthetic?
   a) $CHCl_3$
   b) C_2H_5OH
   c) $C_2H_5OC_2H_5$
   d) $CHCl_3$ and $C_2H_5OC_2H_5$

27. Picric acid is
   a) 2, 4, 6-tribromophenol
   b) *Sym*-trinitrophenol
   c) trinitrophenol
   d) 2, 4, 6-trinitrotoluene

28. The correct order of reactivity of hydrogen halides with ethyl alcohol is
   a) $HF > HCl > HBr > HI$
   b) $HCl > HBr > HF > HI$
   c) $HBr > HCl > HI > HF$
   d) $HI > HBr > HCl > HF$

29. Denatured alcohol is
   a) Ethanol + methanol
   b) Rectified spirit + methanol + naphtha
   c) Undistilled ethanol
   d) Rectified spirit

30. Which of the following reacts with water?
   a) $CHCl_3$
   b) CCl_4
   c) CCl_3CHO
   d) CH_2ClCH_2Cl

31. Formic acid is obtained when:
   a) $(CH_3COO)_2Ca$ is heated with conc. H_2SO_4
   b) Calcium formate is heated with calcium acetate
   c) Glycerol is heated with oxalic acid
   d) Acetaldehyde is oxidized with $K_2Cr_2O_7$ and conc. H_2SO_4

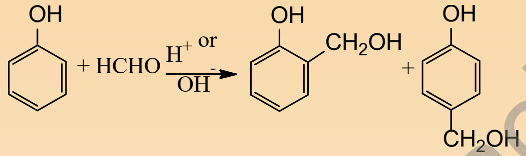
32. Primary, secondary and tetiary alcohols are distinguished from one another by
   a) Ninhydrin test
   b) Tollen’s reagent
   c) Lucas test
   d) Wittig reaction

33. Metal alkoxides contain:
a) Metal-carbon bond b) Metal-oxygen bond c) Metal-methyl bond d) None of these

34. 3-methyl-2-butanol on treatment with HCl gives predominantly:
a) 2-chloro-2-methylbutane
b) 2-chloro-3-methylbutane
c) 2,2-dimethylpentane
d) None of the above

35. No reacts rapidly with:
a) 1° alcohol b) 2° alcohol c) 3° alcohol d) None of these

36.

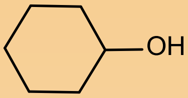


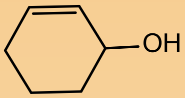
This reaction is called

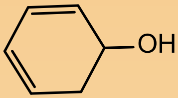
a) Reimer- Tiemann reaction b) Lederer-Manasse reaction
c) Sandmeyer reaction d) Kolbe's reaction

37. The factor adversely affecting the process of fermentation is:
a) Low concentration of sugar
b) High concentration of sugars
c) Presence of ammonium salts
d) Presence of air

38. The correct order of ease of dehydration of following is


I


II


III

a) I > II > III b) III > II > I c) I > III > II d) III > I > II

39. The correct order of boiling point for primary (1°), secondary (2°) and tertiary (3°)alcohols is

a) $1^\circ > 2^\circ > 3^\circ$ b) $3^\circ > 2^\circ > 1^\circ$ c) $2^\circ > 1^\circ > 3^\circ$ d) $2^\circ > 3^\circ > 1^\circ$

40. Phenol can be distinguished from ethanol by the following reagents except

a) Sodium b) $NaOH/I_2$

c) Neutral $FeCI_3$ d) Br_2/H_2O

41. 1-propanol and 2-propanol can be distinguished by

a) Oxidation with alkaline $KMnO_4$ followed by reaction with Fehling solution

b) Oxidation with acidic dichromate followed by reaction with Fehling solution

c) Oxidation by heating with copper followed by reaction with Fehling solution

d) Oxidation with concentrated H_2SO_4 followed by reaction with Fehling solution

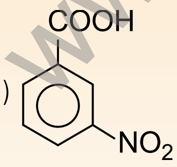
42. Which of the following does not react with sodium metal?

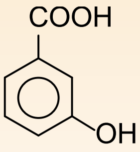
a) $(CH_3)_2O$ b) CH_3CH_2OH c) CH_3COOH d) C_6H_5OH

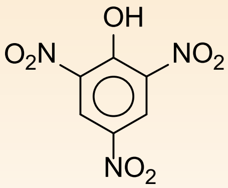
43. Purity of ether before using it as an aesthetic agent is tested by:

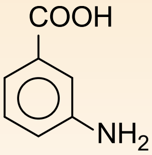
a) KI + starch b) $CuSO_4$ c) H_2SO_4 d) None of these

43. Picric acid is

a) 

b) 

c) 

d) 

HINTS ANS SOLUTIONS

1 (a)

$$C_2H_5OH + [O] \xrightarrow[\text{in } CH_2Cl_2]{\text{PCC}} CH_3CHO$$

(*X*) (*Y*)

$$CH_3CHO + 4NaOH + 3I_2 \rightarrow CHI_3 + HCOONa + 3H_2O + 3NaI$$

(*Y*)

(yellow ppt
tri-iodomethane)

2 (c) Absorbing in sulphuric acid followed by hydrolysis

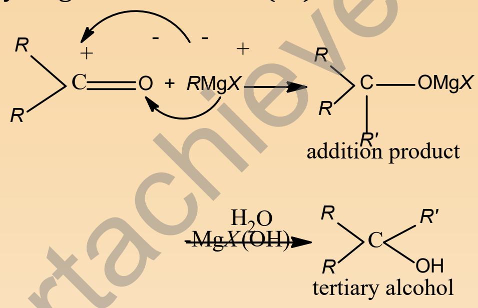
$$C_2H_4 + H_2SO_4 \longrightarrow C_2H_{z5}HSO_4 \xrightarrow{\text{HOH}} C_2H_5OH$$

3 (b) Alcohol group

Tertiary alcohols show replacement of —OH gp. more readily.

4 (c)

Ketones give an addition product having more number of carbon atoms with Grignard reagent, which on hydrolysis gives an alcohol (3°).



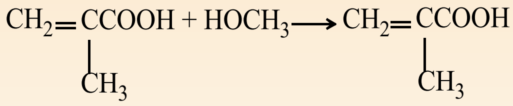
Formaldehyde gives primary alcohol with Grignard reagent while any other aldehyde except formaldehyde give secondary alcohol.

5 (a)

$$CH_3OH \overset{\text{HI}}{\rightarrow} CH_3I$$

6 (b)

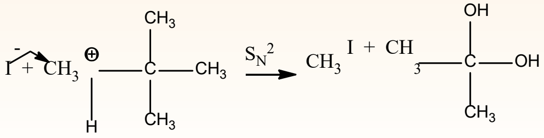
Perspex rubber is polymethyl methyl acrylate (PMMA) is obtained by methyl acrylate obtained as:



$$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}COOH + HOCH_3 \longrightarrow CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}COOH$$

7 (b)

Here, ether is the solvent. Being less polar, it favours S_N2 reaction and the nucleophile I^-attacks the 1^0 carbon of CH_3.



8 (d)

$C_2H_5OC_2H_5 + HI \overset{\Delta}{\rightarrow} 2C_2H_5I + H_2O$

9 (d)

Due to more sites available for H-bonding.

10 (a)

The fermented liquid is technically called wash containing 6-10% ethanol, 3-5% glycerol, higher alcohols (fusel oils), acetaldehyde, etc.

11 (c)

$CH_3COOH + C_2H_5OH \xrightarrow{H_2SO_4} \underset{\text{Fruity smell}}{CH_3COOC_2H_5} + H_2O$

12 (c)

$C_2H_5OH + HOOCCH_3 \longrightarrow C_2H_5OOCCH_3$ Ester possess fruity smell.

13 (d)

Phenol (C_6H_5OH) is carbolic acid.

14 (a)

Conc. HCl+ anhydrous $ZnCl_2$ is called as Lucas reagent. It is used to distinguish primary, secondary and tertiary alcohol.

15 (a)

$CH_3CHO \xrightarrow{\text{Reduction}} CH_3CH_2OH$

16 (c)

$CH_3CHOHCH_3 \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3COCH_3 \xrightarrow[\text{oxidation}]{} CH_3COOH$

2-propanol acetone acetic acid

17 (d)

Phenol reacts with PCl_5 to form chlorobenzene. Halogenation of phenol does not take place with HX

18 c) Intermolecular hydrogen bonding in ethers - Ethers do not have hydrogen atoms bonded to oxygen, so they cannot form intermolecular hydrogen bonds. This makes them more volatile compared to alcohols, which can form hydrogen bonds.

19. b) Cyclic ketals - When glycol condenses with a ketone, it forms a cyclic ketal through a reaction known as ketalization.

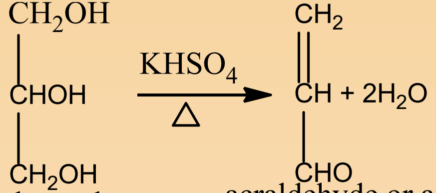
20 (d) A complex compound

The explosive nitroglycerine is a highly sensitive and powerful explosive compound. It is chemically known as trinitroglycerin (C3H5N3O9) and is used in various forms for industrial and military applications. Nitroglycerine is known for its extreme sensitivity to shock, friction, and heat, making it a highly dangerous substance to handle without proper expertise and safety measures. It was first synthesized by Italian chemist Ascanio Sobrero in 1847.

21 b) Hydrogenation - This process involves the addition of hydrogen (H2) to a compound. In this case, CH3CH2CH2Br is converted to CH3CH2CH2OH by replacing the Br (bromine) with an OH (hydroxyl) group through hydrogenation.

22 (c)

Glycerol is dehydrated on heating with $KHSO_4$.



glycerol

acraldehyde or acrolein

23 (d)

Alkyl halides react with sodium alkoxide to give ether. This is called Williamson's synthesis of ether.

$$C_2H_5Cl + C_2H_5ONa \xrightarrow{\Delta} \underset{\text{ether}}{C_2H_5OC_2H_5} + NaCl$$

24 (a)

Alcohols although possess low mol. wt. than thiol but they show H-bonding.

25 (c)

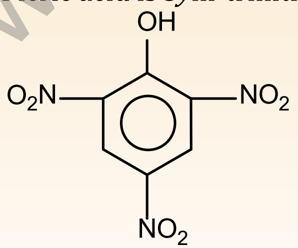
Enzymes are protinous molecules derived from living organisms.

26 (d)

Both ether and chloroform are anaesthetic agents.

27 (b)

Picric acid is *sym*-trinitrophenol.



2,4,6-triniphenol

28 **(d)**Among hydrogen halides, as the size of halide ion increases, its reactivity towards ethyl alcohol also increases. Thus, the order of reactivity of hydrogen halide is
HI > HBr > HCl > HF

29 b) Rectified spirit + methanol + naphtha - Denatured alcohol is ethanol that has been rendered undrinkable by adding substances like methanol and naphtha to it. This makes it unsuitable for consumption but still useful for industrial and technical purposes.

30 (c)
Chloral forms chloral hydrate with water due to H-bonding.

$$CCl_3CHO \longrightarrow CCl_3CH(OH)_2$$

31 d) Acetaldehyde is oxidized with K2Cr2O7 and conc. H2SO4 - Formic acid (HCOOH) is produced when acetaldehyde undergoes oxidation with the help of potassium dichromate (K2Cr2O7) and concentrated sulfuric acid (H2SO4).

32 **(c)**
Primary, secondary and tertiary alcohols are distinguished by Lucas test. A mixture of anhydrous $ZnCl_2$ +conc HCl is called Lucas reagent.

33 b) Metal-oxygen bond - Metal alkoxides are compounds where a metal is bonded to an oxygen atom, typically in an organic group called an alkoxide.

34 a) 2-chloro-2-methylbutane - The treatment of 3-methyl-2-butanol with HCl predominantly leads to the formation of 2-chloro-2-methylbutane.

35 a)1st-degree (1°) alcohol: It reacts rapidly.

36 a) Reimer-Tiemann reaction:This reaction involves the transformation of phenols to salicylaldehydes using chloroform and a strong base like aqueous sodium hydroxide.

37 b) High concentration of sugars: A high concentration of sugars can adversely affect the process of fermentation by creating an environment that is too osmotically stressful for the yeast to thrive.

38 b) III > II > I. The ease of dehydration depends on the stability of the carbocation formed during the process. Tertiary carbocations are the most stable, followed by secondary, and then primary.

39 b) 3° > 2° > 1° Boiling points increase with increasing molecular weight, and branching decreases boiling points. Tertiary alcohols have the highest molecular weight and are the most branched, so they have the highest boiling points

40 a) Sodium will react with both phenol and ethanol, making it unsuitable for distinguishing between the two. The other reagents listed can be used to differentiate between phenol and ethanol.

41 **(a)**Only acidic compounds such as acetic acid, phenol and alcohol react with sodium metal. Ether is not acidic in nature, hence it does react with sodium metal.

$2CH_3CH_2OH + 2Na \rightarrow 2CH_3CH_2ONa + H_2$
Ethanol sodium ethoxide
$2CH_3COOH + 2Na \rightarrow 2CH_3COONa + H_2$
Acetic acid sodium acetate
$2C_6H_5OH + 2Na \rightarrow 2C_6H_5ONa + H_2$
Phenol sodium phenoxide
$CH_3 - O - CH_3 + Na \rightarrow$ No reaction

42 **(a)**Impure ether, *i.e.*, if peroxide ether has formed due to oxidation, the peroxide bond will liberate I_2 from KI which will give blue colour with starch.

43 **(c)**2, 4, 6-trinitrophenol is called picric acid