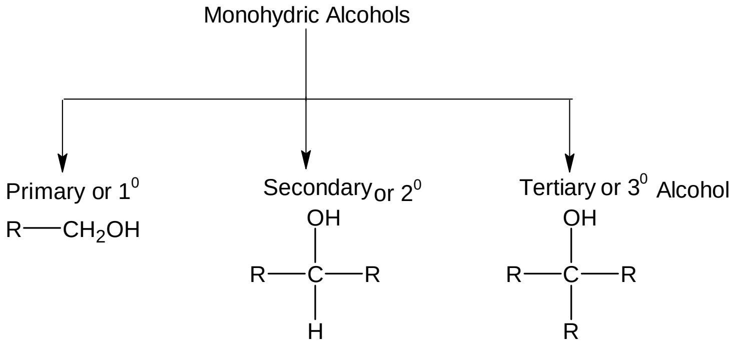
ALCOHOL, ETHER & PHENOL

INTRODUCTION :

Alcohols and **Phenols** are formed when a hydrogen atom in a hydrocarbon, aliphatic and aromatic respectively, is replaced by –OH (hydroxy) group.

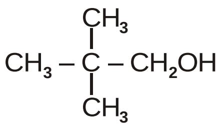
The substitution of a hydrogen atom in a hydrocarbon by an alkoxy or aryloxy group (R–O/Ar–O) yields another class of compounds known as '**Ethers**', for example, CH_3OCH_3 (dimethyl ether) or by substituting the hydrogen atom of hydroxyl group of an alcohol or phenol by an alkyl or aryl group.

(a) Monohydric alcohols (only one hydroxy group present) are of three types.



Solved Example :

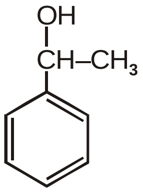
Qus. Classify the following as primary, secondary and tertiary alcohols :

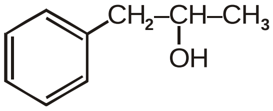
(i) 

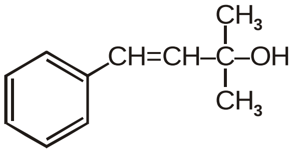
$CH_3 - \overset{CH_3}{\underset{CH_3}{C}} - CH_2OH$

(ii) $H_2C = CH - CH_2OH$

(iii) $CH_3 - CH_2 - CH_2 - OH$

(iv) 

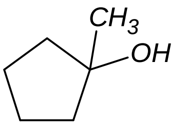
(v) 

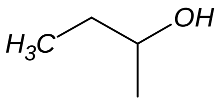
(vi) 

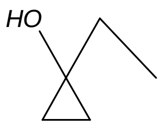
Ans. Primary alcohol (i), (ii) and (iii)
Secondary alcohol (iv) and (v)
Tertiary alcohol (vi)

Solved Example :

Qus. Classify the following into primary, secondary and tertiary alcohols:

(a) 

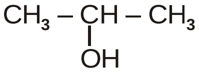
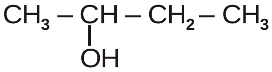
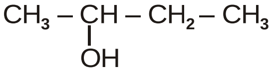
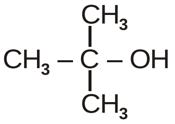
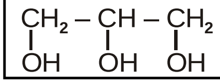
(b) 

(c) 

Ans. (a) Tertiary
(b) Secondary
(c) Tertiary

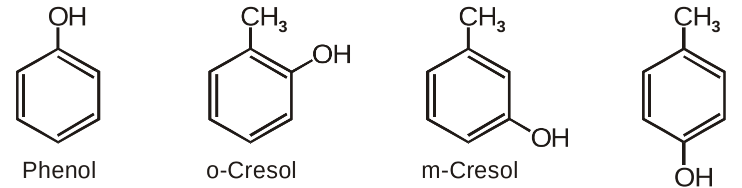
ALCOHOLS :

Common and IUPAC names of some Alcohols :

Compound	**Common name**	**IUPAC name**
CH_3-OH	Methyl alcohol	Methanol
$CH_3-CH_2-CH_2-OH$	n-Propyl alcohol	Propan-1-ol
 $CH_3-\underset{OH}{\underset{\vert}{CH}}-CH_3$	Isopropyl alcohol	Propan-2-ol
$CH_3-CH_2-CH_2-CH_2-OH$	n-Butyl alcohol	Butan-1-ol
 $CH_3-\underset{OH}{\underset{\vert}{CH}}-CH_2-CH_3$	sec-Butyl alcohol	Butan-2-ol
 $CH_3-\underset{OH}{\underset{\vert}{CH}}-CH_2-CH_3$	Isobutyl alcohol	2-Methylpropan-1-ol
 $CH_3-\overset{CH_3}{\overset{\vert}{\underset{CH_3}{\underset{\vert}{C}}}}-OH$	tert-Butyl alcohol	2-Methylpropan-2-ol
 $\underset{OH}{\underset{\vert}{CH_2}}-\underset{OH}{\underset{\vert}{CH}}-\underset{OH}{\underset{\vert}{CH_2}}$	Glycerol	Propan-1,2, 3-triol

(b) **Phenols :** The simplest hydroxy derivative of benzene is phenol. It is its common name and also an accepted IUPAC name.

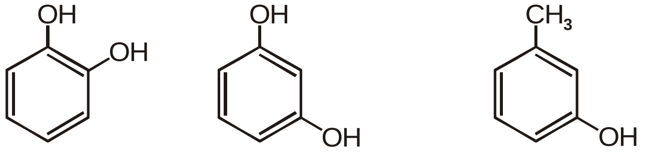
Common name IUPAC Name :



Common names :	Phenol	o-Cresol	m-Cresol	o-Cresol
IUPAC names :	Phenol	2-Methylphenol	3-Methylphenol	4-Methylphenol

Dihydroxy derivatives of benzene are known as 1,2-, 1, 3-and 1, 4-benzenediol.

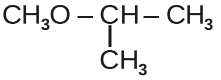
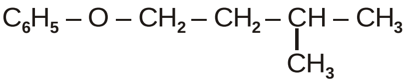
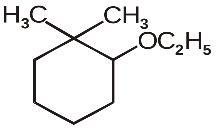
Common name IUPAC Name :



Common names :	Catechol	Resorcinol	Hydroquinone or quinol
IUPAC names :	Benzene-1,2-diol	Benzene-1,3-diol	Benzene-1,4-diol

(c) **Ethers :** Common names of ethers are derived from the names of alkyl/aryl groups written as separate words in alphabetical order and adding the word 'ether' at the end. For example, $CH_3OC_2H_5$ is ethylmethyl ether.

Table : Common and IUPAC names of some Ethers :

Compound	**Common name**	**IUPAC name**
CH_3OCH_3	Dimethyl ether	Methoxymethane
$C_2H_5OC_2H_5$	Diethyl ether	Ethoxyethane
$CH_3OCH_2CH_2CH_3$	Methyl n-propyl ether	1-Methoxypropane
$C_6H_5OCH_3$	Methylphenyl ether (Anisole)	Methoxybenzene (Anisole)
$C_6H_5OCH_2CH_3$	Ethylphenyl ether (Phenetole)	Ethoxybenzene
$C_6H_5O(CH_2)_6-CH_3$	Heptylphenyl ether	1-Phenoxyheptane
 $CH_3O-\underset{CH_3}{\underset{\vert}{CH}}-CH_3$	methyl isopropyl ether	2-Methoxypropane
 $C_6H_5-O-CH_2-CH_2-\underset{CH_3}{\underset{\vert}{CH}}-CH_3$	Phenylisopentyl ether	3-Methylbutoxybenzene
$CH_3-O-CH_2-CH_2-OCH_3$	–	1,2-Dimethoxyethane
	–	2-Ethoxy-1,1-dimethylcylohexane

Solved Example :

Qus. Give the structures and IUPAC names of the products expected from the following reactions :

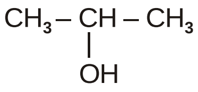
(a) Catalytic reduction of butanol

(b) Hydration of propene in the presence of dilute sulphuric acid.

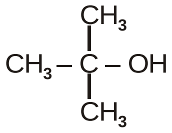
(c) Reaction of propanone with methylmagnesium bromide followed by hydrolysis.

Ans. (a) $CH_3-CH_2-CH_2-CH_2-OH$

Butan-1-ol

(b)

$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$

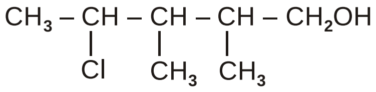
Propan-2-ol

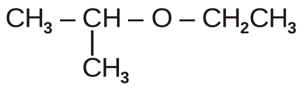
(c)

$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\underset{\displaystyle CH_3}{|}}{C}}}-OH$

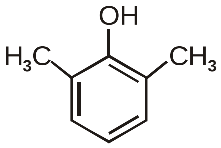
2-Methylpropan-2-ol

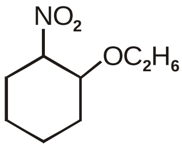
Solved Example :

Qus. Given IUPAC names of the following compounds :

(i)

$CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2OH$

(ii)

$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-O-CH_2CH_3$

(iii)


(iv)


Ans. (i) 4-Chloro-2, 3-dimethylpentan-1-ol

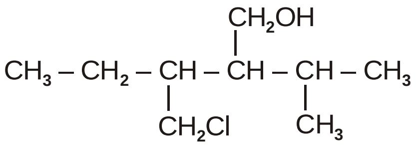
(ii) 2-Ethoxypropane

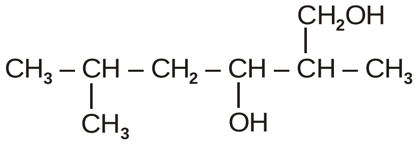
(iii) 2, 6-Dimethylphenol

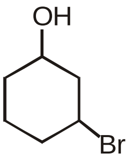
(iv) 1-Ethoxy-2-nitrocyclohexane

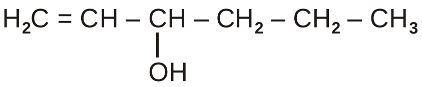
Solved Example :

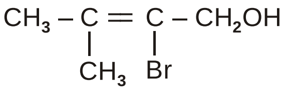
Qus. Name the following compounds according to IUPAC system.

(i)

$CH_3-CH_2-\underset{\displaystyle CH_2Cl}{\underset{|}{CH}}-\overset{\displaystyle CH_2OH}{\overset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

(ii)

$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-\overset{\displaystyle CH_2OH}{\overset{|}{CH}}-CH_3$

(iii)


(iv)

$H_2C=CH-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-CH_2-CH_3$

(v)

$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=\underset{\displaystyle Br}{\underset{|}{C}}-CH_2OH$

Ans. (i) 3-chloromethyl-2-isopropylpentene-2-ol

(ii) 2,5-dimethylhexene-1,5-diol

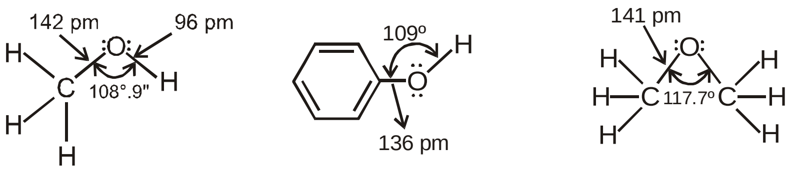
(iii) 3-Bromohexenol

(iv) Hex-1-en-3-ol

(v) 2-Bromo-3-methylbut-2-en-1-ol

Structures of functional groups :

In alcohols, the oxygen of the –OH group is attached to carbon by a sigma (σ) bond formed by the overlap of a sp^3 hybridised orbital of carbon with a sp^3 hybridised orbital of oxygen. Following figure depicts structural aspects of methanol, phenol and methoxymethane.



Methanol Phenol Methoxymethane

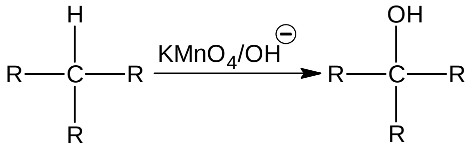
Structures of methanol, phenol and methoxymethane

Bond angle between C-O-C is 117.7° in ether because of steric repulsion between methyl groups

PREPARATION OF ALCOHOLS

1. From Alkanes :

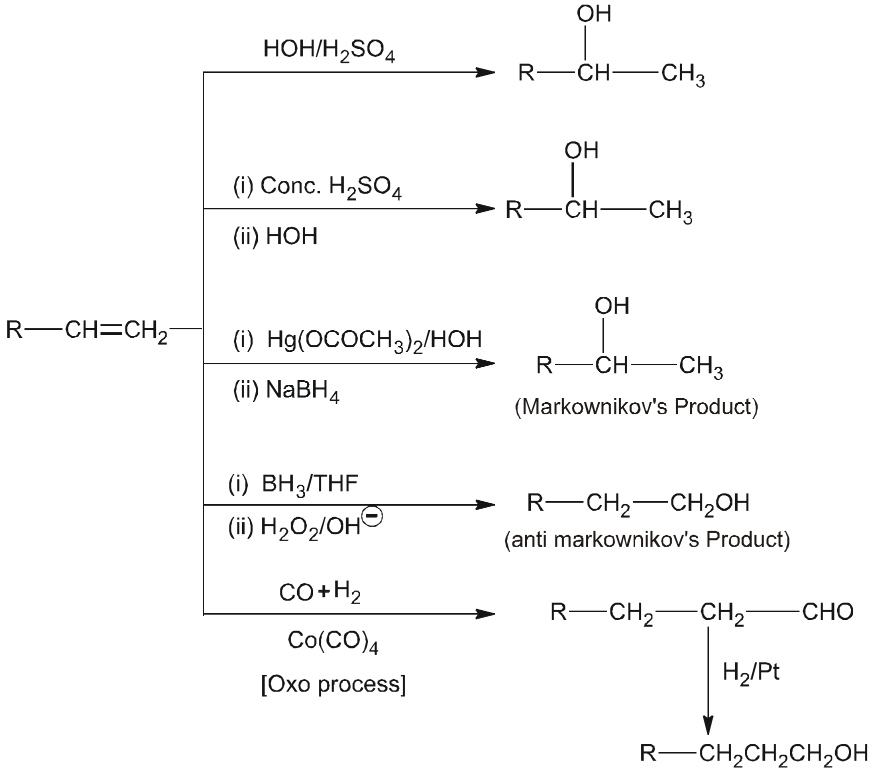
Alkanes having tertiary carbon on oxidation with cold alkaline $KMnO_4$ give tertiary alcohol.



$$R_3C{-}H \xrightarrow{KMnO_4/OH^{\ominus}} R_3C{-}OH$$

2. From Alkenes :

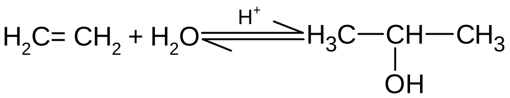
Alkenes can be converted into alcohol by the following reactions:



From alkenes :

A wide variety of electrophilic additions involve similar mechanisms. First, a strong electrophile attracts the loosely held electrons from the π-bond of an alkene. The electrophile forms a sigma bond to one of the carbons of the (former) double bond, while the other carbon becomes a carbocation. The carbocation (a strong electrophile) reacts with a nucleophile (often a weak nucleophile) to form another sigma bond.

By acid-catalysed hydration :

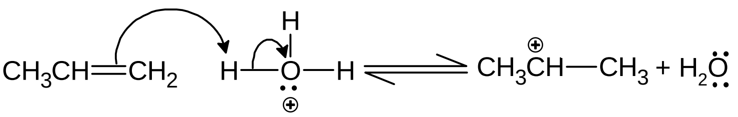


$$H_2C{=}CH_2 + H_2O \overset{H^+}{\rightleftharpoons} H_3C{-}CH(OH){-}CH_3$$

Mechanism:

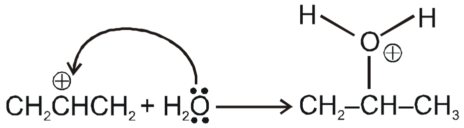
Step 1 - Protonation of alkene by electrophilic attack of H_3O^+ to form carbocation

$H_2O + H^+ \longrightarrow H_3O^+$



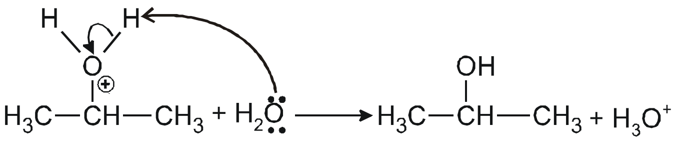
$$CH_3CH{=}CH_2 + H_3O^+ \rightleftharpoons CH_3\overset{\oplus}{C}H{-}CH_3 + H_2\ddot{O}$$

Step 2 - Nucleophilic attack of water on the carbocation



$$CH_2\overset{\oplus}{C}HCH_2 + H_2\ddot{O} \longrightarrow CH_2{-}CH(\overset{\oplus}{O}H_2){-}CH_3$$

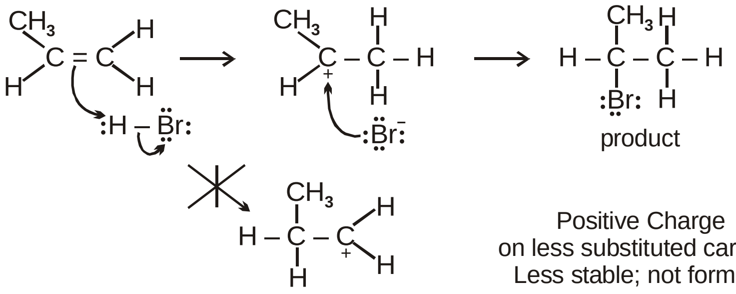
Step 3 - Deprotonation to form alcohol



$$H_3C-\underset{\overset{|}{\overset{+}{O}H_2}}{CH}-CH_3 + H_2\ddot{O}: \longrightarrow H_3C-\overset{OH}{\overset{|}{C}H}-CH_3 + H_3O^+$$

Example :

The ionic addition of HBr to propene shows protonation of the less substituted carbon to give the more substituted carbocation. Reaction with bromide ion completes the addition.

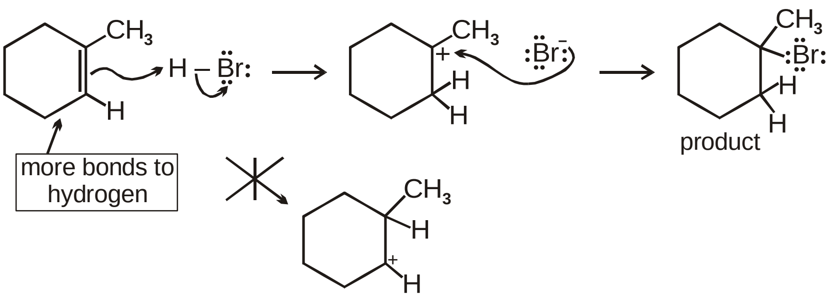


Positive Charge
on less substituted carbon.
Less stable; not formed.

Markovnikov's Rule : A Russian chemist, Vladimir Markovnikov, first showed the orientation of addition of HBr to alkenes in 1869. Markovnikov stated :

MARKOVNIKOV'S RULE : The addition of a proton acid to the double bond of an alkene result in a product with the acid proton bonded to the carbon atom that already holds the greater number of hydrogen atoms. This is the original statement of Markovnikov's rule. Reactions that follow this rule are said to follow **Markovnikov orientation** and give the **Markovnikov product**. We are often interested in adding electrophiles other than proton acids to the double bonds of alkenes. Markovnikov's rule can be extended to include a wide variety of other additions, based on the addition of the electrophile in such a way as to produce the most stable carbocation.

MARKOVNIKOV'S RULE (extended) : In an electrophilic addition to an alkene, the elctrophile adds in such a way as to generate the most sable intermediate.



Positive Charge
on less substituted carbon.
Less stable; not formed.

Free-Radical Addition of HBr : Anti-Markovnikov Addition :

In 1933, M. S. Kharasch and F.W. Mayo showed that anti-Markovnikov products result from addition of HBr (but not HCl or HI) in the presence of peroxides. Peroxides give rise to free radicals that act as catalysts to accelerate the addition, causing it to occur by a different mechanism. The oxygen-oxygen bond in peroxides is rather weak. It can break to give two radicals.

$$R-\ddot{\underset{..}{O}}-\ddot{\underset{..}{O}}-R \xrightarrow{\Delta} R-\ddot{\underset{..}{O}}\cdot + \cdot\ddot{\underset{..}{O}}-R \qquad \Delta H^o = +150 \text{ kJ } (+36 \text{ kcal})$$

Alkoxy radicals (R – O·) catalyze the anti-Markovnikov addition of HBr. The mechanism of this free-radical chain reaction is shown next.

Free-Radical Addition of HBr to Alkenes :

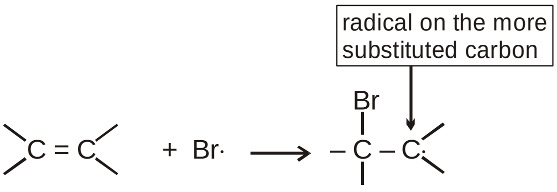
Initiation : Radicals are formed

$$R-O-O-R \xrightarrow{\Delta} R-O\cdot + \cdot O-R$$

$$R-O\cdot + H-Br \longrightarrow R-O-H + Br\cdot$$

Propagation : A radical reacts to generate another radical.

Step-I : A bromine radical adds to the double bond to generate an alkyl radical on the more substituted carbon atom.



Step-II : The alkyl radical abstracts a hydrogen atom from HBr to generate the product and a bromine radical.

The bromine radical generated in Step 2 gassan to react in Step 1, continuing the chain.

Example : Free-radical addition of HBr to propene.

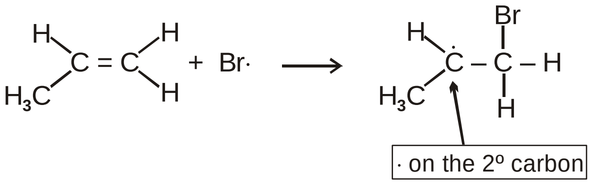
Initiation : Radicals are formed.

$$R-O-O-R \xrightarrow{\Delta} R-O\cdot + \cdot O-R$$

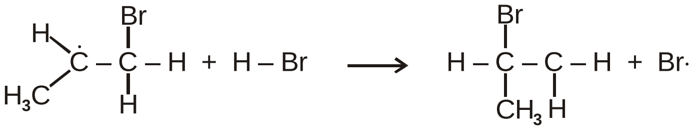
$$R-O\cdot + H-Br \longrightarrow R-O-H + Br\cdot$$

Propagation : A radical reacts to generate another radical.

Step-I : A bromine radical adds to the double bond to generate an alkyl radical on the secondary carbon atom.



Step-II : The alkyl radical abstracts a hydrogen atom from HBr to generate the product and a bromine radical.



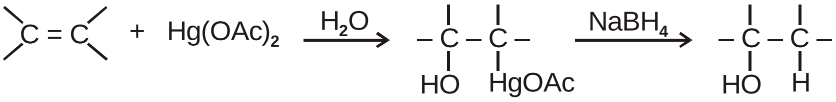
The bromine radical generated in Step 2 goes on to react in Step 1, continuing the chain.

Hydration by Oxymercuration Demercuration (OMDM) :

Many alkanes do not easily undergo hydration in aqueous acid.

Oxymercuration-demercuration is another method for converting alkenes to alcohols with Markovnikov orientation.

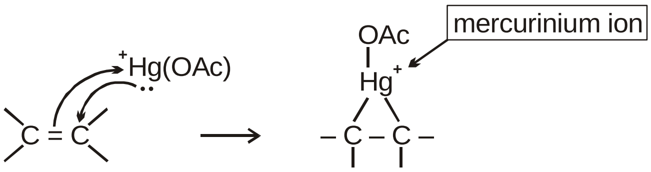
Oxymercuration-Demercuration :



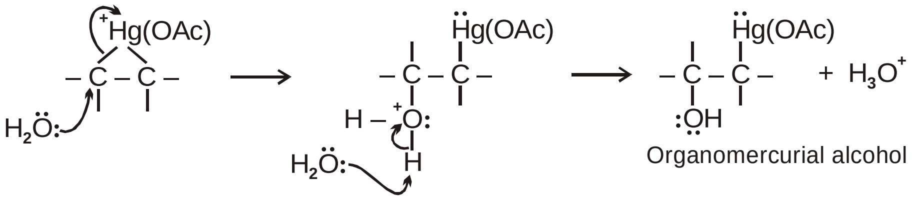
(Markovnikov orientation)

Oxymercuration of an Alkene :

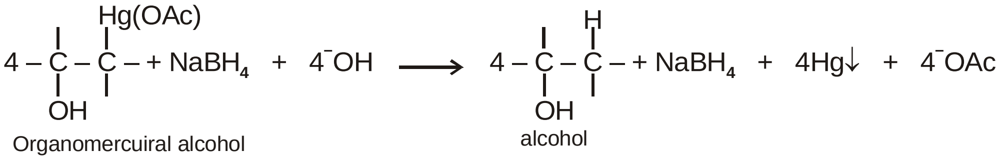
Step-I : Electrophilic attack forms a mercurinium ion.



Step-II : Water opens the ring to give an organomercurial alcohol.

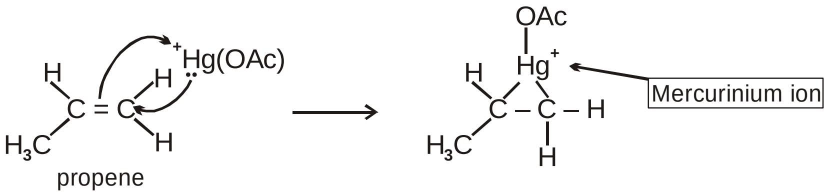


Demercuration replaces the mercuric fragment with hydrogen to give the alcohol.

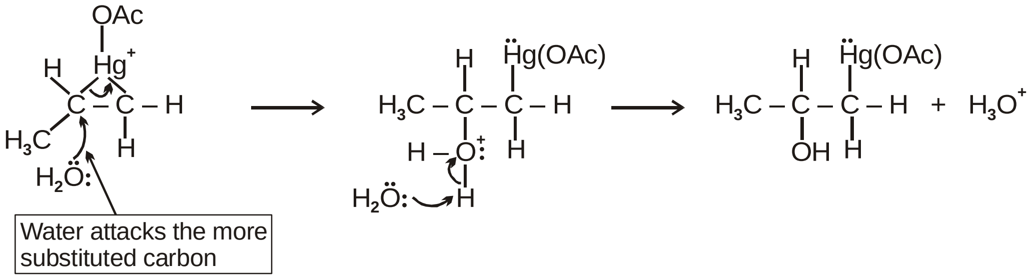


Example : Oxymercuration-demercuration of propene.

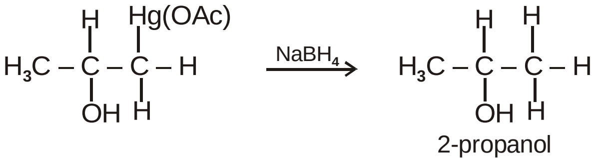
Step-1 : Electrophilic attack forms a mercurinium ion.



Step-2 : Water opens the ring to give an organomercurial alcohol.



Demercuration replaces the mercuric fragment with hydrogen to give the alcohol.



Solved Example :

Qus. Predict the major products of the following reactions.

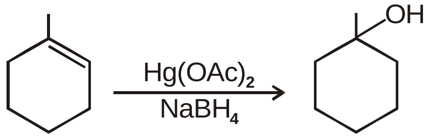
(a) 1-methylcyclohexene + aqueous $Hg(OAc)_2$

(b) The product from part (a), treated with $NaBH_4$

(c) 4-chlorocycloheptene + $Hg(OAc)_2$ in CH_3OH

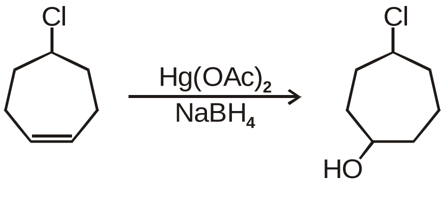
(d) The product from part (c), treated with $NaBH_4$

Ans. a, b



;

c, d



Solved Example :

Qus. Show how you would accomplish the following synthetic conversions.

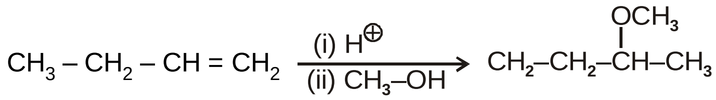
(a) 1-butene → 2-methoxybutane

(b) 1-iodo-2-methylcyclopentane → 1-methylcyclopentanol

(c) 3-methyl-1-pentene → 3-methyl-2-pentanol

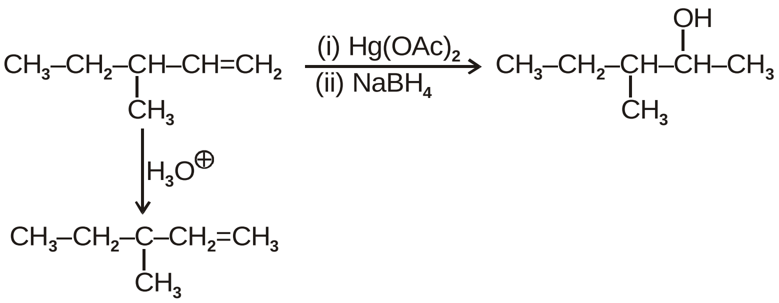
Explain why acid-ctatalyzed hydration would be a poor choice for the reaction in (c).

Ans. (a)



$$CH_3-CH_2-CH=CH_2 \xrightarrow[\text{(ii) } CH_3-OH]{\text{(i) } H^{\oplus}} CH_2-CH_2-\overset{OCH_3}{\overset{|}{CH}}-CH_3$$

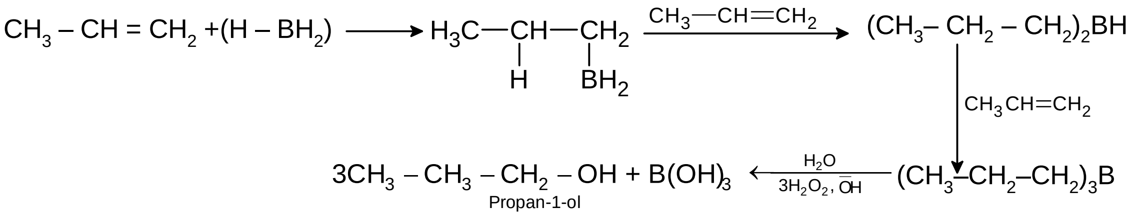
(c)



$$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH=CH_2 \xrightarrow[\text{(ii) } NaBH_4]{\text{(i) } Hg(OAc)_2} CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-\overset{OH}{\overset{|}{CH}}-CH_3$$

$$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH=CH_2 \xrightarrow{H_3O^{\oplus}} CH_3-CH_2-\underset{\underset{CH_3}{|}}{C}-CH_2=CH_3$$

Hydration by hydroboration-oxidation (HBO) :



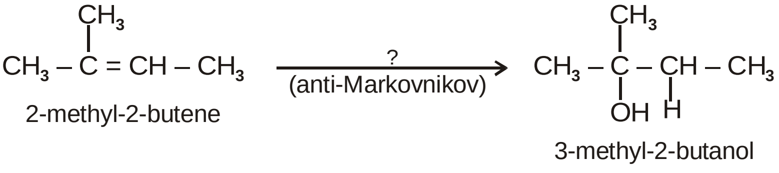
$$CH_3-CH=CH_2+(H-BH_2) \longrightarrow H_3C-\underset{\underset{H}{|}}{CH}-\underset{\underset{BH_2}{|}}{CH_2} \xrightarrow{CH_3-CH=CH_2} (CH_3-CH_2-CH_2)_2BH \xrightarrow{CH_3CH=CH_2} (CH_3-CH_2-CH_2)_3B$$

$$(CH_3-CH_2-CH_2)_3B \xrightarrow[3H_2O_2,\ \overset{-}{O}H]{H_2O} \underset{\text{Propan-1-ol}}{3CH_3-CH_3-CH_2-OH} + B(OH)_3$$

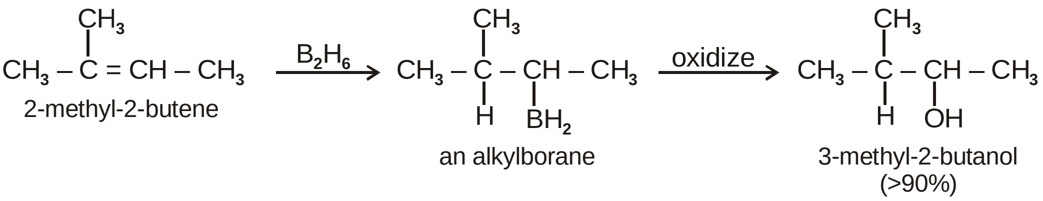
The product so formed looks as if it were formed by the addition of water to the alkene in a way opposite to Markovnikov's rule.

Hydroboration of Alkenes :

We have seen two methods for hydrating an alkene with Markovnikov orientation. What if we need to convert an alkene to the anti-Markovnikov alcohol? For example, the following transformation cannot be accomplished using the hydration procedures covered thus far.

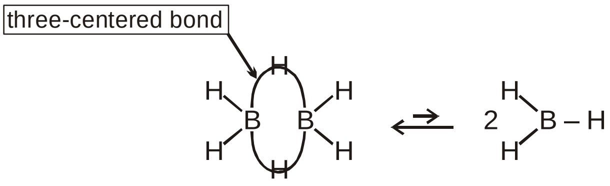


$$\underset{\text{2-methyl-2-butene}}{CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_3} \xrightarrow[\text{(anti-Markovnikov)}]{?} \underset{\text{3-methyl-2-butanol}}{CH_3-\overset{CH_3}{\overset{|}{\underset{\underset{OH}{|}}{C}}}-\underset{\underset{H}{|}}{CH}-CH_3}$$



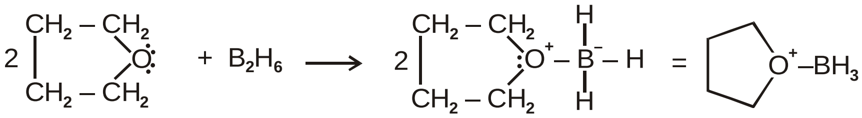
$$\underset{\text{2-methyl-2-butene}}{CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_3} \xrightarrow{B_2H_6} \underset{\text{an alkylborane}}{CH_3-\overset{CH_3}{\overset{|}{\underset{\underset{H}{|}}{C}}}-\underset{\underset{BH_2}{|}}{CH}-CH_3} \xrightarrow{\text{oxidize}} \underset{\substack{\text{3-methyl-2-butanol}\\(>90\%)}}{CH_3-\overset{CH_3}{\overset{|}{\underset{\underset{H}{|}}{C}}}-\underset{\underset{OH}{|}}{CH}-CH_3}$$

Diborane (B_2H_6) is a dimer composed of two molecules of borane (BH_3). The bonding in diborane is unconventional, using three-centered (banana-shaped) bonds with protons in the middle of them. Diborane is in equilibrium with a small amount of borane (BH_3), a strong Lewis acid with only six valence electrons.



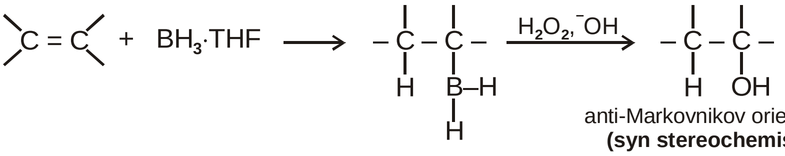
diborane borane

Diborane is an inconvenient reagent. It is a toxic, flammable, and explosive gas. It is more easily used as a complex with tetrahydrofuran (THF), a cyclic ether. This complex reacts like diborane, yet the solution is easily measured and transferred.



tetrahydrofuran (THF) diborane borane-THF complex = $BH_3{\cdot}THF$

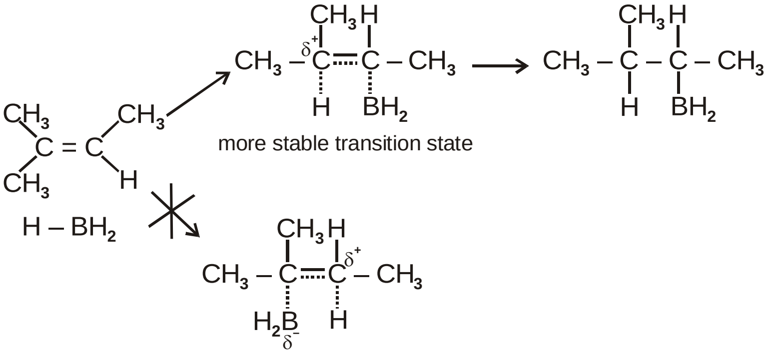
Hydroboration-oxidation :



anti-Markovnikov orientation
(syn stereochemistry)

Mechanism : Hydroboration of an Alkene :

Borane adds to the double bond in a single step. Boron adds to the less hindered, less substituted carbon, and hydrogen adds to the more substituted carbon.



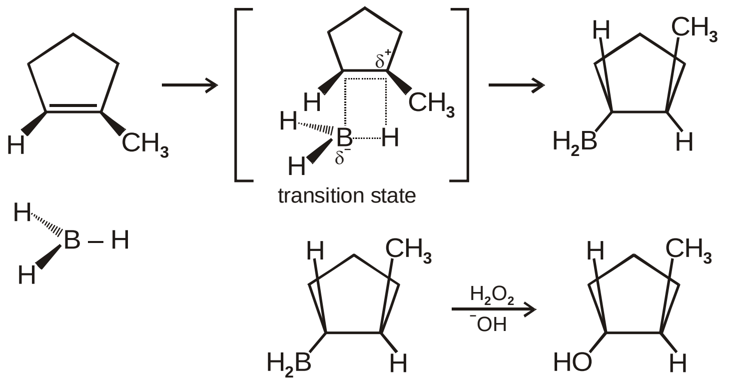
more stable transition state

less stable transition state

Stereochemistry of Hydroboration :

The simultaneous addition of boron and hydrogen to the double bond leads to a syn addition: Boron and hydrogen add across the double bond on the same side of the molecule. (If they added to opposite sides of the molecule, the process would be an anti addition.)

The stereochemistry of the hydroboration-oxidation of 1-methylcyclopentene is shown next. Boron and hydrogen add to the same face of the double bond (syn) to form a trialkylborane. Oxidation of the trialkylborane replaces boron with a hydroxyl group in the same stereochemical position. The product is trans-2-methylcyclopentanol. A racemic mixture is expected because a chiral product is formed from achirl reagents.

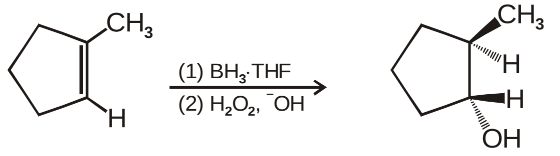


trans-2-methylcyclopentanol
(85% overall)
(racemic mixture of enantiomers)

Solved Example :

Qus. Show how you would convert 1-methylcyclopentene to 2-methylcyclopentanol.

Ans. Working backward, use hydroboration-oxidation to form 2-methyl-cyclopentanol from 1-methylcyclopentene. The use of (1) and (2) above and below the reaction arrow indicates individual steps in a two-step sequence.



1-methylcyclopentene trans-2-methylcyclopentanol

The 2-methylcyclopentanol that results from this synthesis is the pure trans isomer.

Solved Example :

Qus. Predict the major products of the following reactions.

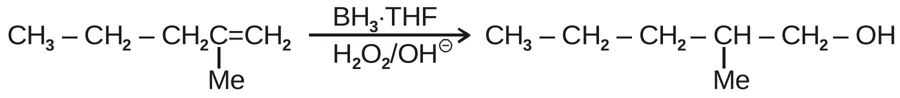
(a) propene + $BH_3 \cdot THF$ (b) The product from part (a) + H_2O_2/OH^-

(c) 2-methyl-2-pentene + $BH_3 \cdot THF$ (d) The product from part (c) + H_2O_2/OH^-

(e) 1-methylcyclohexene + $BH_3 \cdot THF$ (f) The product from part (e) + H_2O_2/OH^-

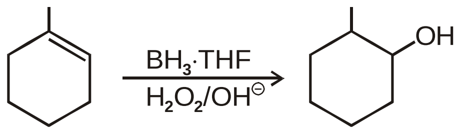
Ans. **a, b** $CH_3-CH=CH_2 \xrightarrow[H_2O_2/OH^{\ominus}]{BH_3 \cdot THF} CH_3-CH_2-CH_2-OH$

c, d



$$CH_3-CH_2-CH_2\underset{\substack{|\\ Me}}{C}=CH_2 \xrightarrow[H_2O_2/OH^{\ominus}]{BH_3 \cdot THF} CH_3-CH_2-CH_2-\underset{\substack{|\\ Me}}{CH}-CH_2-OH$$

e, f



Solved Example :

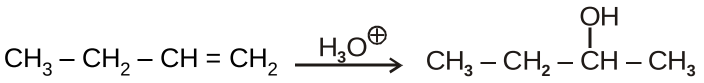
Qus. Show how you would accomplish the following synthetic conversions.

(a) 1-butene → 1-butanol

(b) 1-butene → 2-butanol

Ans. (a) $CH_3-CH_2-CH=CH_2 \xrightarrow[H_2O_2/OH^{\ominus}]{BH_3 \cdot THF} CH_3-CH_2-CH_2-CH_2-OH$

(b)

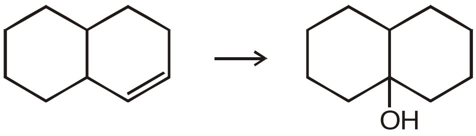


$$CH_3-CH_2-CH=CH_2 \xrightarrow{H_3O^{\oplus}} CH_3-CH_2-\overset{\substack{OH\\ |}}{CH}-CH_3$$

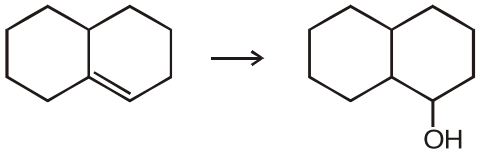
Solved Example :

Qus. Show how you would accomplish the following transformations.

(a)



(b)



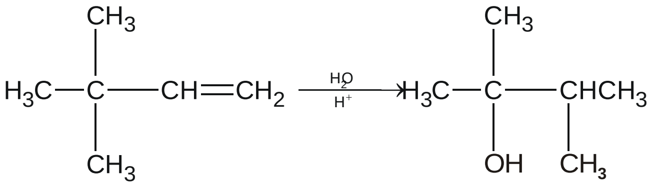
(c) 1-methylcycloheptanol → 2-methylcycloheptanol

Ans. (a) by $H_3O^{\oplus}$

(b) by HBO

Hydration, hydroboration and oxymercuration – demercuration of alkenes.

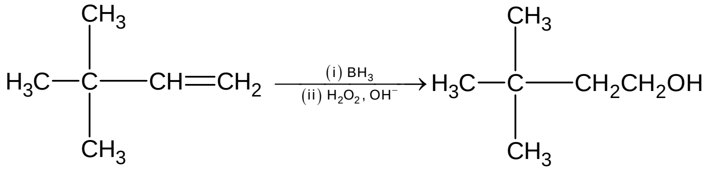
Hydration :



$$H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH{=}CH_2 \xrightarrow[H^+]{H_2O} H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-\underset{\underset{CH_3}{|}}{C}HCH_3$$

According to Markovnikov's rule, rearrangement possible

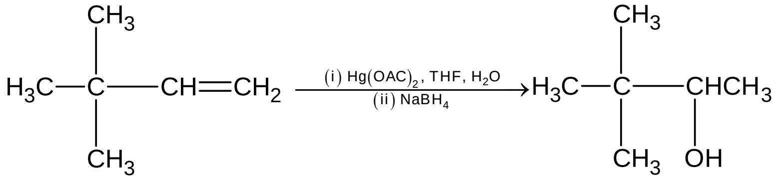
Hydroboration :



$$H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH{=}CH_2 \xrightarrow[\text{(ii) } H_2O_2,\ OH^-]{\text{(i) } BH_3} H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2CH_2OH$$

According to anti Markovnikov's rule and rearrangement not possible (anti addition)

Oxymercuration – demercuration :

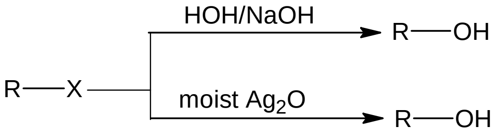


$$H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH{=}CH_2 \xrightarrow[\text{(ii) } NaBH_4]{\text{(i) } Hg(OAC)_2,\ THF,\ H_2O} H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\underset{\underset{OH}{|}}{C}HCH_3$$

According to Markovnikov's rule but rearrengement not possible

3. **From alkyl halides**

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

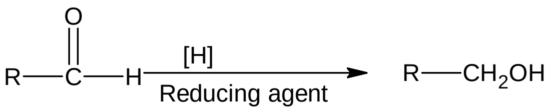


$$R-X \xrightarrow{HOH/NaOH} R-OH$$
$$R-X \xrightarrow{\text{moist } Ag_2O} R-OH$$

4. **Reduction of aldehydes and ketones**

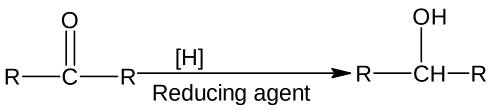
(a) **Reduction by reducing agents**

(i) Aldehyde gives primary alcohol



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

(ii) Ketone gives secondary alcohol



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

Reducing agents

(i) $LiAlH_4$

(ii) $NaBH_4$

(iii) Metal (Zn, Fe or Sn)/Acid (HCl, dil H_2SO_4 or CH_3COOH)

(iv) Aluminium isopropoxide/isopropylalcohol

(v) H_2/Ni

$$CH_3-CH=CH-CHO \xrightarrow{NaBH_4} CH_3-CH=CH-CH_2OH$$

- $LiAlH_4$ has no effect on double and triple bonds but if compound is β - aryl, α, β - unsaturated carbonyl compound then double bond also undergoes reduction.

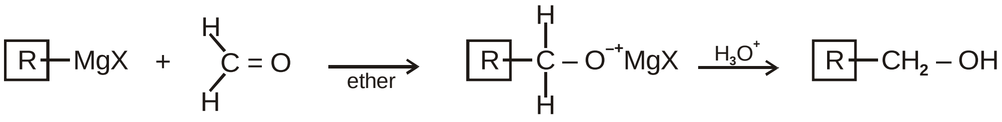
$$H_5C_6-CH=CH-CHO \xrightarrow{LiAlH_4} H_5C_6-CH_2-CH_2-CH_2OH$$

(b) Reduction by Grignard reagents

Addition followed by hydrolysis

Addition to Formaldehyde : Formation of Primary Alcohols :

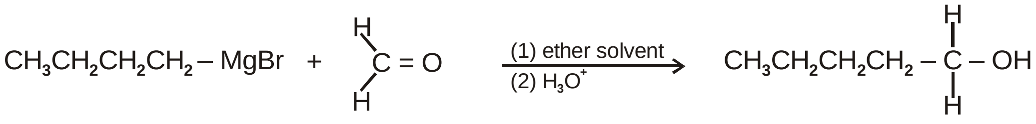
Addition of a Grignard reagent to formaldehyde, followed by protonation, gives a primary alcohol with one more carbon atom than in the Grignard reagent.



Grignard reagent formaldehyde primary alcohol

$$\boxed{R}-MgX + H_2C=O \xrightarrow[\text{ether}]{} \boxed{R}-CH_2-O^{-+}MgX \xrightarrow{H_3O^+} \boxed{R}-CH_2-OH$$

For example,

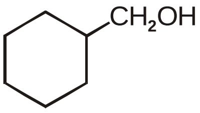


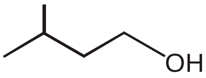
butylmagnesium bromide formaldehyde 1-pentanol (92%)

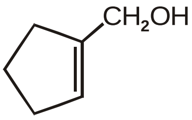
$$CH_3CH_2CH_2CH_2-MgBr + H_2C=O \xrightarrow[(2)\ H_3O^+]{(1)\ \text{ether solvent}} CH_3CH_2CH_2CH_2-CH_2-OH$$

Solved Example :

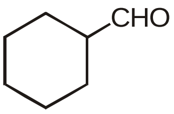
Qus. Show how you would synthesize the following alcohols by adding anappropriate Grignard reagent to formaldehyde.

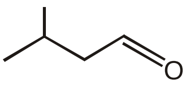
(a)


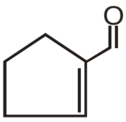
(b)


(c)


Ans. By reaction of CH_3MgBr with

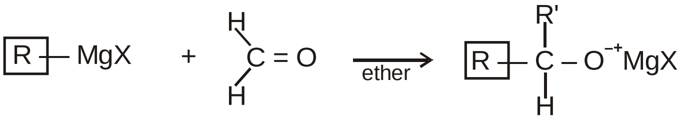
(a)


(b)


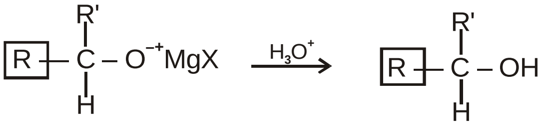
(c)


Addition to Aldehydes : Formation of Secondary Alcohols :

Grignard reagents add to aldehydes to give, after protonation, secondary alcohols.

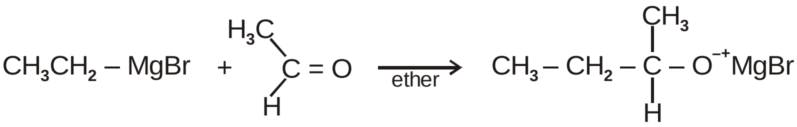


Grignard reagent aldehyde

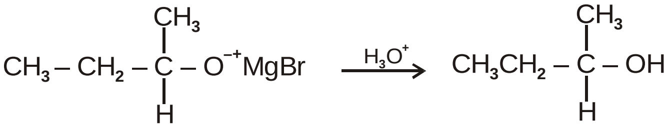


$$\boxed{R}-\overset{R'}{\underset{H}{C}}-O^{-+}MgX \xrightarrow{H_3O^+} \boxed{R}-\overset{R'}{\underset{H}{C}}-OH$$

The two alkyl groups of the secondary alcohol are the alkyl group from the Grignard reagent and the alkyl group that was bonded to the carbonyl group of the aldehyde.



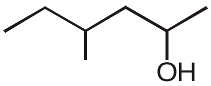
$$CH_3CH_2-MgBr + (H_3C)(H)C=O \xrightarrow{ether} CH_3-CH_2-\overset{CH_3}{\underset{H}{C}}-O^{-+}MgBr$$

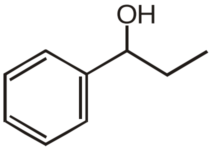


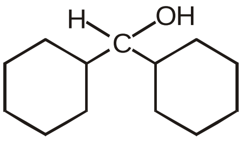
$$CH_3-CH_2-\overset{CH_3}{\underset{H}{C}}-O^{-+}MgBr \xrightarrow{H_3O^+} CH_3CH_2-\overset{CH_3}{\underset{H}{C}}-OH$$

Solved Example :

Qus. Show two ways you could synthesize each of the following alcohols by adding an appropriate Grignard reagent to an aldehyde.

(a) 

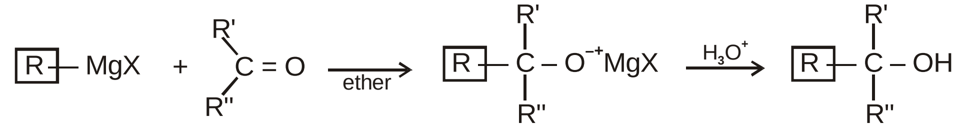
(b) 

(c) 

Ans. A secondary alcohol has two groups on the carbinol carbon atom. Consider two possible reactions, with either group added as the Grignard reagent.

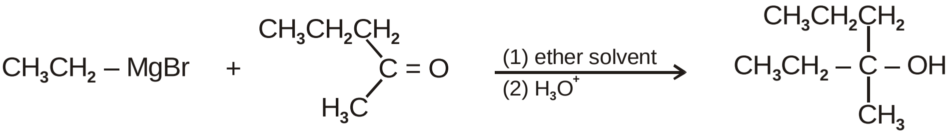
Addition to Ketones : Formation of Tertiary Alcohols :

A ketone has two alkyl groups bonded to its carbonyl carbon atom. Addition of a Grignard reagent, followed by protonation, gives a tertiary alcohol, with three alkyl groups bonded to the carbinol carbon atom.



$$\boxed{R}-MgX + (R')(R'')C=O \xrightarrow{ether} \boxed{R}-\overset{R'}{\underset{R''}{C}}-O^{-+}MgX \xrightarrow{H_3O^+} \boxed{R}-\overset{R'}{\underset{R''}{C}}-OH$$

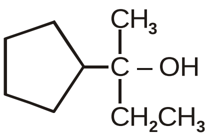
Two of the alkyl groups are the two originally bonded to the ketone carbonyl group. The third alkyl group comes from the Grignard reagent.



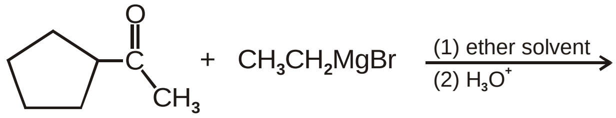
$$CH_3CH_2-MgBr + (CH_3CH_2CH_2)(H_3C)C=O \xrightarrow[(2)\ H_3O^+]{(1)\ ether\ solvent} CH_3CH_2-\overset{CH_3CH_2CH_2}{\underset{CH_3}{C}}-OH$$

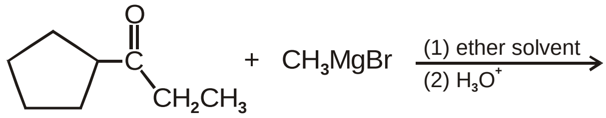
Solved Example :

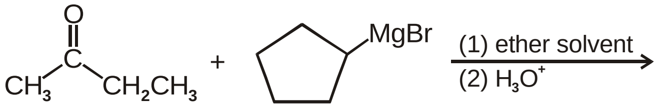
Qus. Show how you would synthesize the following alcohol from compounds containing no more than five carbon atoms.



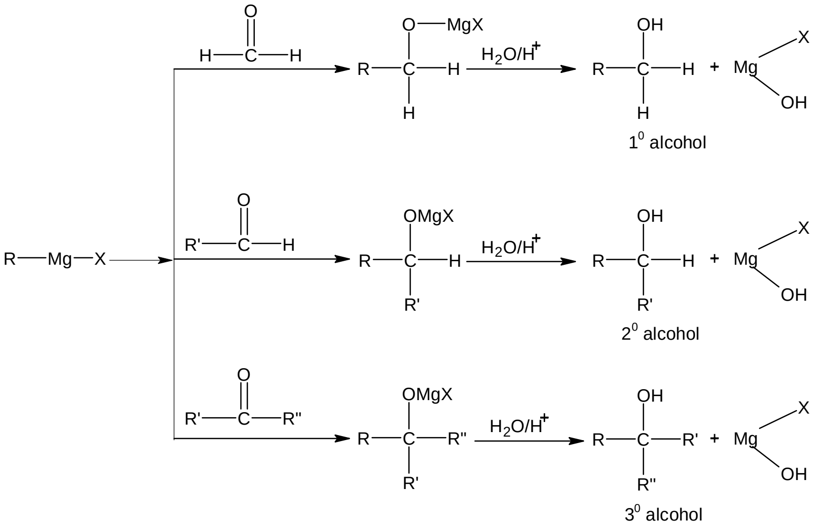
Ans. This is a tertiary alcohol; any one of the three alkyl groups might be added in the form of a Grignard reagent. We can propose three combinations of Grignard reagents with ketones :







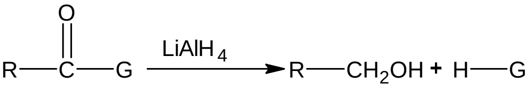
Any of these three syntheses would probably work, but only the third begins with fragments containing no more than five carbon atoms. The other two syntheses would require further steps to generate the ketones from compounds containing no more than five carbon atoms.



- Methanol can not be prepared by this method.

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

(a) **Reduction by $LiAlH_4$**

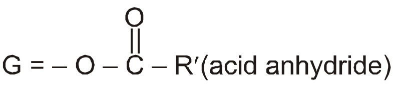


$$R-\overset{O}{\overset{\|}{C}}-G \xrightarrow{LiAlH_4} R-CH_2OH + H-G$$

G = OH (acid)

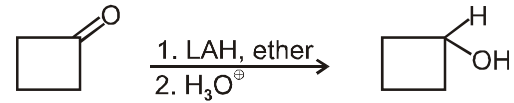
G = Cl (acid chloride)

G = OR′ (ester)



$$G = -O-\overset{O}{\overset{\|}{C}}-R'\text{(acid anhydride)}$$

Ex.



Cyclobutanone Cyclobutanol

Ex. **Acids**

$$\underset{\text{Palmitic}}{CH_3-(CH_2)_{14}-COOH} \xrightarrow[2.\ H_3O^{\oplus}]{1.\ LAH,\ ether} \underset{\text{Hexadecanol-1 (cetyl alcohol)}}{CH_3-(CH_2)_{14}-CH_2OH}$$

Ex. $\underset{\text{Palmitic}}{CH_3 - CH = CH - COOH} \xrightarrow[2.\ H_3O^{\oplus}]{1.\ \text{LAH, ether}} \underset{\text{Crotyl alcohol}}{CH_3 - CH = CH - CH_2OH}$

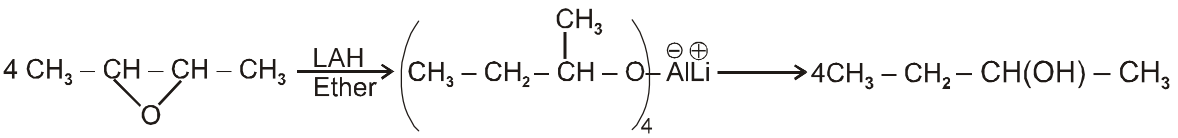
Ex. $\underset{\beta\text{-Alanine}}{CH_2(NH_2)CH_2COOH} \xrightarrow[2.\ H_3O^{\oplus}]{1.\ \text{LAH, ether}} \underset{\text{3-Aminopropanol-1}}{CH_2 - (NH_2)CH_2CH_2OH}$

Ex. Acid chlorides $CH_3COCl \xrightarrow[2.\ H_3O^{\oplus}]{1.\ \text{LAH, ether}} CH_3CH_2OH$

Acid anhydrides $(CH_3CO)_2O \xrightarrow[2.\ H_3O^{\oplus}]{1.\ \text{LAH, ether}} 2CH_3CH_2OH$

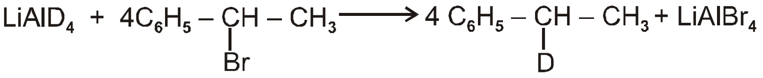
Esters $CH_3 - CH = CH - COOC_2H_5 \xrightarrow[2.\ H_3O^{\oplus}]{1.\ \text{LAH, ether}} \underset{\text{But}-2-\text{ene}-1-\text{ol}}{CH_3 - CH = CH - CH_2OH}$

Ex.



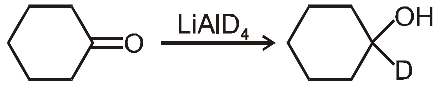
Ex. $4\ ROH + LiAlH_4 \longrightarrow (RO)_4\overset{\ominus}{Al}\ \overset{\oplus}{Li} + 4H_2$

Ex. **(i)**



$LiAlD_4 + 4C_6H_5 - \underset{Br}{\underset{|}{CH}} - CH_3 \longrightarrow 4\ C_6H_5 - \underset{D}{\underset{|}{CH}} - CH_3 + LiAlBr_4$

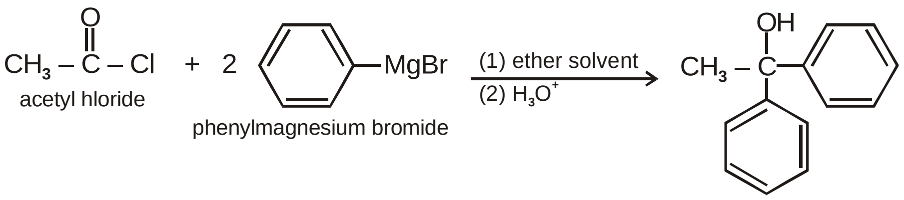
(ii)



Cyclohexanone Cyclohexanol-1-d

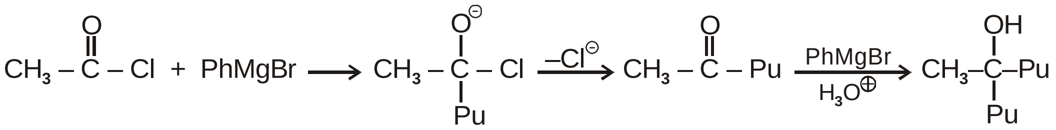
Solved Example :

Qus. Propose a mechanism for the reaction of acetyl chloride with phenylmagnesium bromide to give 1,1-diphenylethanol.



1,1-diphenylethanol

Ans.



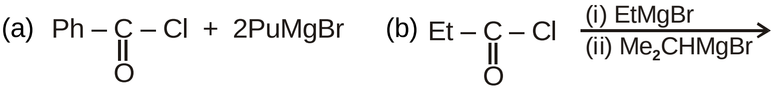
$CH_3 - \overset{O}{\overset{||}{C}} - Cl + PhMgBr \longrightarrow CH_3 - \underset{Pu}{\underset{|}{\overset{O^{\ominus}}{\overset{|}{C}}}} - Cl \xrightarrow{-Cl^{\ominus}} CH_3 - \overset{O}{\overset{||}{C}} - Pu \xrightarrow[H_3O^{\oplus}]{PhMgBr} CH_3 - \underset{Pu}{\underset{|}{\overset{OH}{\overset{|}{C}}}} - Pu$

Solved Example :

Show how you would add Grignard reagents to acid chlorides or esters to synthesize the following alcohols.

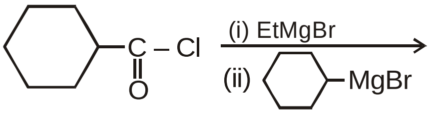
(a) $Ph_3C - OH$ (b) 3-ethyl-2-methyl-3-pentanol (c) dicyclohexylphenylmethanol

Ans.



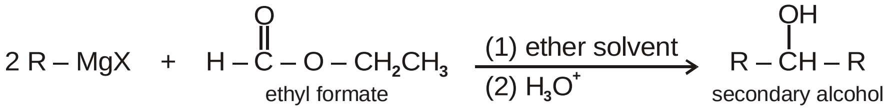
(a) $Ph - \underset{O}{\underset{||}{C}} - Cl + 2PuMgBr$ (b) $Et - \underset{O}{\underset{||}{C}} - Cl \xrightarrow[(ii)\ Me_2CHMgBr]{(i)\ EtMgBr}$

(c)



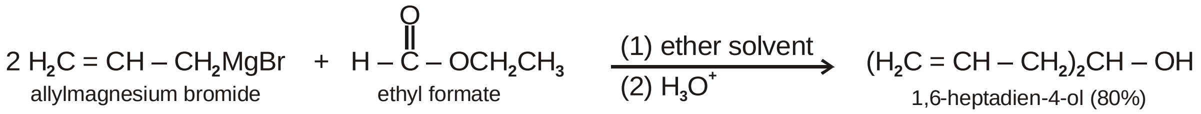
Solved Example :

A formate ester, such as ethyl formate, reacts with an excess of a Grignard reagent to give (after protonation) secondary alcohols with two identical alkyl groups.



$$2\,R-MgX + H-\overset{\overset{O}{\|}}{C}-O-CH_2CH_3 \xrightarrow[(2)\ H_3O^+]{(1)\ \text{ether solvent}} R-\overset{\overset{OH}{|}}{C}H-R$$

(a) Propose a mechanism to show how the reaction of ethyl formate with an excess of allyl magnesium bromide gives, after protonation, 1,6-heptadien-4-ol.



$$2\,H_2C=CH-CH_2MgBr + H-\overset{\overset{O}{\|}}{C}-OCH_2CH_3 \xrightarrow[(2)\ H_3O^+]{(1)\ \text{ether solvent}} (H_2C=CH-CH_2)_2CH-OH$$

(b) Show how you would use reactions of Grignard reagents with ethyl formate to synthesize the following secondary alcohols.

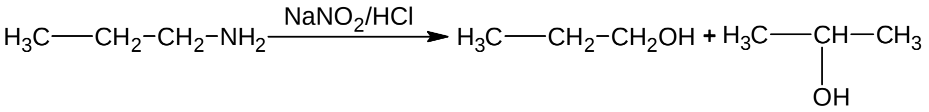
(i) 3-pentanol (ii) diphenylmethanol

6. **From aliphatic primary amines :**

It react with nitrous acid to give alcohol.

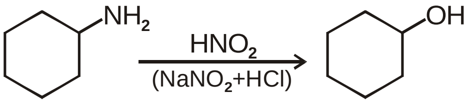
- Nature of alcohol depends on the nature of carbon having —NH_2 group.
- Reaction proceeds through carbocation hence rearranged alcohol is obtained.

Ex.

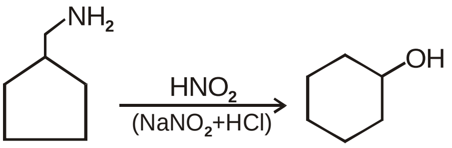


$$H_3C-CH_2-CH_2-NH_2 \xrightarrow{NaNO_2/HCl} H_3C-CH_2-CH_2OH + H_3C-\underset{\underset{OH}{|}}{C}H-CH_3$$

Ex.

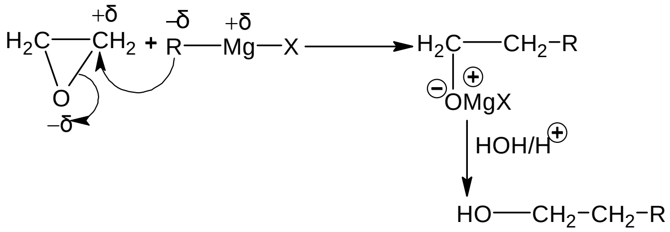


Ex.



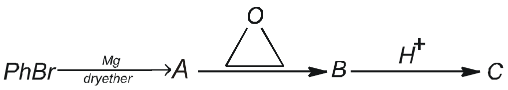
7. From Oxiranes *:*

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.



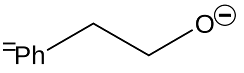
Solved Example :

Qus. (a) Find A, B, C, D, E.

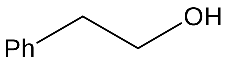


(b) $CH_3COOC_2H_5 \xrightarrow[(ii)\ H_2O/H^+]{(i)\ CH_3MgBr} D + E$

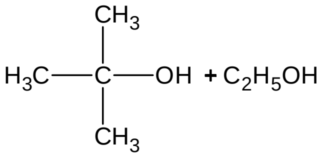
Ans. (a) A = PhMgBr B =



C =



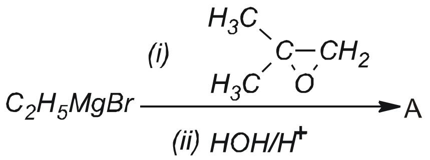
(b)



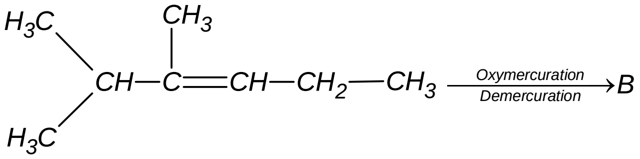
$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH + C_2H_5OH$$

Solved Example :

Qus. (i)

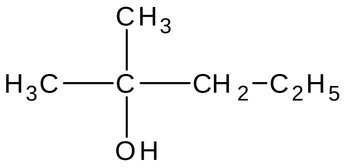


(ii)



Ans.

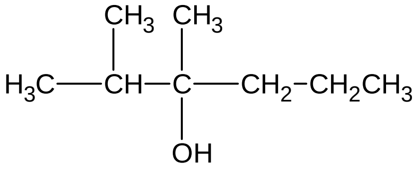
(i)



$$H_3C-C(CH_3)(OH)-CH_2-C_2H_5$$

(2 methyl 2 pentanol)

(ii)

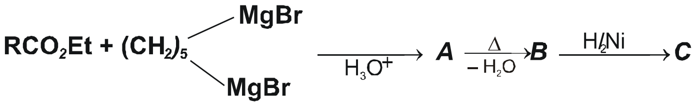


$$H_3C-CH(CH_3)-C(CH_3)(OH)-CH_2-CH_2CH_3$$

(3^0 alcohol)

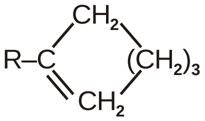
Solved Example :

Qus. (i) Identify A, B & C

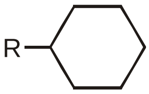


Account the reason for the above reactions.

Ans. **(i)** (A)



(B)



Physical properties of alcohols :

The hydroxyl group is quite polar and, most important, contains hydrogen bonded to the highly electronegative element oxygen. Through the hydroxyl group, an alcohol is capable of hydrogen bonding : The physical properties show some of the effects of this hydrogen bonding.

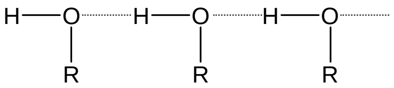
Polyhydroxy alcohols provide more than one site per molecule for hydrogen bonding, and their properties reflect this. The simplest diol,1,2-ethanediol (ethylene glycol), boils at 197ºC.

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 decreases.

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.

Solved Example :

Qus. Arrange the following sets of compounds in order of their increasing boiling points :

(a) Pentan-1-ol, butan-1-ol, butan-2-ol, ethanol, propan-1-ol, methanol.

(b) Pentan-1-ol, n-butane, pentanal, ethoxyethane.

Ans. (a) Methanol, ethanol, propan-1-ol, butan-2-ol, butan-1-ol, pentan-1-ol.

(b) n-Butane, ethoxyethane, pentanal and pentan-1-ol.

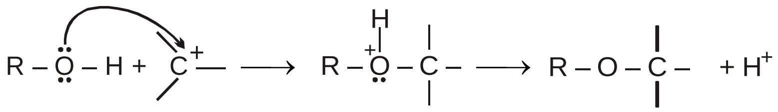
CHEMICAL PROPERTIES :

Chemical properties of alcohols can be discussed under following categories :

(A) Reaction involving breaking of oxygen – hydrogen bond.
(B) Reaction involving breaking of carbon – oxygen bond.
(C) Oxidation of alcohols.
(D) Dehydrogenation of alcohols.
(E) Some miscellaneous reactions of monohydric alcohol.

(A) Reactions due to breaking of oxygen hydrogen bond. (Reactions due to acidic character of alcohols) :

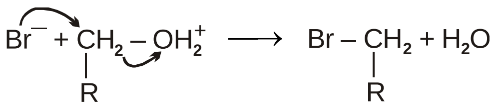
Alcohols as nucleophiles :

(i) 

(ii) The bond between C – O is broken when they react as electrophiles. Protonated alcohols react in this manner.

Protonated alcohols as electrophiles :

$$R-CH_2-OH + H^+ \longrightarrow R-CH_2-\overset{+}{O}H_2$$



(a) Alcohols are acidic in nature because hydrogen is present on electro negative oxygen atom.

(b) Alcohol is weaker acid

$$R—O—H \longrightarrow H^+ + R—O^{\ominus}$$

acidity ∝ stability of acid anions.
Acidity of 1° > 2° > 3°
Alcohols give following reactions due to breaking of oxygen – hydrogen bond.

Talbe : pKa values of some phenols and Ethanol :

Compound	**Formula**	**pKa**
o-Nitrophenol	o-$O_2N-C_6H_4-OH$	7.2
m-Nitrophenol	m-$O_2N-C_6H_4-OH$	8.3
p-Nitrophenol	p-$O_2N-C_6H_4-OH$	7.1
Phenol	C_6H_5-OH	10.0
o-Cresol	o-$CH_3-C_6H_4-OH$	10.2
m-Cresol	m-$CH_3C_6H_4-OH$	10.1
p-Cresol	p-$CH_3-C_6H_4-OH$	10.2
Ethanol	C_2H_5OH	15.9

Solved Example :

Qus. Arrange the following compounds in increasing order of their acid strength:

Propan-1-ol, 2,4,6-trinitrophenol, 3-nitrophenol, 3, 5-dinitrophenol, phenol, 4-methylphenol.

Ans. Propan-1-ol, 4-methylphenol, phenol, 3-nitrophenol, 3,5-dinitrophenol, 2,4, 6-trinitrophenol.

(i) Reaction with metal

$$R-O-H + M \longrightarrow R-\overset{\ominus}{O}\ \overset{\oplus}{M} + 1/_2\, H_2$$

Metal alkoxide

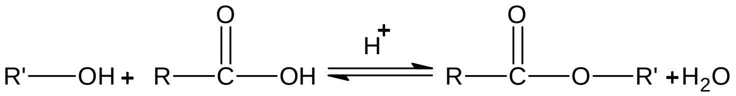
M = 1st group metal.

M = Al, Mg, Zn

$$3R-OH + Al \longrightarrow (RO)_3\, Al + \frac{3}{2}H_2$$

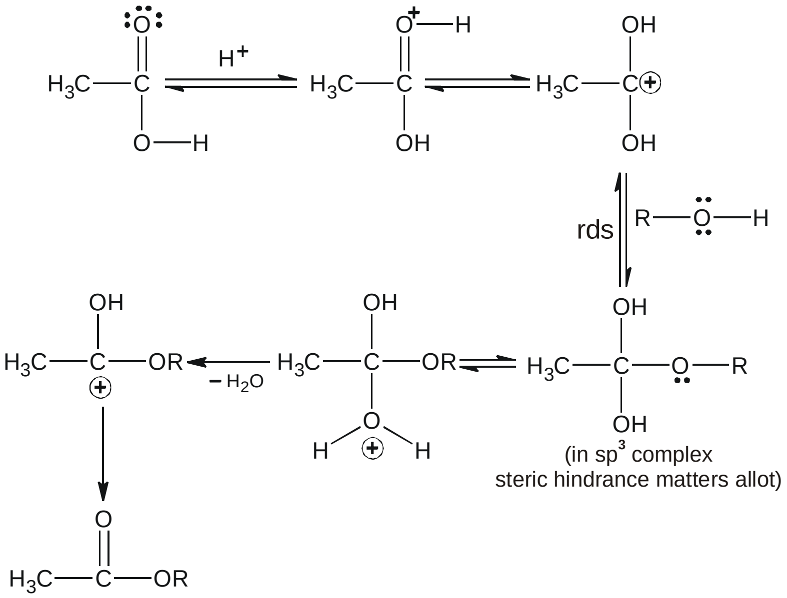
Aluminium alkoxide

(ii) Esterification (With carboxylic acid)



$$R'-OH + R-\overset{\overset{O}{\|}}{C}-OH \overset{H^+}{\rightleftharpoons} R-\overset{\overset{O}{\|}}{C}-O-R' + H_2O$$

It is reversible acid catalysed reaction. It follow SN_1 mechanism.



Increasing the size of alkyl group on alcohol part decreases the nucleophilic character because steric hindrance increases.

$$\left[\text{Reactivity} \propto \frac{1}{\text{Steric hindrence in RCOOH/ROH}}\right]$$

Order of reactivity of alcohols CH_3OH > 1° alcohol > 2° alcohol > 3° alcohol

⇒ $Ar/R-OH + R'-COOH \xleftrightarrow{H^+} Ar/ROCOR' + H_2O$

Carboxylic acid

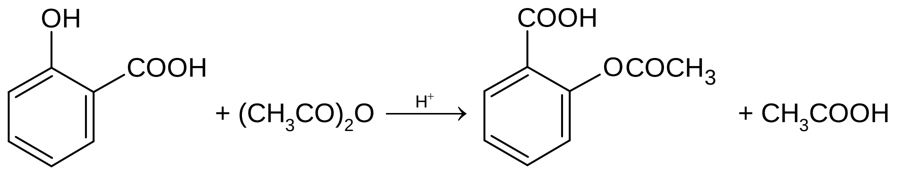
- $Ar/R-OH + (R'CO)_2O \xleftrightarrow{H^+} Ar/ROCOR' + R'COOH$

  Acid anhydride

- $Ar/R-OH + R'COCl \xleftrightarrow{\text{Pyridine}} Ar/ROCOR' + HCl$

  Acid Chloride

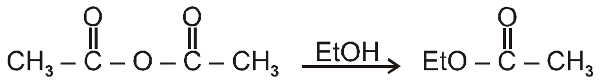
Example - Acetylation of salicylic acid



Salicylic acid

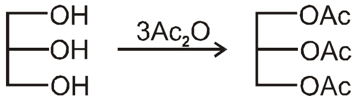
Acetylsalicylic acid
(aspirin)

Acylation of Alcohol :



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow{EtOH} EtO-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

(MOL.WEIGHT OF ALCOHOL INCREASED BY 42 amu OR BY C_2H_2O)

Ex. 

(MOL.WEIGHT OF ALCOHOL INCREASED BY 126 amu)

(iv) **Alkylation of Alcohol**

$$R-O-H\xrightarrow[\substack{\text{or}\\ CH_3I/K_2CO_3}]{(CH_3)_2SO_4/NaOH}R-O-CH_3$$

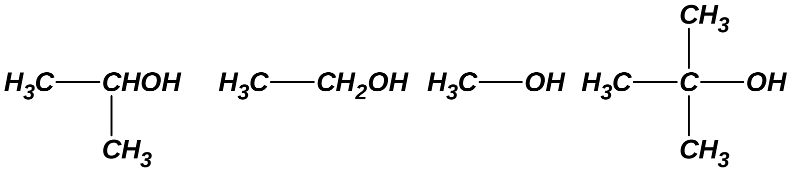
Methylation is mainly used for determination of hydroxyl groups in an unknown compound.

$$\text{No. of hydroxyl groups} = \frac{\text{Molecular weight of methylated ether prodcued} - \text{molecular weight of reactant}}{14}$$

Solved Example :

Qus. Arrange the following in increasing order of acidic strength.

(a)



(i) ***(ii)*** ***(iii)*** ***(iv)***

(b) Arrange the following in increasing order of esterification:

MeCOOH	EtCOOH	$(Et)_2CHCOOH$
(i)	(ii)	(iii)

Ans. **(a)** (iii) > (ii) > (i) > (iv) **(b)** (i) > (ii) > (iii)

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

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

Reaction with hydrogen halides :

$$R-OH + HX \xrightarrow[\text{anhy}-]{ZnCl_2} R\text{–}Cl + H_2O$$

- Lucas test [test with Lucas regent (conc. HCl and $ZnCl_2$)] -Used for distinguishing the three classes of alcohols.

Reaction with phosphorus trihalides :

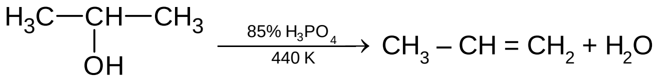
$$3R-OH + PX_3 \longrightarrow 3R\text{–}X + H_3PO_3\ (X = Cl, Br)$$

Dehydration:

From 1° alcohol

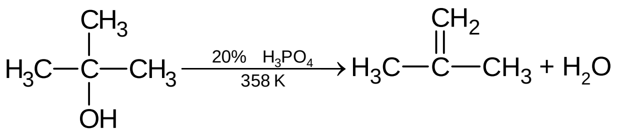
$$C_2H_5OH \xrightarrow[443K]{Conc.\ H_2PO_4} CH_2 = CH_2 + H_2O$$

From 2° alcohol



$$H_3C-\underset{OH}{CH}-CH_3 \xrightarrow[440\text{ K}]{85\%\ H_3PO_4} CH_3-CH=CH_2+H_2O$$

From 3° alcohol

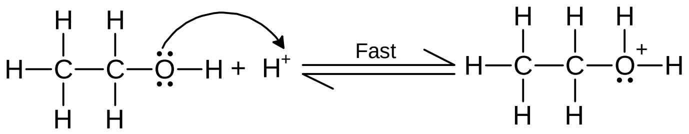


$$H_3C-\overset{CH_3}{\underset{OH}{C}}-CH_3 \xrightarrow[358\text{ K}]{20\%\ H_3PO_4} H_3C-\overset{CH_2}{\overset{||}{C}}-CH_3+H_2O$$

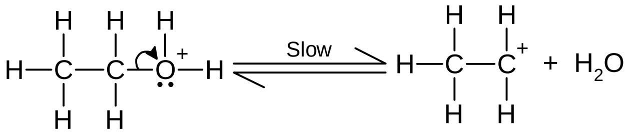
Therefore, the order reactivity can be observed as 1° < 2° < 3°

- Mechanism of dehydration

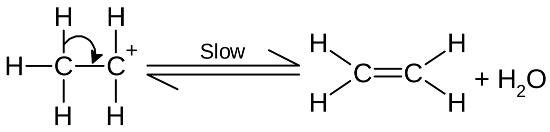
Step 1 - Formation of protonated alcohols



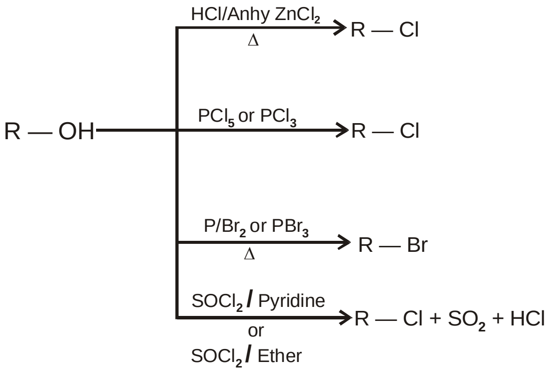
Step 2 - Formation of carbocation



Step 3 - Formation of alkene by elimination of a proton



(i) SN reaction :



(ii) Dehydration of alcohol :

Dehydration of alcohol to give alkene.

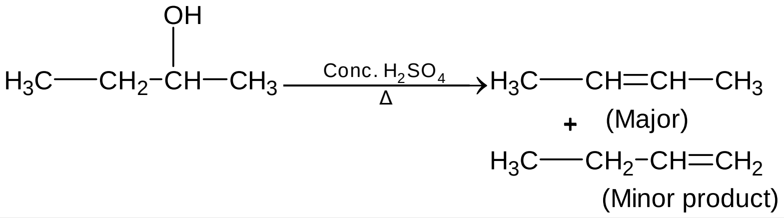
(a) Dehydrating agents are

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

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

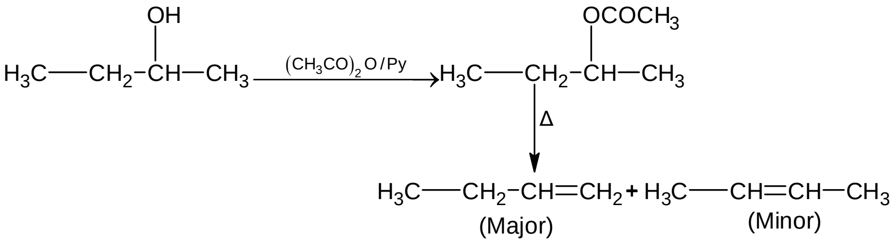
3° > 2° > 1°

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



$$H_3C-CH_2-\overset{OH}{CH}-CH_3 \xrightarrow[\Delta]{Conc.\ H_2SO_4} H_3C-CH=CH-CH_3\ (\text{Major}) + H_3C-CH_2-CH=CH_2\ (\text{Minor product})$$

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



Mechanism in presence of acidic medium :

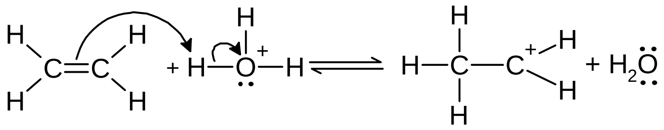
E_1 mechanism : follow saytzeff's rule.

$CH_2{=}CH_2 + H_2O/H^+ \longrightarrow CH_3{-}CH_2{-}OH$

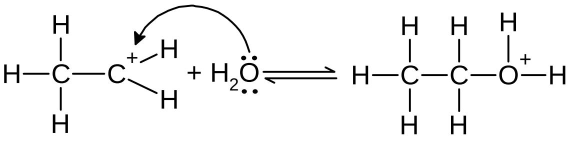
The mechanism of hydration of ethene to form ethanol involves three steps.

Step 1: Protonation of ethene to form carbocation by electrophilic attack of H_3O^+:

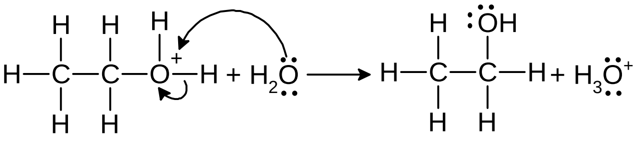
$H_2O + H^+ \longrightarrow H_3O^+$



Step 2: Nucleophilic attack of water on carbocation:



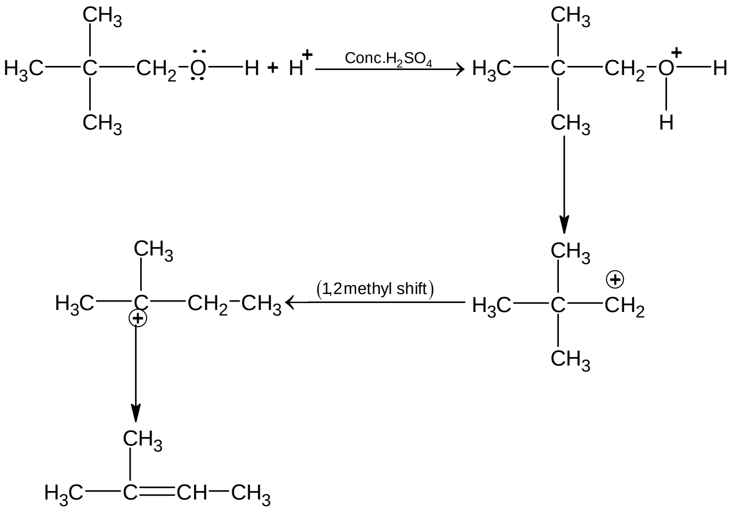
Step 3: Deprotonation to form ethanol:



Solved Example :

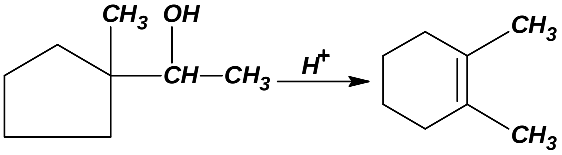
Qus. Write the product with mechanism when neopentyl alcohol reacts with H_3O^+ ?

Ans.

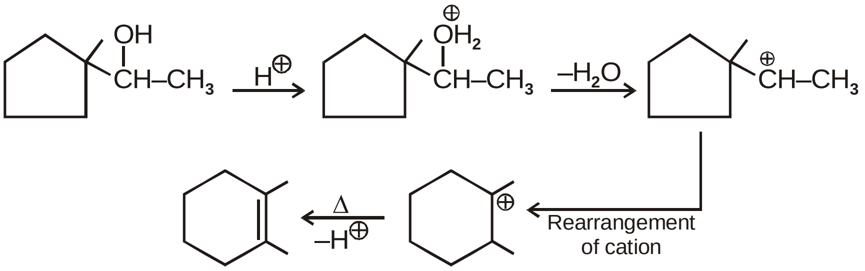


Solved Example :

Qus. Write mechanism

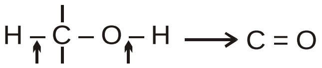


Ans.



(C) Oxidation of alcohol :

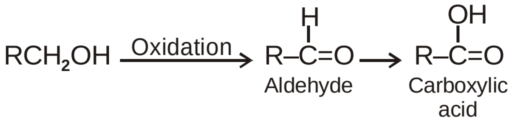
Oxidation of alcohols involves the formation of a carbon-oxygen double bond with cleavage of an O–H and C–H bonds.



$$H-\overset{|}{\underset{|}{C}}-O-H \longrightarrow C=O$$

Bond breaking

Such a cleavage and formation of bonds occur in oxidation reactions. These are also known as **dehydrogenation** reactions as these involve loss of dihydrogen from an alcohol molecule. Depending on the oxidising agent used, a primary alcohol is oxidised to an aldehyde which in turn is oxidised to a carboxylic acid.



$$RCH_2OH \xrightarrow{\text{Oxidation}} \underset{\text{Aldehyde}}{R-\overset{H}{\overset{|}{C}}=O} \longrightarrow \underset{\text{Carboxylic acid}}{R-\overset{OH}{\overset{|}{C}}=O}$$

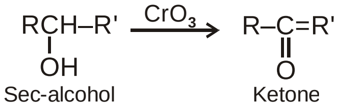
Strong oxidising agents such as acidified potassium permanganate are used for getting carboxylic acids from alcohols directly. CrO_3 in anhydrous medium is used as the oxidising agent for the isolation of aldehydes.

$$RCH_2OH \xrightarrow{CrO_3} RCHO$$

A better reagent for oxidation of primary alcohols to aldehydes in good yield is pyridinium chlorochromate (PCC), a complex of chromium trioxide with pyridine and HCl.

$$CH_3-CH=CH-CH_2OH \xrightarrow{PCC} CH_3-CH=CH-CHO$$

Secondary alcohols are oxidised to ketones by chromic anhydride (CrO_3).

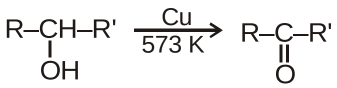


$$\underset{\text{Sec-alcohol}}{R\underset{OH}{\underset{|}{C}}H-R'} \xrightarrow{CrO_3} \underset{\text{Ketone}}{R-\underset{O}{\underset{\|}{C}}=R'}$$

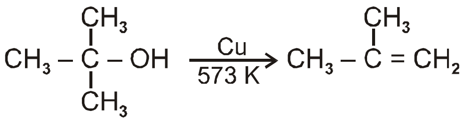
Tertiary alcohols do not undergo oxidation reaction. Under strong reaction conditions such as strong oxidising agents ($KMnO_4$) and elevated temperatures, cleavage of various C – C bonds takes place and a mixture of carboxylic acids containing lesser number of carbon atoms is formed.

When the vapours of a primary or a secondary alcohol are passed over heated copper at 573 K, dehydrogenation takes place and an aldehyde or a ketone is formed respectively while tertiary alcohols undergo dehydration (removal of H_2O because H-atom is not present on carbon for dehydrogenation).

$$RCH_2OH \xrightarrow[573\text{ K}]{Cu} RCHO$$



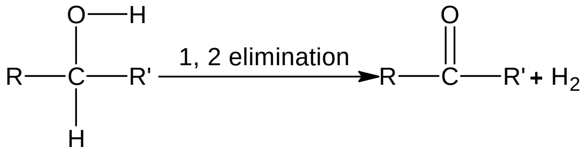
$$R{-}\underset{OH}{CH}{-}R' \xrightarrow[573\text{ K}]{Cu} R{-}\underset{O}{\overset{}{C}}{-}R'$$



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH \xrightarrow[573\text{ K}]{Cu} CH_3-\overset{CH_3}{C}=CH_2$$

Biological oxidation of methanol and ethanol in the body produces the corresponding aldehyde followed by the acid. At times the alcoholics, by mistake, drink ethanol, mixed with methanol also called denatured alcohol. In the body, methanol is oxidised first to methanal and then to methanoic acid, which may cause blindness and death. A methanol poisoned patient is treated by giving intravenous infusions of diluted ethanol. The enzyme responsible for oxidation of aldehyde (HCHO) to acid is swamped allowing time for kidneys to excrete methanol.

Oxidation of alcohol is dehydrogenation reaction which is 1, 2 – elimination reaction.



$$R-\overset{O-H}{\underset{H}{C}}-R' \xrightarrow{1,\ 2\text{ elimination}} R-\overset{O}{\overset{\|}{C}}-R' + H_2$$

So oxidation of alcohol $\propto$ numbers of α - hydrogen atom.

(a) With mild oxidising agents :

Like

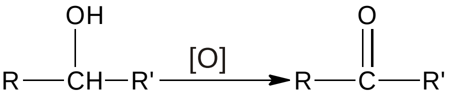
(i) X_2

(ii) Fenton reagent $[FeSO_4/H_2O_2]$

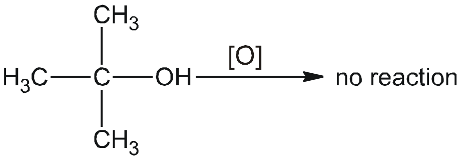
(iii) Jones reagent / CH_3COCH_3 $[CrO_3/\text{dil. } H_2SO_4]$

(iv) $K_2Cr_2O_7/H^+$ cold

$$R-CH_2OH \xrightarrow{[O]} RCHO$$



$$R-\overset{OH}{CH}-R' \xrightarrow{[O]} R-\overset{O}{\overset{\|}{C}}-R'$$



$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-OH \xrightarrow{[O]} \text{no reaction}$$

Note :

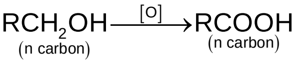
PCC (Pyridinium chloro chromate) is a selective reagent which converts 1° alc to aldehyde.

(b) With strong oxidising agent

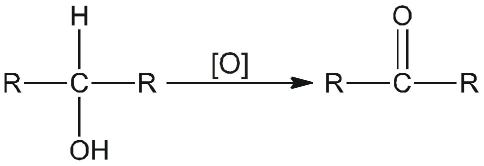
Oxidising agents are

(i) $KMnO_4/OH^-/\Delta$ (ii) $KMnO_4/H^+/\Delta$

(iii) $K_2Cr_2O_7/H^+/\Delta$ (iv) Conc. HNO_3/Δ



$$\underset{(n\text{ carbon})}{RCH_2OH} \xrightarrow{[O]} \underset{(n\text{ carbon})}{RCOOH}$$



$$R-\overset{H}{\underset{OH}{C}}-R \xrightarrow{[O]} R-\overset{O}{\overset{\|}{C}}-R$$

(D) Dehydrogenation with Cu/573K or Ag/573K

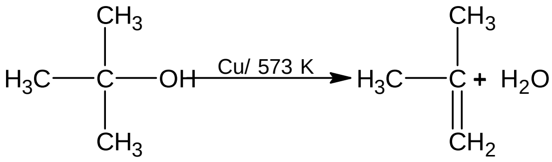
(a) 1° alcohol $\longrightarrow$ aldehyde

$$R-CH_2OH \xrightarrow{Cu/573K} RCHO$$

(b) 2° alcohol $\longrightarrow$ ketone

$$R-CHOH-R \xrightarrow{Cu/573K} R-CO-R$$

(c) 3° alc $\longrightarrow$ undergo dehydration to form alkene.



$$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-OH \xrightarrow{Cu/\ 573\ K} H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_2}{\|}}{C}} + H_2O$$

Reduction :

$$R-O-H \xrightarrow{HI/Red\ P} R-H$$

Solved Example :

Qus. **(i)** Out of these compound which gives iodoform test.

(a) $CH_3-CH_2-CHOHCH_3$

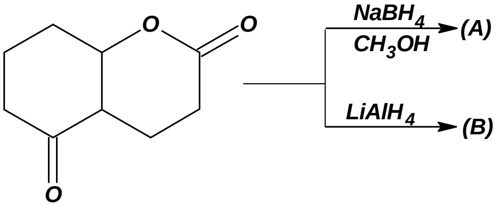
(b) $PhCH_2CHOHCH_3$

(c) $PhCHOHCH_3$

(d) CH_3CH_2OH

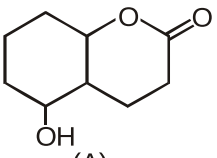
(e) $CH_3COCH_2-COOC_2H_5$

(ii)

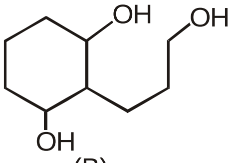


Ans. **(i) a, c, d and e**

(ii)

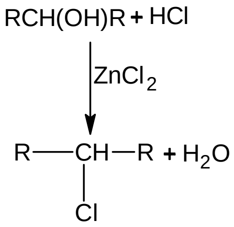
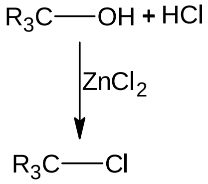
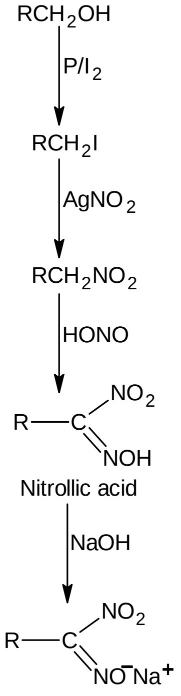
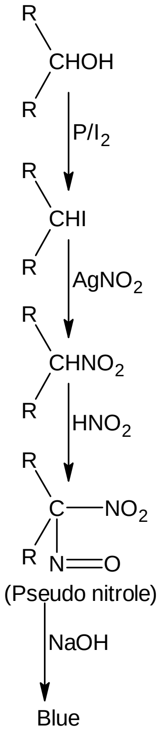
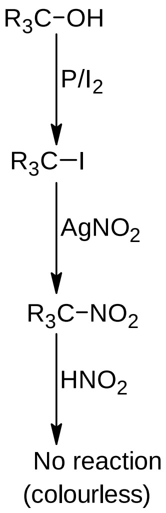


(A)



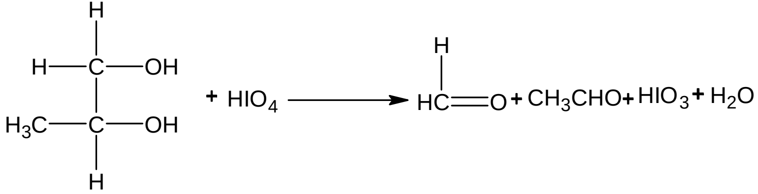
(B)

Distinguishing 1°, 2°, 3° alcohol

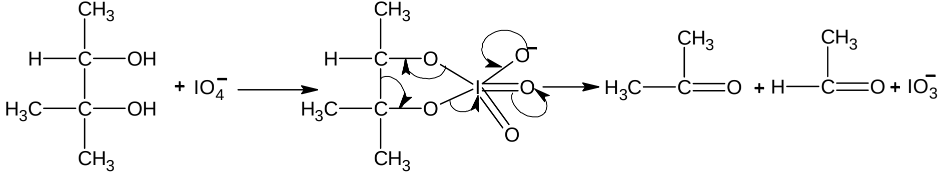
Test	1° alc	2° alc	3° alc
(I) Lucas test [$ZnCl_2$ + HCl] 5 – 10 min.	No reaction at room temperature	White turbidity after 	White turbidity instantaneously 
(II) Victor Meyer test (P/I_2, $AgNO_2$, HNO_2, NaOH)	Red colour	Blue colour	Colourless
	 Sodium nitrolate (red)		

PERIODATE OXIDATION :

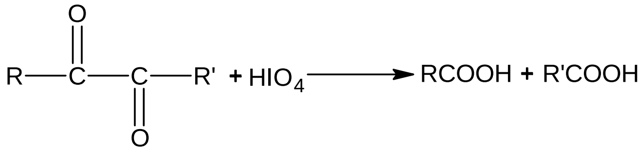
Compounds that have hydroxyl group on adjacent atoms undergo oxidation cleavage when they are treated with aq. Periodic acid (HIO_4). The reaction breaks carbon carbon bonds and produced carbonyl compounds (aldehyde, ketones or acids)



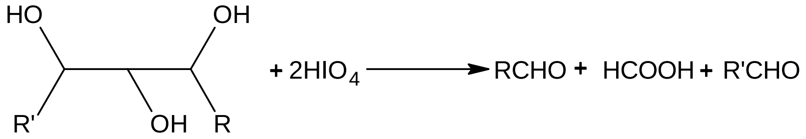
It takes place through a cyclic intermediate.



Other examples



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle O}{\|}}{C}-R' + HIO_4 \longrightarrow RCOOH + R'COOH$$



This oxidation is useful in determination of structure.

Ex. $R-CHOH \vdots CHOH-R' + HIO_4 \xrightarrow{-HIO_3} R-CHO + R'CHO$

Ex. $R_2C(OH) \vdots CHOH-R' + HIO_4 \xrightarrow{-HIO_3} R_2CO + R'CHO$

Ex. $R-CHOH \vdots CHOH \vdots CHOH-R' + 2HIO_4 \xrightarrow{-2HIO_3} RCHO + HCOOH + R'CHO$

Ex. $R'-CO \vdots CHOH-R + HIO_4 \xrightarrow{-HIO_3} R'-COOH + R-CHO$

Ex. $CH_2OH \vdots CO-CH_2OH + HIO_4 \xrightarrow{-HIO_3} HCHO + HOOC-CH_2OH$

Ex. $R'-CO \vdots CHOH-R + HIO_4 \xrightarrow{-HIO_3} R'-COOH + R-CHO$

Ex. $CH_2OH \vdots CO-CH_2OH + HIO_4 \xrightarrow{-HIO_3} HCHO + HOOC-CH_2OH$

Ex. $R-CO \vdots CO-R' + HIO_4 \xrightarrow{-HIO_3} R-COOH + R'-COOH$

Ex. $RCHNH_2 \vdots CHOH-R' + HIO_4 \xrightarrow{-HIO_3} RCHO + R'CHO + NH_3$

Ex. $R-CHOH-CH_2-CHOH-R \xrightarrow{HIO_4}$ No reaction

Ex. $CH_2OH \vdots CHOH \vdots CHOH + CHOH-CHO + 4HIO_4 \longrightarrow 4HCOOH + HCHO + 4HIO_3$

Aldopentose

Ex. $CH_2OH \vdots CHOH \vdots CHOH \vdots CHOH \vdots CHOH \vdots CHO + 5HIO_3 \longrightarrow 5HCOOH + HCHO + 5HIO_3$

Aldopentose

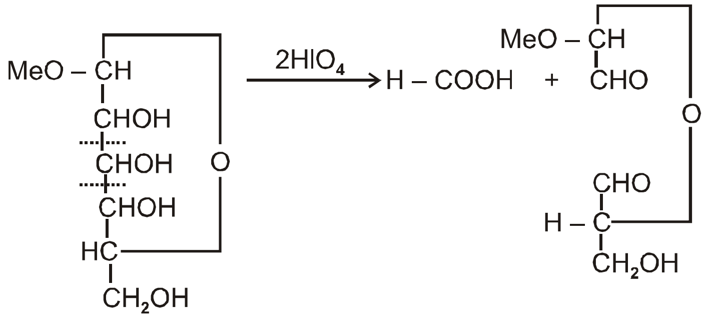
Ex. $CH_2OH \vdots CHOH \vdots CHOH \vdots CHOH \vdots CHOH \vdots CHO \xrightarrow{5HIO_4} 5HCOOH + HCHO + 5HIO_3$

Aldopentose (glucose)

Ex. $CH_2OH \vdots CHOH \vdots CHOH \vdots CHOH \vdots CO-CH_2OH \xrightarrow{4HIO_4} HCHO + 3HCOOH + HOOC-CH_2OH + 4HIO_3$

Ketohexose (fructose)

Ex.



Methyl glucoside (I) Acetaldialdehyde

Solved Example :

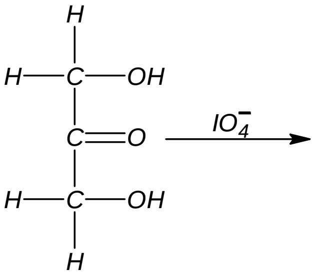
Qus. Write the products of the reaction of t-butyl alcohol with PBr_3, conc. H_2SO_4, CH_3COCl, Na, CH_3MgBr, $Na_2Cr_2O_7/H_2SO_4$.

Ans. $(CH_3)_3CBr$, $(CH_3)_3C=CH_2$; $(CH_3)_3COCOCH_3$, $(CH_3)_3CO^-Na^+$, CH_4, no reaction.

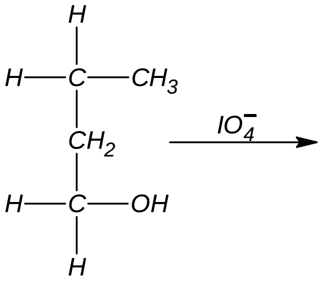
Solved Example :

Qus. Write products

(a)



(b)



Ans. (a) $2HCHO + CO_2$

(b) No reaction (as it is not a vicinal diol)

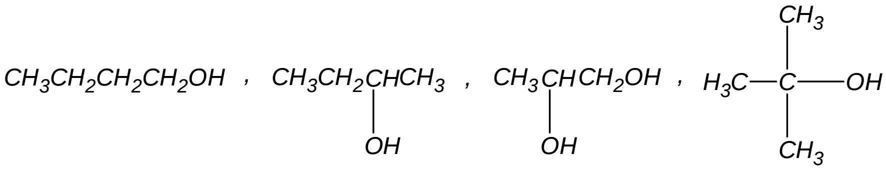
Migratory preference of the group

Migration depends on the stability of Transition state.

In general migration of C_6H_5 > alkyl

Solved Example :

Qus. Which of the following alcohols would react fastest with Lucas reagent?



$CH_3CH_2CH_2CH_2OH$, $CH_3CH_2\underset{OH}{CH}CH_3$, $CH_3\underset{OH}{CH}CH_2OH$, $H_3C-\underset{CH_3}{\overset{CH_3}{C}}-OH$

Ans. $(CH_3)_3COH$, it being a tertiary alcohol.

Industrial source of alcohols :

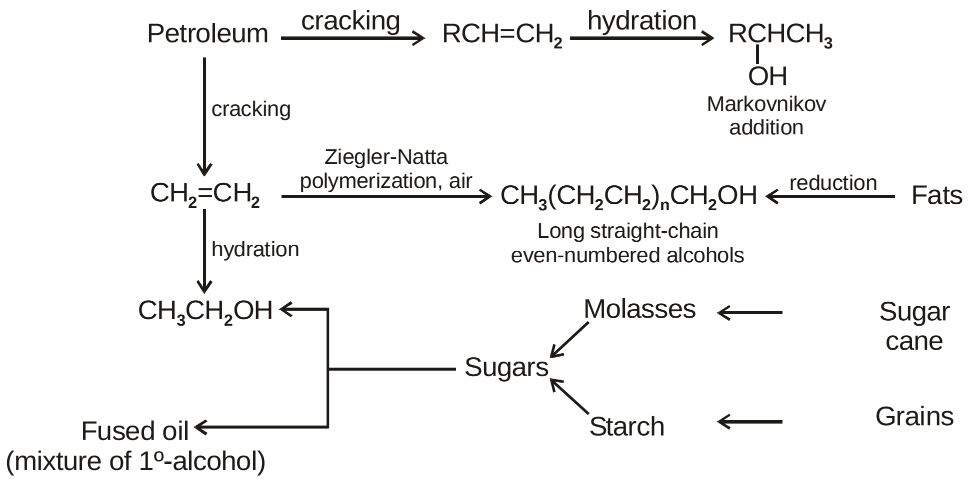


Figure : Industrial sources of alcohols.

Methanol and ethanol are among the two commercially important alcohols :

1. **Methanol :**

Methanol, CH_3OH, also known as 'wood spirit', was produced by destructive distillation of wood. Today, most of the methanol is produced by catalytic hydrogenation of carbon monoxide at high pressure and temperature and in the presence of ZnO – Cr_2O_3 catalyst.

$$CO + 2H_2 \xrightarrow[\substack{200-300\text{ atm} \\ 573-673\text{ K}}]{ZnO-Cr_2O_3} CH_3OH$$

Methanol is a colourless liquid and boils at 337 K. It is highly poisonous in nature. Ingestion of even small quantities of methanol can cause blindness and large quantities causes even death. Methanol is used as a solvent in paints, varnishes and chiefly for making formaldehyde.

2. **Ethanol :**

Ethanol, C_2H_5OH, is obtained commercially by fermentation, the oldest method is from sugars. The sugar in molasses, sugarcane or fruits such as grapes is converted to glucose and fructose, (both of which have the formula $C_6H_{12}O_6$), in the presence of an enzyme, invertase. Glucose and fructose undergo fermentation in the presence of another enzyme, zymase, which is found in yeast.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

In wine making, grapes are the source of sugars and yeast. As grapes ripen, the quantity of sugar increases and yeast grows on the outer skin. When grapes are crushed, sugar and the enzyme come in contact and fermentation starts. Fermentation takes place in anaerobic conditions i.e. in absence of air. Carbon dioxide is released during fermentation.

The action of zymase is inhibited once the percentage of alcohol formed exceeds 14 percent. If air gets into fermentation mixture, the oxygen of air oxidises ethanol to ethanoic acid which in turn destroys the taste of alcoholic drinks.

Ethanol is a colourless liquid with boiling point 351 K. It is used as a solvent in paint industry and in the preparation of a number of carbon compounds. The commercial alcohol is made unfit for drinking by mixing in it some copper sulphate (to give it a colour) and pyridine (a foul smelling liquid). It is known as **denaturation** of alcohol.

Nowadays, large quantities of ethanol are obtained by hydration of ethene.

$$CH_2 = CH_2 \xrightarrow{H^{\oplus}/H_2O} CH_3 - CH_2 - OH$$

ETHER

Diethyl ether has been used widely as an inhalation anaesthetic. But due to its slow effect and an unpleasant recovery period, it has been replaced, as an anaesthetic, by other compounds. However it safest anaesthetic agent.

- $R — O — R'$ Alkoxy alkane (Di alkyl ether)
- $R = R'$ Symmetrical ether.

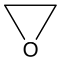
$R \neq R'$ Unsymmetrical or mixed ether.

'O' is to be counted with least number of C atom for IUPAC naming

$CH_3 — O — C_2H_5$ Methoxy ethane (ethymethyl ether)

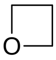
$CH_3 — O — C_6H_5$ Methoxy benzene (Anisol)

There are various types of cyclic ethers also.



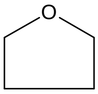
Oxirane

(Epoxide)



Oxetane

(Oxacyclo butane)



Tetra hydro furan

(Oxacyclo pentane)

PREPARATION OF ETHERS :

(i) From 1° alcohol

(a) With H_2SO_4

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

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

(b) With diazomethane

$$R-O-H \xrightarrow[(C_2H_5O)_3\,Al]{CH_2N_2} R-O-CH_3+N_2$$

Williamson's synthesis

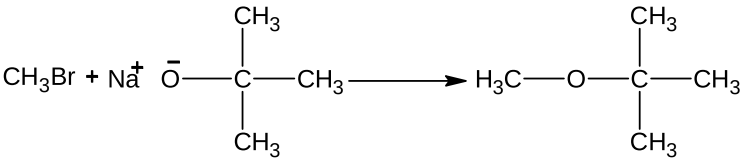
S_N2 reaction of a sodium alkoxide with alkyl halide, alkyl sulphonate or alkyl sulphate is known as Williamson synthesis of ethers.

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

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

- 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.

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



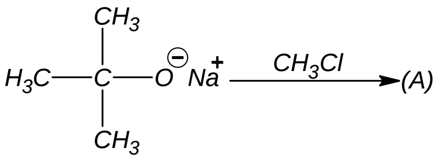
$$CH_3Br + Na^+\ \bar{O}—C(CH_3)_2—CH_3 \longrightarrow H_3C—O—C(CH_3)_2—CH_3$$

Sodium ter. butoxide ter. butyl methyl ether

Solved Example :

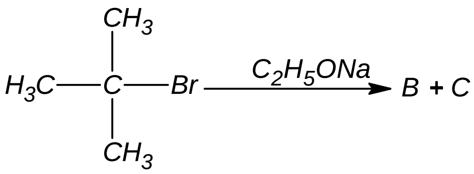
Qus. Write the product

(i)



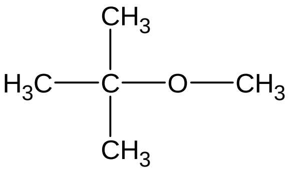
$(CH_3)_3C-\overset{\ominus}{O}\overset{+}{Na} \xrightarrow{CH_3Cl} (A)$

(ii)



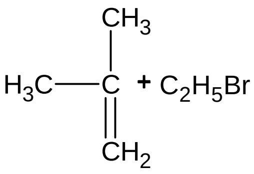
$(CH_3)_3C-Br \xrightarrow{C_2H_5ONa} B + C$

Ans. (i)



$H_3C-C(CH_3)_2-O-CH_3$

(ii)

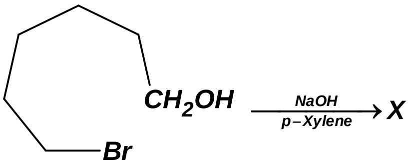


$H_3C-C(CH_3)=CH_2 + C_2H_5Br$

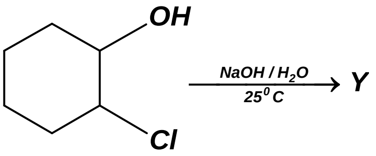
Solved Example :

Qus. Find product

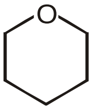
(i)



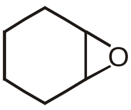
(ii)



Ans. X =

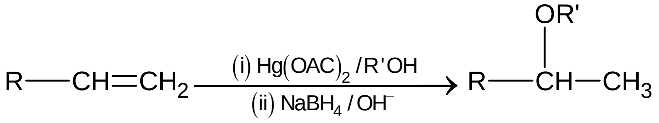


Y =

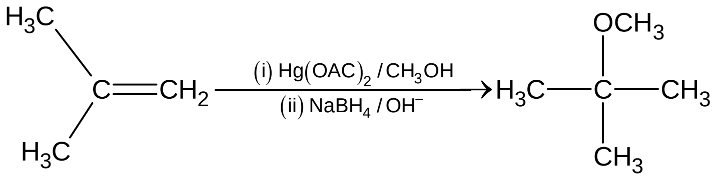


(3) From Alkane by Alkoxy mercuration demercuration (AOMDM) :

(a)

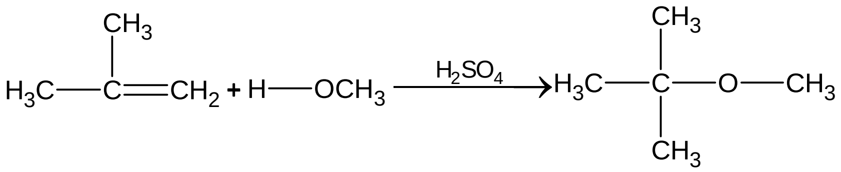


$R-CH=CH_2 \xrightarrow[\text{(ii) } NaBH_4/OH^-]{\text{(i) } Hg(OAC)_2/R'OH} R-CH(OR')-CH_3$



$(H_3C)_2C=CH_2 \xrightarrow[\text{(ii) } NaBH_4/OH^-]{\text{(i) } Hg(OAC)_2/CH_3OH} H_3C-C(OCH_3)(CH_3)-CH_3$

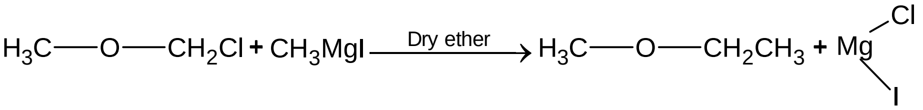
(b)



$H_3C-C(CH_3)=CH_2 + H-OCH_3 \xrightarrow{H_2SO_4} H_3C-C(CH_3)_2-O-CH_3$

(4) From Grignard reagent :

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



$H_3C-O-CH_2Cl + CH_3MgI \xrightarrow{\text{Dry ether}} H_3C-O-CH_2CH_3 + Mg(Cl)(I)$

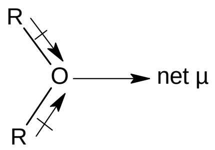
(5) From Alkyl halide

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

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 :

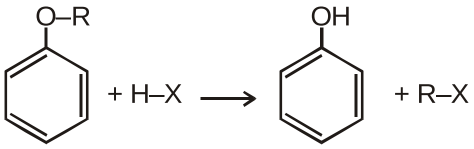
Cleavage of C–O bond in ethers :

Ethers are the least reactive of the functional groups. The cleavage of C–O bond in ethers takes place under drastic conditions with excess of hydrogen halides. The reaction of dialky ether gives two alkyl halide molecules.

$R–O–R + HX \longrightarrow RX + R–OH$

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

Alkyl aryl ethers are cleaved at the alkyl-oxygen bond due to the more stable aryl-oxygen bond. The reaction yields phenol and alkyl halide.



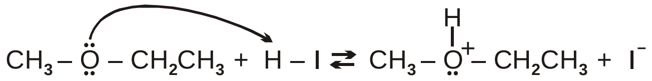
Ethers with two different alkyl groups are also cleaved in the same manner.

$R–O–R' + HX \longrightarrow R–X + R'–OH$

The order of reactivity of hydrogen halides is as follows : HI > HBr > HCl. The cleavage of ethers takes place with concentrated HI or HBr at high temperature.

The reaction of an ether with concentrated HI starts with protonation of ether molecule.

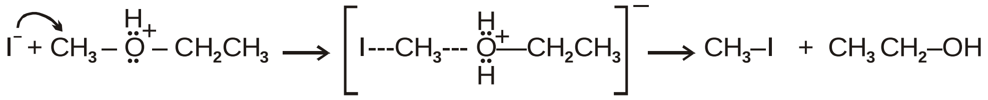
Step-I :



$$CH_3–\ddot{O}–CH_2CH_3 + H–I \rightleftarrows CH_3–\overset{H}{\overset{|}{\ddot{O}^+}}–CH_2CH_3 + I^-$$

The reaction takes place with HBr or HI because these reagents are sufficiently acidic.

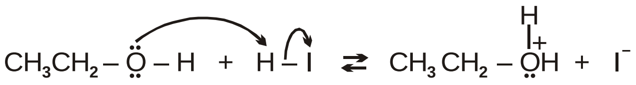
Step-II : Iodide is a good nucleophile. It attacks the least substituted carbon of the oxonium ion formed in step 1 and displaces an alcohol molecule by SN_2 mechanism. Thus, in the cleavage of mixed ethers with two different alkyl groups, the alcohol and alkyl iodide formed, depend on the nature of alkyl groups. When primary or secondary alkyl groups are present, it is the lower alkyl group that forms alkyl iodide (SN_2 reaction).



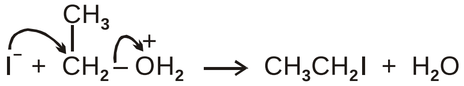
$$I^- + CH_3-\overset{H}{\overset{+}{\ddot{\underset{..}{O}}}}-CH_2CH_3 \longrightarrow \left[I\text{---}CH_3\text{---}\overset{H}{\underset{H}{\overset{+}{O}}}-CH_2CH_3\right]^- \longrightarrow CH_3-I + CH_3CH_2-OH$$

When HI is in excess and the reaction is carried out at high temperature, ethanol reacts with another molecule of HI and is converted to ethyl iodide.

Step-III :

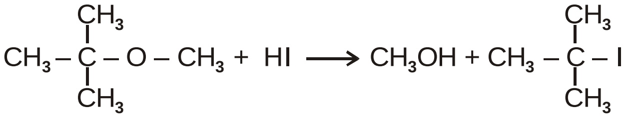


$$CH_3CH_2-\ddot{\underset{..}{O}}-H + H-I \rightleftharpoons CH_3CH_2-\overset{H}{\overset{|+}{\underset{..}{O}}}H + I^-$$



$$I^- + \overset{CH_3}{\overset{|}{CH_2}}-\overset{+}{O}H_2 \longrightarrow CH_3CH_2I + H_2O$$

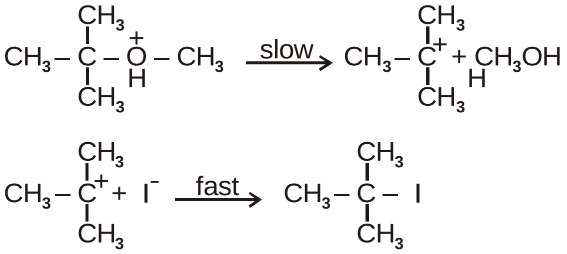
However, when one of the alkyl group is a tertiary group, the halide formed is a tertiary halide.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-CH_3 + HI \longrightarrow CH_3OH + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-I$$

It is because in step 2 of the reaction, the departure of leaving group ($HO-CH_3$) creates a more stable carbocation [$(CH_3)_3C^+$], and the reaction follows SN_1 mechanism.

In case of anisole, methylphenyl oxonium ion, $C_6H_5-\underset{H}{\overset{+}{O}}-CH_3$ is formed by protonation of ether. The bond between $O-CH_3$ is weaker than the bond between $O-C_6H_5$ because the carbon of phenyl group is sp^2 hybridised and there is a partial double bond character.



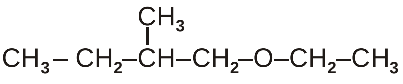
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{H}{\overset{+}{O}}-CH_3 \xrightarrow{slow} CH_3-\underset{CH_3}{\overset{CH_3}{C^+}} + \underset{H}{CH_3OH}$$

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

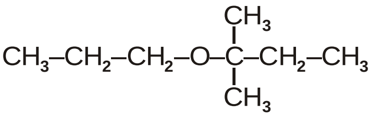
Therefore the attack by I^- ion breaks $O-CH_3$ bond to form CH_3I. Phenols do not react further to give halides because the sp^2 hybridised carbon of phenol cannot undergo nucleophilic substitution reaction needed for conversion to the halide.

Solved Example :

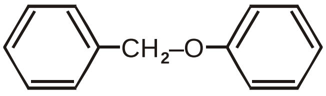
Qus. Give the major products that are formed by heating each of the following ethers with HI.

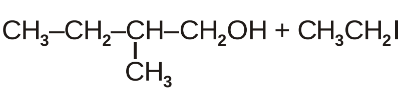
(i) 

$CH_3-CH_2-\overset{CH_3}{\overset{|}{C}H}-CH_2-O-CH_2-CH_3$

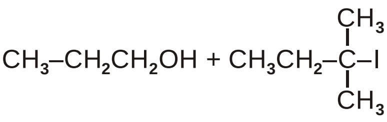
(ii) 

$CH_3-CH_2-CH_2-O-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-CH_3$

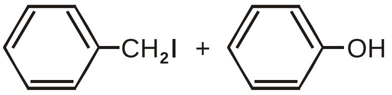
(iii) 

Ans. (i) 

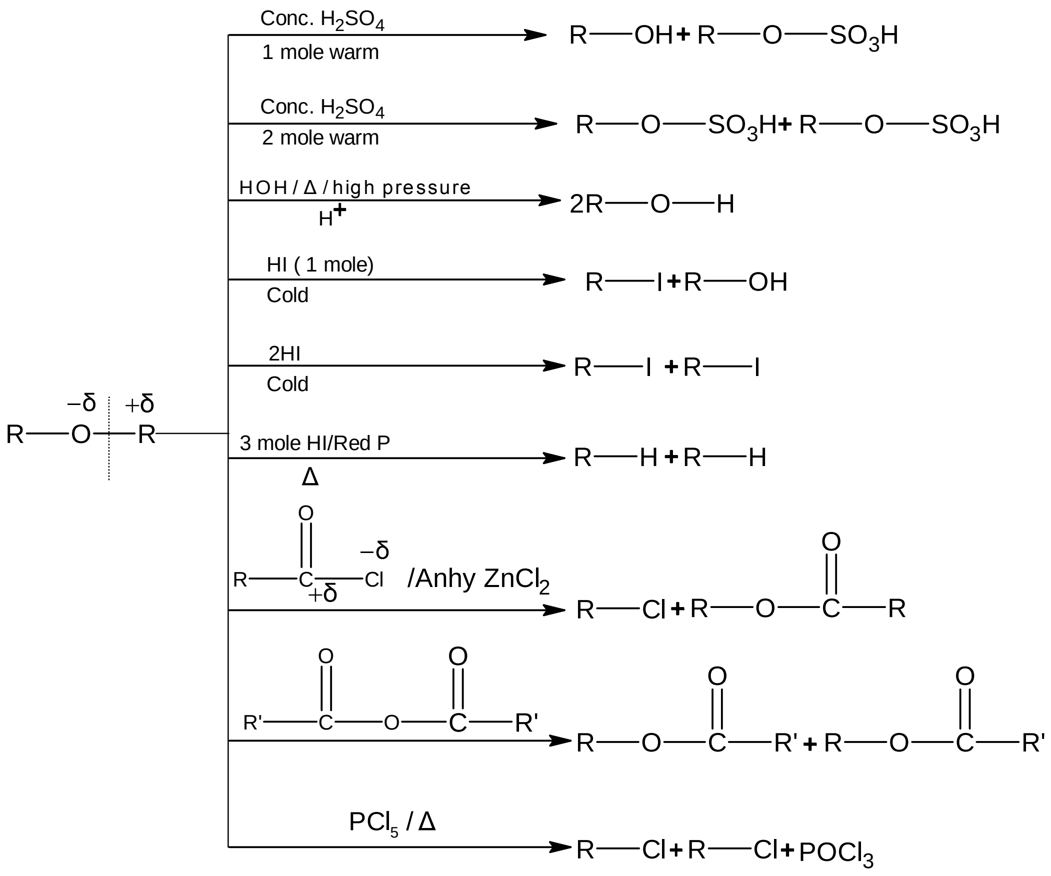
$CH_3-CH_2-\underset{CH_3}{\underset{|}{C}H}-CH_2OH + CH_3CH_2I$

(ii) 

$CH_3-CH_2CH_2OH + CH_3CH_2-\underset{CH_3}{\overset{CH_3}{C}}-I$

(iii) 

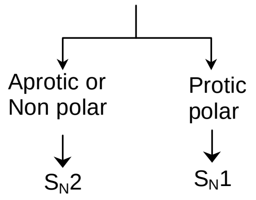
1. Nucleophilic substitution reactions



Note :

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

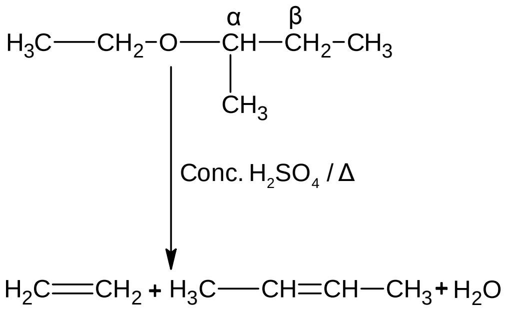
Combinations	**Mechanism follows**
1°R + 2°R	Less sterically hindered ⇒ S_N2
2°R + 3°R	More sterically hindered ⇒ S_N1
1°R + 3°R	Nature of mechanism decoded by nature of solvent.



Methyl cation is stabler than phenyl cations

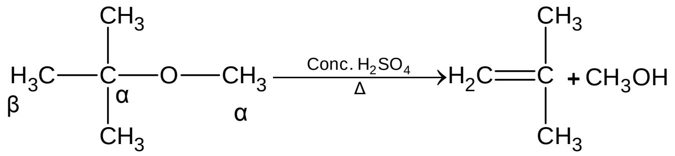
(B) Dehydration with H_2SO_4/Δ and Anhy Al_2O_3/Δ

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



$$H_3C-CH_2-O-\overset{\alpha}{C}H(CH_3)-\overset{\beta}{C}H_2-CH_3 \xrightarrow{\text{Conc. } H_2SO_4 / \Delta} H_2C=CH_2 + H_3C-CH=CH-CH_3 + H_2O$$

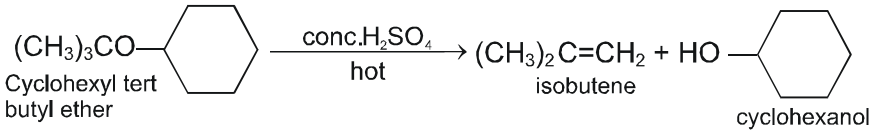
(ii) When only alkyl group has β - hydrogen.



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

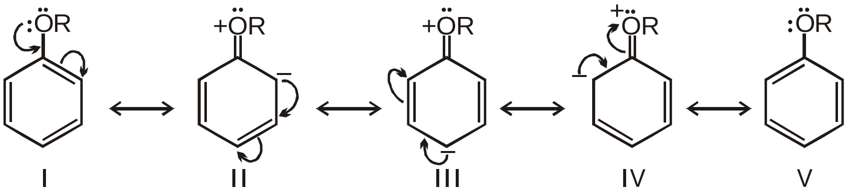
- Hot conc. H_2SO_4 react with secondary and tertiary ethers to give a mixture of alcohols and alkenes.

$$(CH_3)_3CO—CH_3 \xrightarrow[\text{hot}]{\text{Conc.}H_2SO_4} (CH_3)_2C = CH_2 + CH_3OH$$

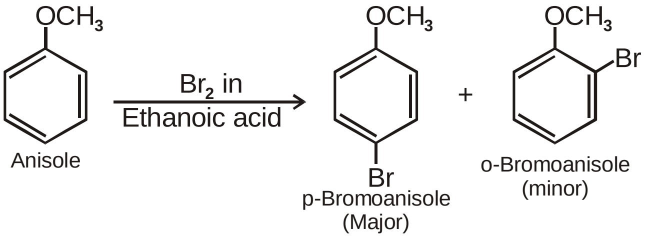


(C) Electrophilic substitution Reactions (S_E) of ether :

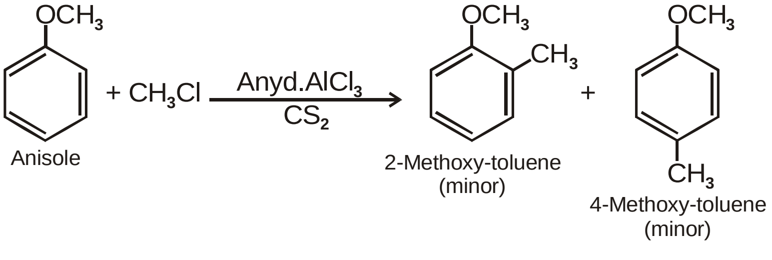
The alkoxy group (–OR) is ortho, para directing and activates the aromatic ring towards electrophilic substitution in the same way as in phenol.

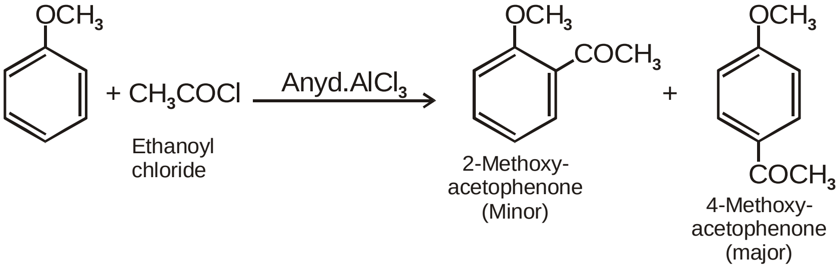


(i) Halogenation : Phenylalkyl ethers undergo usual halogenation in the benzene ring, e.g., anisole undergoes bromination with bromine in ethanoic acid even in the absence of iron (III) bromide catalyst. It is due to the activation of benzene ring by the methoxy group. Para isomer is obtained in 90° yield.

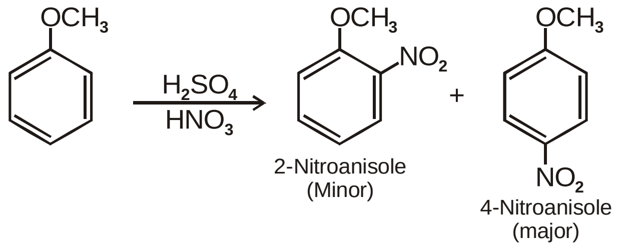


(ii) **Friedel-Crafts reaction :** Anisole undergoes Friedel-Crafts reaction, i.e., the alkyl and acyl groups are introduced at ortho and para positions by reaction with alkyl halide and acyl halide in the presence of anhydrous aluminium chloride (a Lewis acid) as catalyst.





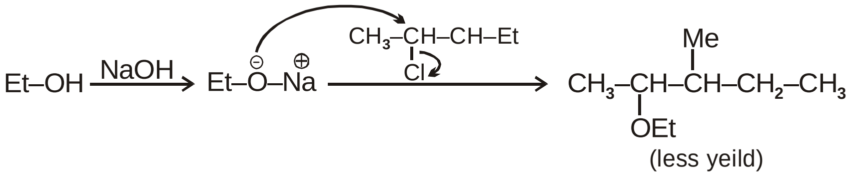
(iii) **Nitration :** Anisole reacts with a mixture of concentrated sulphuric and nitric acids to yield a mixture of ortho and para nitroanisole.



Solved Example :

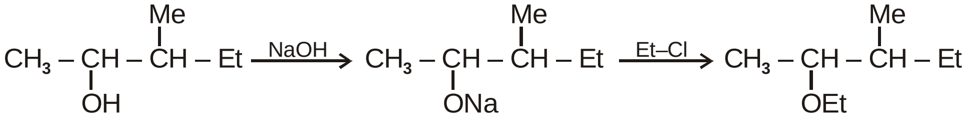
Qus. Write the reactions of Williamson synthesis of 2-ethoxy-3-methylpentane starting from ethanol and 3-methylpentan-2-ol.

Ans.


$$\text{Et–OH} \xrightarrow{\text{NaOH}} \text{Et–}\overset{\ominus}{\text{O}}\text{–}\overset{\oplus}{\text{Na}} \xrightarrow{CH_3\text{–}\underset{Cl}{CH}\text{–}CH\text{–}Et} CH_3\text{–}\underset{OEt}{CH}\text{–}\overset{Me}{CH}\text{–}CH_2\text{–}CH_3$$

(less yeild)

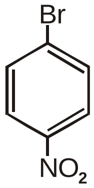
or


$$CH_3 - \underset{OH}{CH} - \overset{Me}{CH} - Et \xrightarrow{\text{NaOH}} CH_3 - \underset{ONa}{CH} - \overset{Me}{CH} - Et \xrightarrow{\text{Et–Cl}} CH_3 - \underset{OEt}{CH} - \overset{Me}{CH} - Et$$

Solved Example :

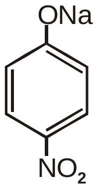
Qus. Which of the following is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene and why ?

(i)



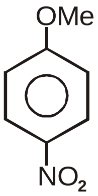
\+ CH_3ONa

(ii)



\+ CH_3Br

Ans. (i) No reaction due to double bond charecter of C – Br bond (ii)

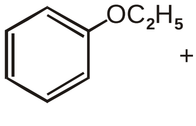


Solved Example :

Qus. Predict the products of the following reactions :

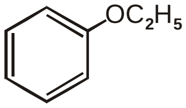
(i) $CH_3 - CH_2 - CH_2 - O - CH_3 + HBr \longrightarrow$

(ii)



\+ HBr $\longrightarrow$

(iii)



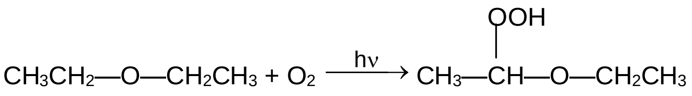
$\xrightarrow[\text{Conc.}HNO_3]{\text{Conc.}H_2SO_4}$

(iv) $(CH_3)_3C - OC_2H_5 \xrightarrow{HI}$

Solved Example :

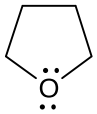
Qus. Explain why sometimes explosion occurs while distilling ethers.

Ans. It is due to formation of peroxide


$$CH_3CH_2\text{—}O\text{—}CH_2CH_3 + O_2 \xrightarrow{h\nu} CH_3\text{—}\overset{OOH}{CH}\text{—}O\text{—}CH_2CH_3$$

Solved Example :

Qus. The basicity of the ethers towards BF_3 has the following order, explain.

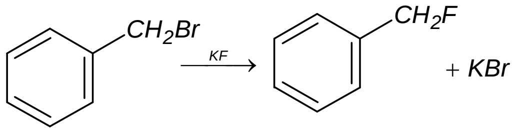


$> (CH_3)_2\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}} > (C_2H_5)_2\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}} > [(CH_3)_2CH]_2\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}$

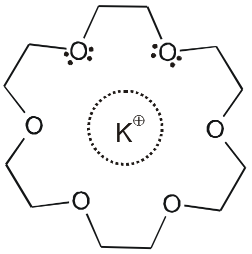
Ans. There are steric effects in the Lewis acid-Lewis base complex formation between BF_3 and the respective ethers.

Solved Example :

Qus. What are crown ethers? How can the following reaction be made to proceed?



Ans. Crown ethers are large ring polyethers and are basically cyclic oligomers of oxirane which may have annulated rings. They are designated according to ring size and the number of complexing oxygen atoms, thus 18-crown – 6 denotes an 18-membered ring with 6-oxygens. The molecule is shaped like a "dough-nut", and has a hole in the middle.

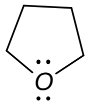


These are phase transfer catalysts. This is a unique example of "host-guest relationship". The crown ether is the host, the cation is the guest. The cavity is well suited to fit a K^+ or Rb^+ which is held as a complex. Interaction between host and guest in all these complexes are mainly through electrostatic forces and hydrogen bonds.

The reaction can be made to process by using catalytic amount of crown ether, 18-crown-6.

Solved Example :

Qus. Explain why



is much more soluble than furan in water.

Ans. THF is more soluble than furan. In THF, in contrast to furan the electron pairs are available for H-bonding with water which makes it more soluble in water.

Solved Example :

Qus. What chemical methods can be used to distinguish between the following pairs of compounds?

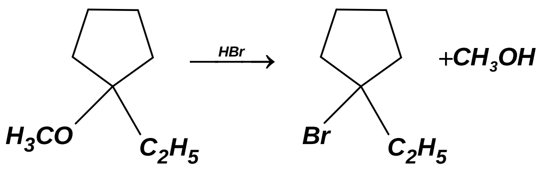
(a) Ethoxy ethanol and methyl isopropyl ether.

(b) Butyl iodide and butyl ethyl ether.

(c) Ethyl propyl ether and ethyl allyl ether.

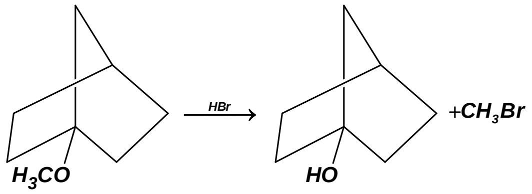
Solved Example :

Qus. Ether A cleaves much faster than B with conc. HI. Explain.



(A)

;

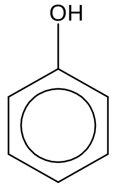


(B)

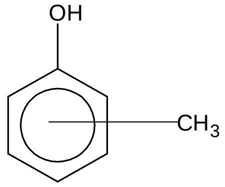
Ans. Cation is not stable on bridge head carbon on B. (Violation of Bredicts rule).

PHENOL

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



Phenol or carbolic acid



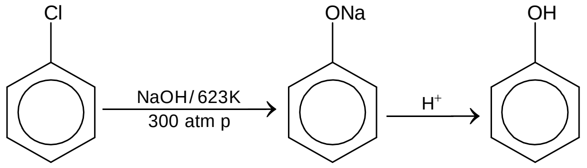
(o , p , m)
Cresol

Preparation :

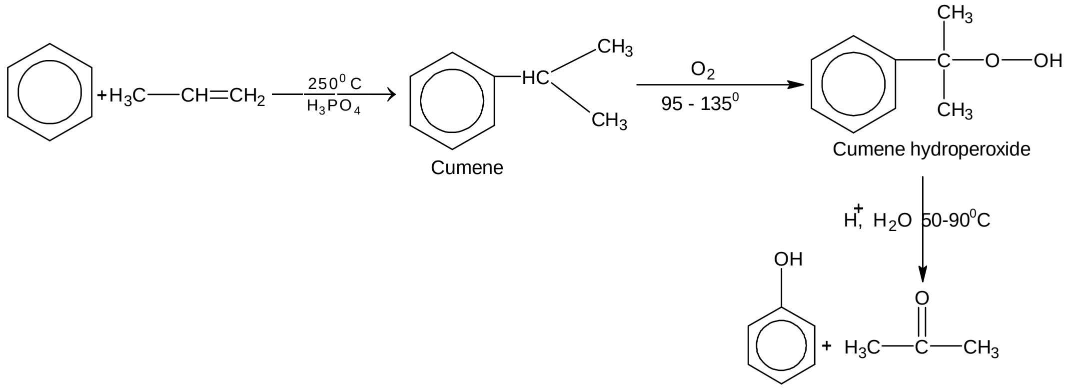
Industrial Method :

(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.

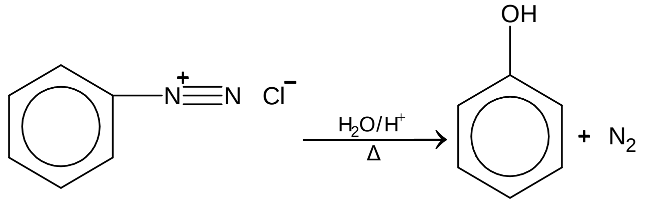


(iii) **From benzene sulphonic acid**

It is fused with NaOH gives sodium salt of phenol.

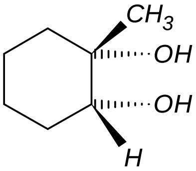
$$C_6H_5SO_3H \xrightarrow[\text{Fusion}]{\text{NaOH}} C_6H_5SO_3Na \longrightarrow C_6H_5ONa \xrightarrow{H_2O^+/H^+} C_6H_5OH$$

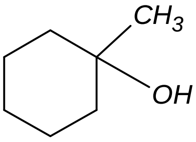
(iv) **From benzene diazonium chloride :**
This gives Ar SN1 reaction with H_2O to form phenol.

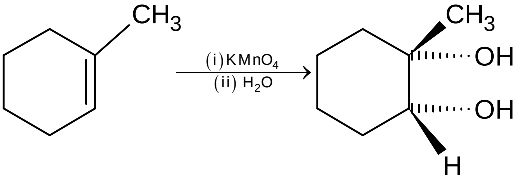


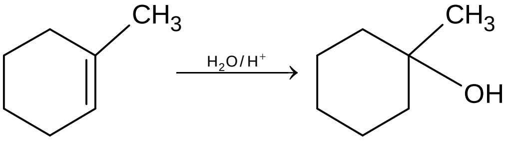
Solved Example :

Qus. Starting from 1-methyl cyclohexene, prepare the following:

(a)


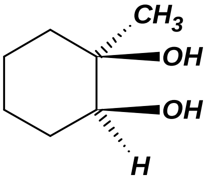
(b)


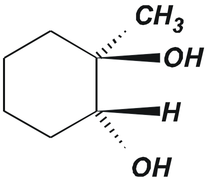
Ans. (a)


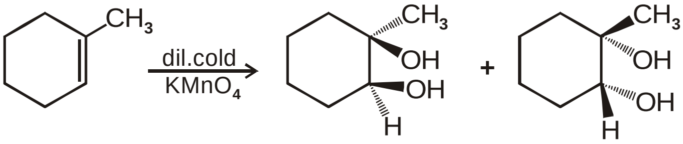
(b)


Solved Example :

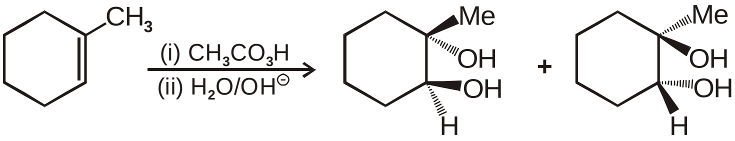
Qus. Starting from 1-methyl cyclohexene, prepare the following :

(a)


(b)


Ans. (a)


(Syn addition)

(b)


(Antiaddition)

PHYSICAL PROPERTIES :

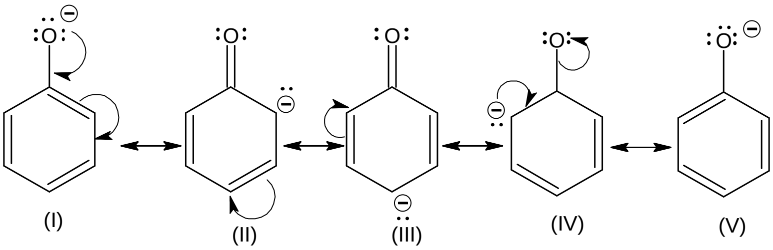
Phenol is needle shaped solid, soon liquefies due to high hygroscopic nature. It is less soluble in water, but readily soluble in organic solvents.

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.

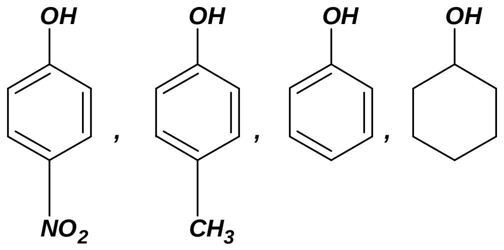
For example: (cresol are less acidic then phenol)

PHYSICAL PROPERTIES :

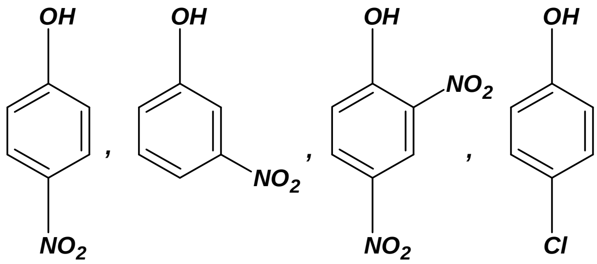
Solved Example :

Qus. Arrange each group of compounds in order of decreasing acidity:

(a)



(b)

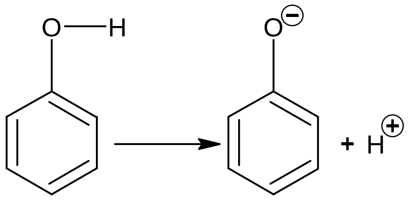


CHEMICAL REACTIONS :

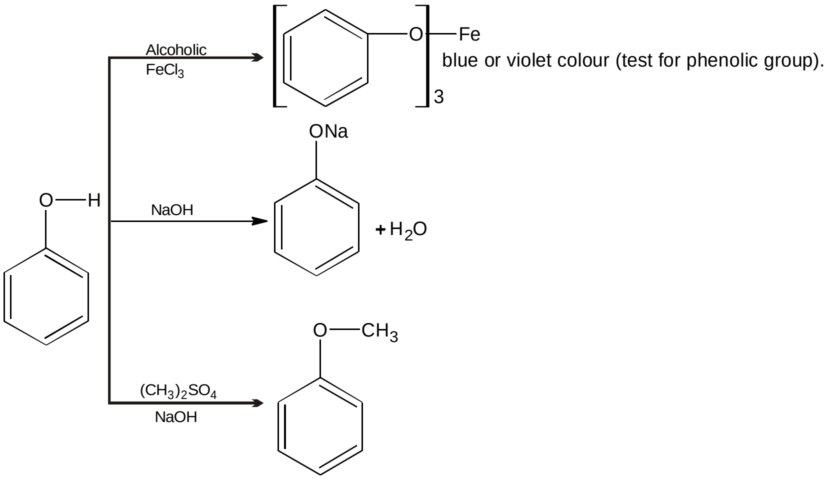
(A) Reaction due to breaking of O – H bond

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

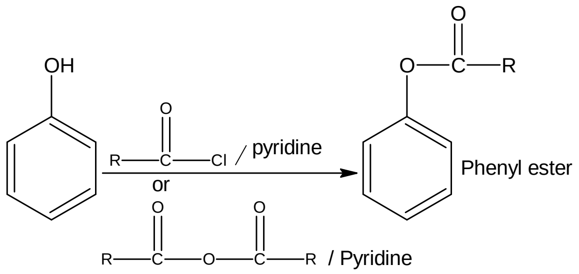
$$R-O-H \longrightarrow R-\overset{\ominus}{O} + H^{\oplus}$$



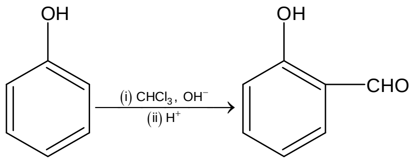
Reactions of phenol due to breaking of —O — H bond are given below:



Acylation (By SN_2 mechanism) :

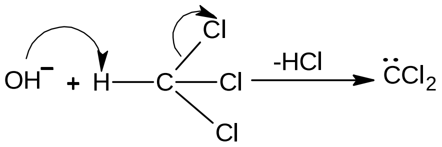


Reimer Tieman reaction :

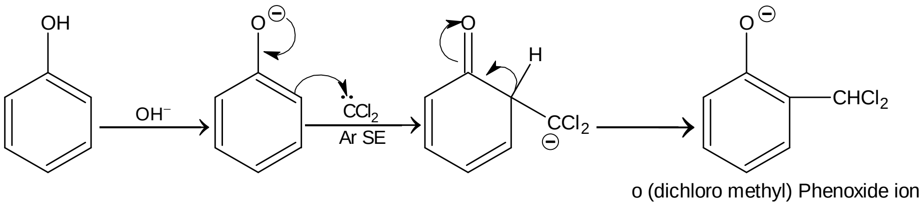


The electrophile is the dichloro carbene, $:CCl_2$, formation of carbene is an example of α - elimination.

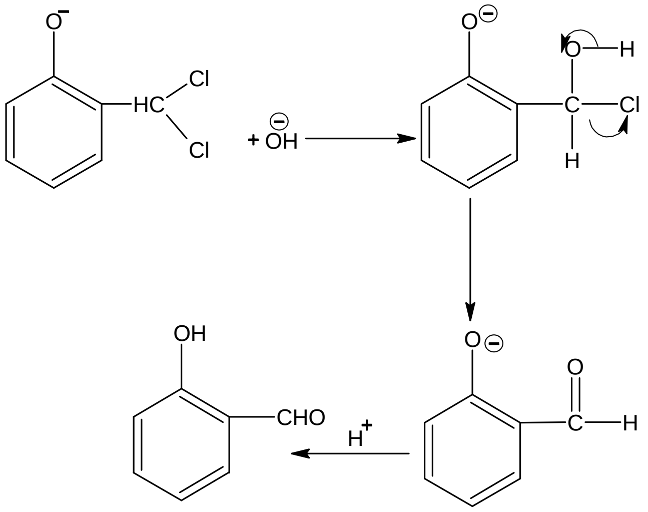
(i)



(ii)

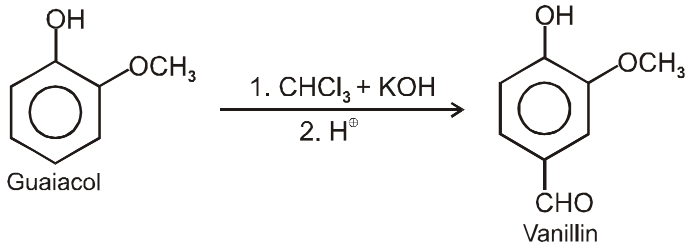


(iii)

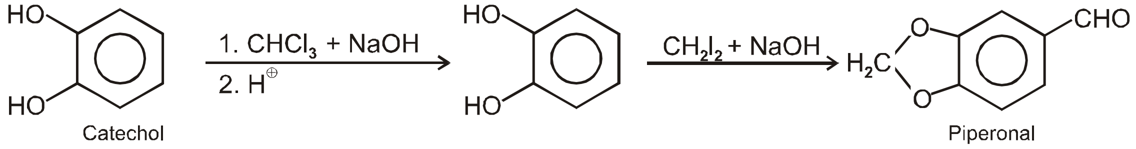


APPLICATION OF REIMER TIEMAN :

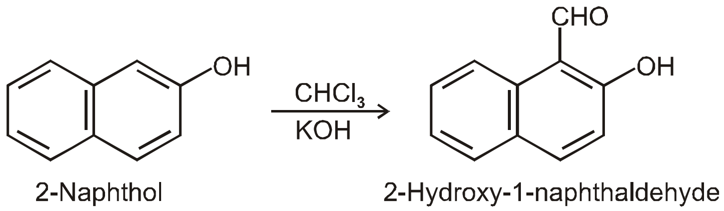
1. Preparation of vanillin



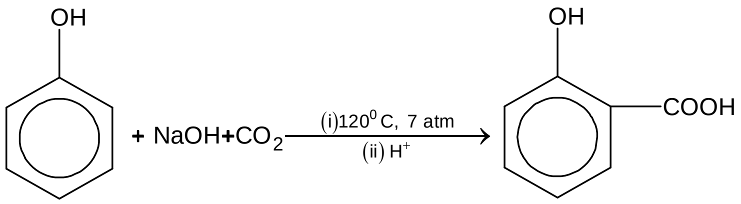
2. Preparation of piperonal



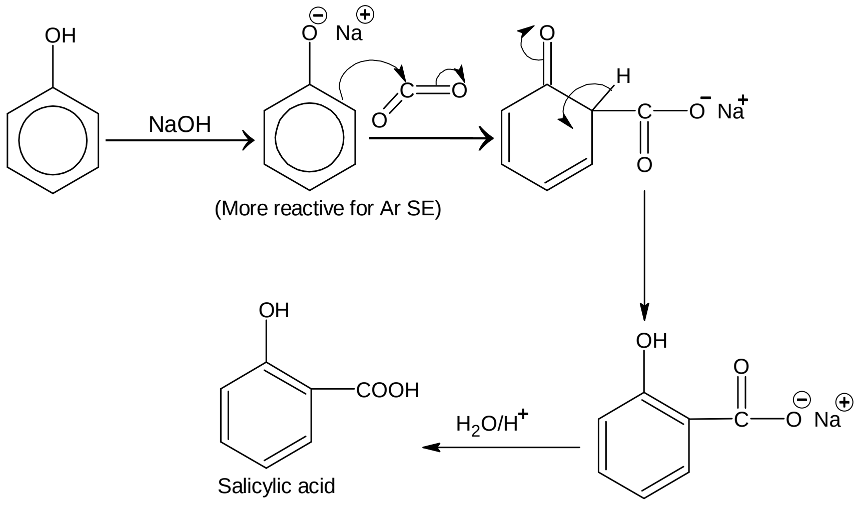
3. Formylation of naphthol



2. Kolbe's reaction



Mechanism :

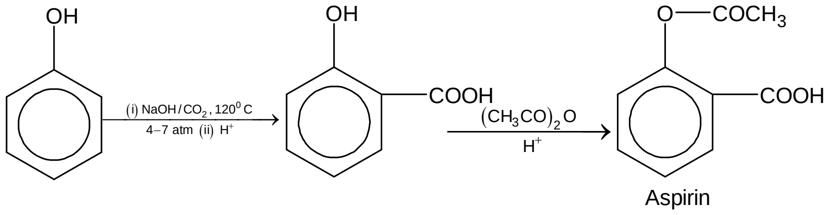


Solved Example :

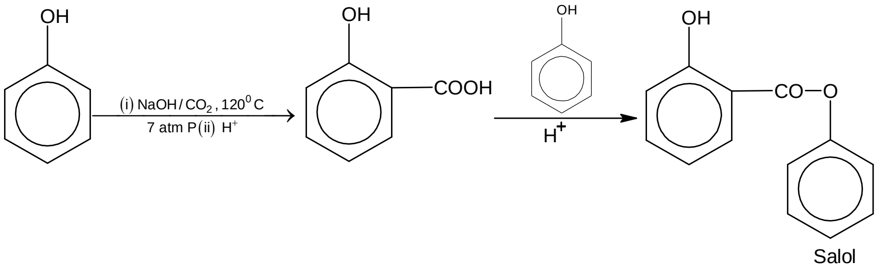
Qus. How will you convert ?

(i) phenol to aspirin
(ii) phenol to salol.
(iii) phenol to oil of winter green.
(iv) phenol to benzoic acid.

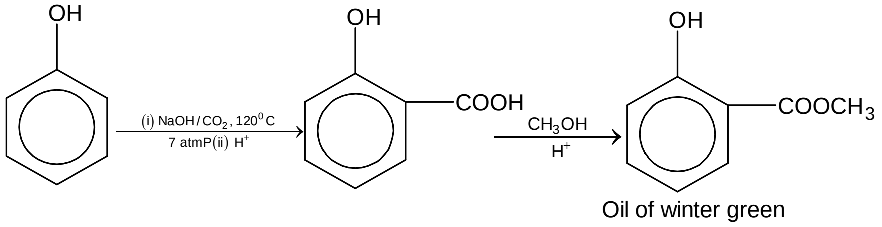
Ans. (i)



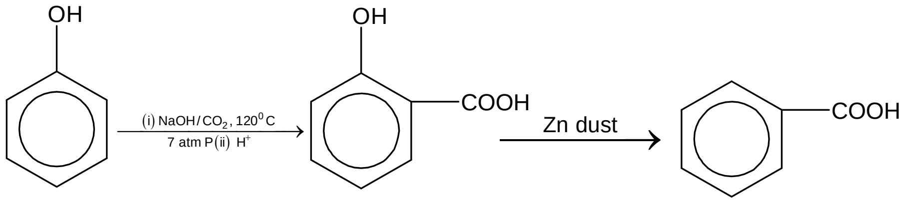
(ii)



(iii)

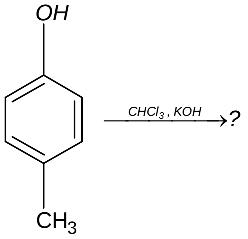


(iv)

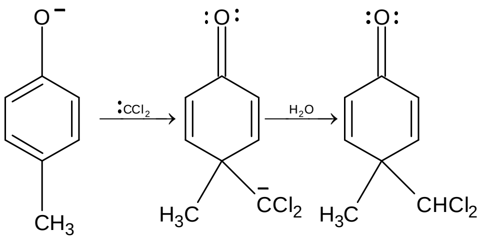


Solved Example :

Qus. What product would you expect in the following reaction? Explain.



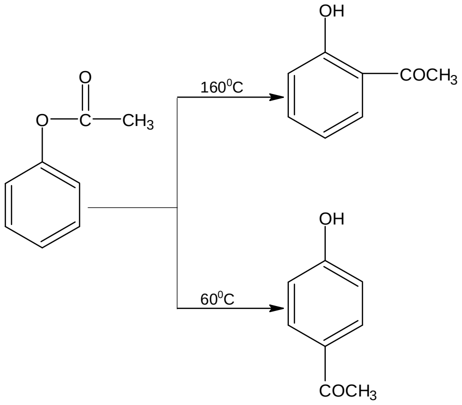
Ans. $CHCl_3 + aq.\ KOH \longrightarrow :CCl_2$



It is an 'abnormal' product formed in the Reimer-Tiemann reaction when the dienone cannot tautomerize to regenerate a phenolic system.

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:

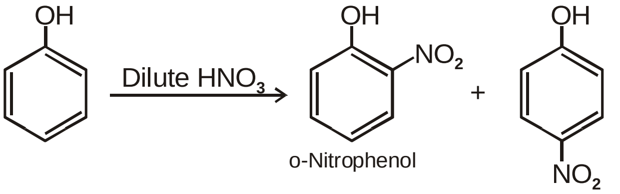
(i) —OH group is present on sp^2 hybridised carbon. This makes C — O bond stronger.

(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) Electrophilic aromatic substitution (S_E) in Phenol : It is strong activating group.

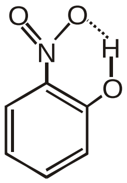
(i) Nitration : With dilute nitric acid at low temperature (298K), phenol yields a mixture of ortho and para nitrophenols.



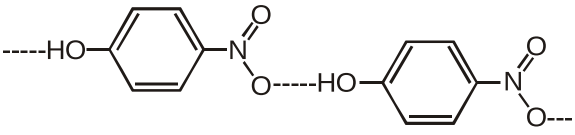
o-Nitrophenol

p-Nitrophenol

The ortho and para isomers can be separated by steam distillation. o-Nitrophenol is steam volatile due to intramolecular hydrogen bonding while p-nitriphenol is less volatile due to intermolecular hydrogen bonding which causes the association of molecules.

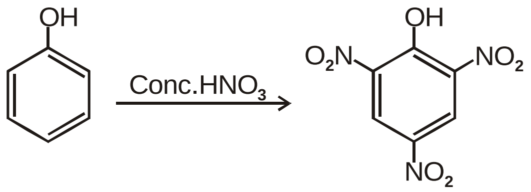


o-Nitrophenol
(Intramolecular
H-bonding)



p-Nitrophenol
(Intramolecular
H-bonding)

With concentrated nitric acid, phenol is converted to 2,4,6-trinitrophenol. The product is commonly known as picric acid. The yield of the reaction product is poor (due to deactivating $-NO_2$ groups toward electrophilic towards electrophillic aromatic substitution).



2,4,6-Trinitrophenol
(Picric acid)

2,4,6-Trinitrophenol is a strong acid due to the presence of three electron withdrawing –NO$_2$ groups which facilitate the release of hydrogen ion.

Nowadays picric acid is prepared by treating phenol first with concentrated sulphuric acid which converts it to phenol-2,4-disulphonic acid, and then with concentrated nitric acid to get 2,4,6-trinitrophenol. Can you write the equations of the reactions involved ?

Solved Example :

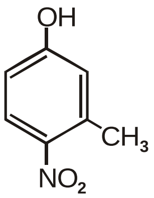
Qus. Write the structures of the major products expected from the following reactions :

(a) Mononitration of 3-methylphenol (b) Dinitration of 3-methylphenol

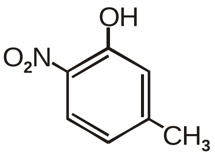
(c) Mononitration of phenyl methanoate.

Ans. The combined influence of –OH and –CH$_3$ groups determine the position of the incoming group.

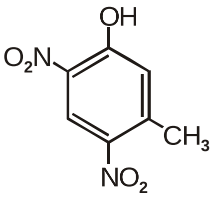
(a)



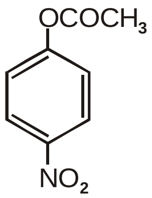
and

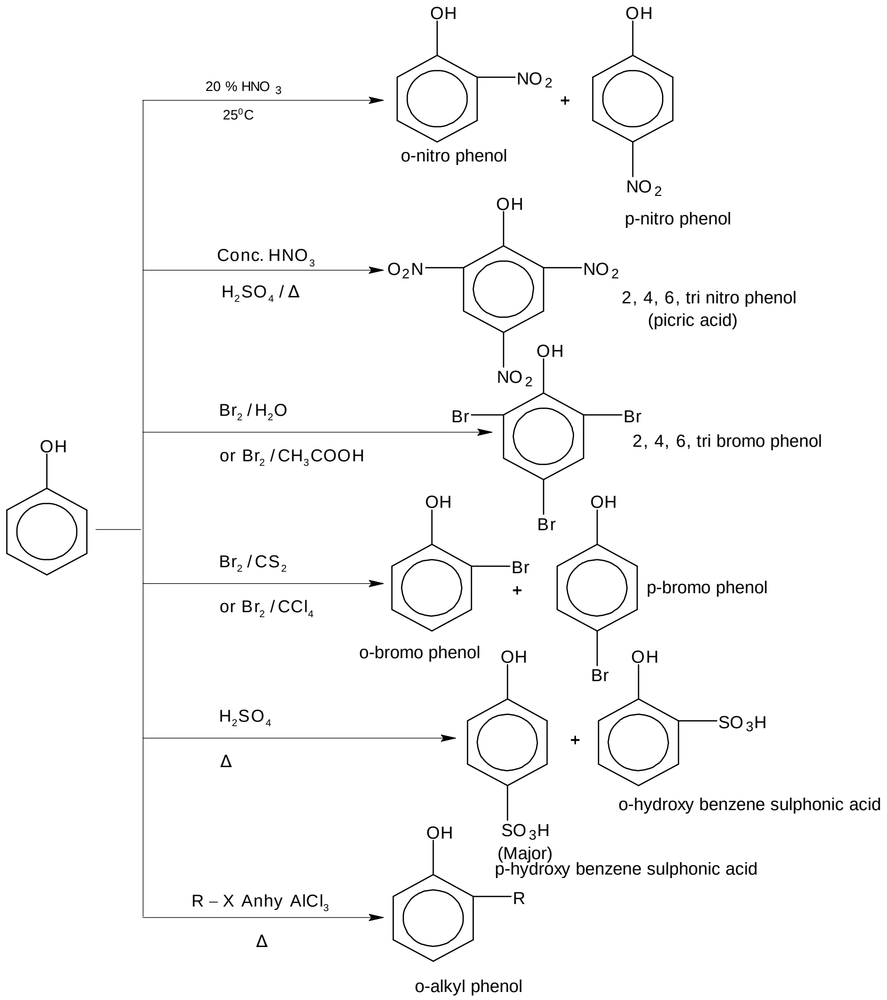


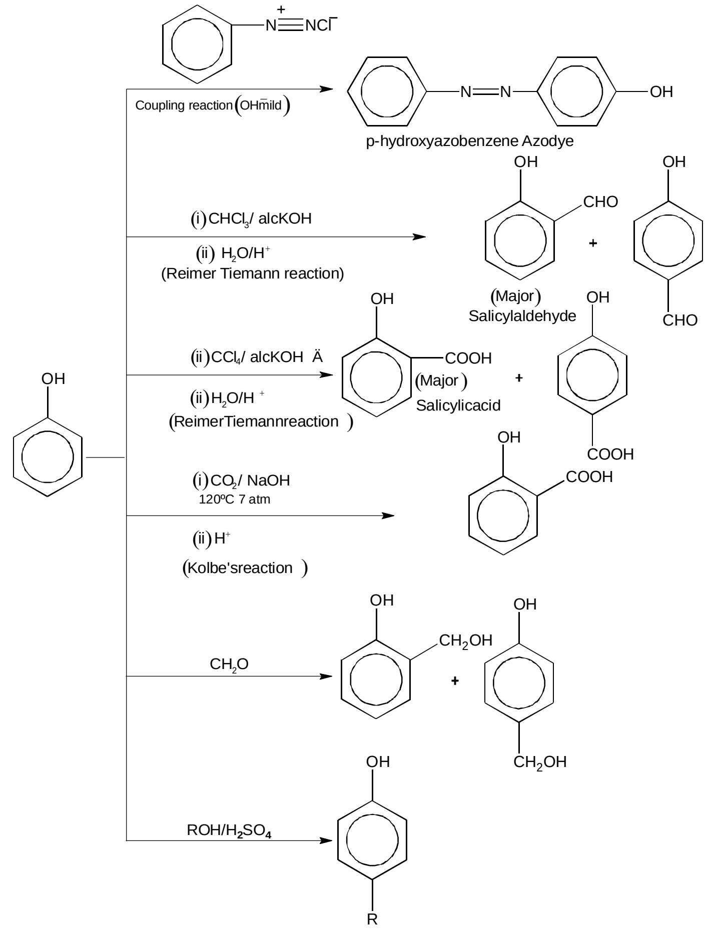
(b)



(c)

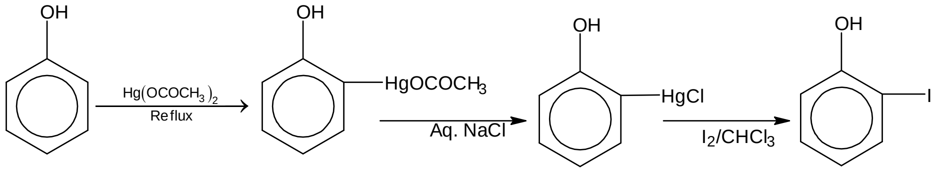






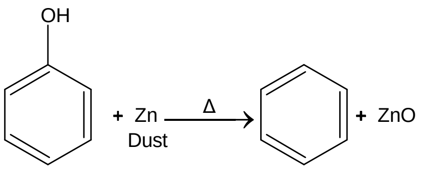
MERCURATION :

Mercuric acetate cation. $[HgOAC]^+$ is a weak electrophile which substitutes in ortho and para position of phenol. Usually donating product is O–acetoxy mercuriphenol. The mercuric compound can be converted to iodophenol.



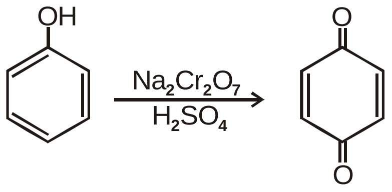
MISCELLANEOUS REACTION :

(i) Reaction with Zn dust :



(ii) Oxidation :

Oxidation of phenol with chromic acid produces a conjugated diketone known as benzoquinone. In the presence of air, phenols are slowly oxidised to dark coloured mixtures containing quinones.

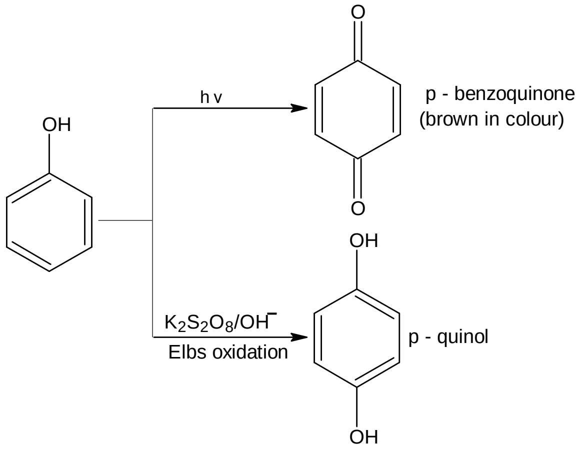


benzoquinone

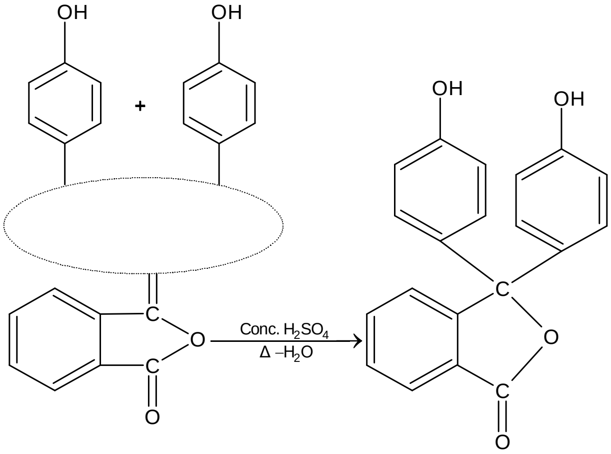
Solved Example :

Qus. Give structures of the products you would expect when each of the following alcohol reacts with (a) HCl – $ZnCl_2$ (b) HBr and (c) $SOCl_2$.

(i) Butan-1-ol (ii) 2-Methylbutan-2-ol



(iii) Condensation with phthalic anhydride



Penolphthalein

(Acid base indicator)

Solved Example :

Qus. Discuss the product formed in the bromination of p-phenol sulfonic acid.

Mechanism of some important reactions

Solved Example :

Qus. How would you distinguish between the following pairs?

(a) Phenol and cyclohexanol

(b) Ethyl alcohol and methyl alcohol

Ans. (a) Phenol gives coloration with $FeCl_3$ solution

(b) Ethyl alcohol responds to the iodoform test

Solved Example :

Qus. How would you distinguish between the following pairs?

(a) 2-Pentanol and 3-pentanol

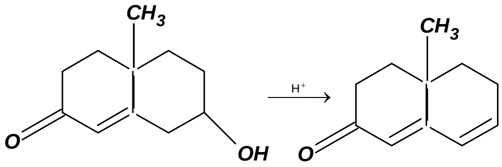
(b) 1-Propanol and phenol

Solved Example :

Qus. Offer explanation for the following observations:

(a) Why is phenol unstable in the keto-form?

(b) The following dehydration is extremely facile:



(c) Why does thionyl chloride provide alkyl chlorides of high purity?

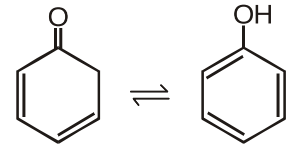
(d) 2-Methyl -2- pentanol dehydrates faster than 2 – methyl – 1 – pentanol.

(e) Phenol is acidic but ethyl alcohol is neutral.

(f) Ethanol responds to Iodoform test but tert- butanol does not.

(g) A tertiary alcohol reacts faster than a primary alcohol in the Lucas test.

Ans. (a)



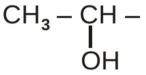
Non-aromatic Aromatic (more stable)

(b) Resonance stablished product

(c) By product (SO_2) is gasseous in nature.

(d) Due to formation of more stable carbocation.

(e) Due to resonance stabilised conjugate base (Anion)

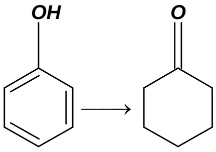
(f)  $CH_3-\underset{\mathrm{OH}}{\underset{|}{C}}H-$ must be present in alcohol for iodoform test

(g) Due to more stable carbocation

Solved Example :

Qus. How will you effect the following conversion?

(a)

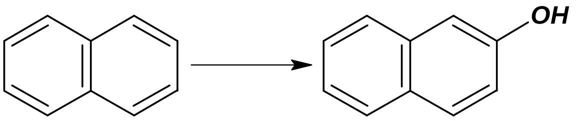


(b) $C_2H_5OH \longrightarrow CH_3CH_2CH_2OH$

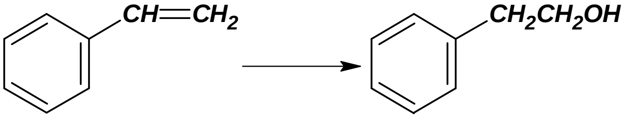
Solved Example :

Qus. How will you effect the following conversion?

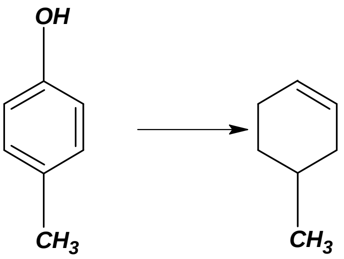
(a)



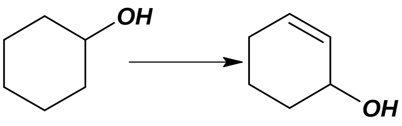
(b)



(c)



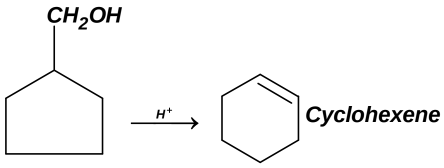
(d)



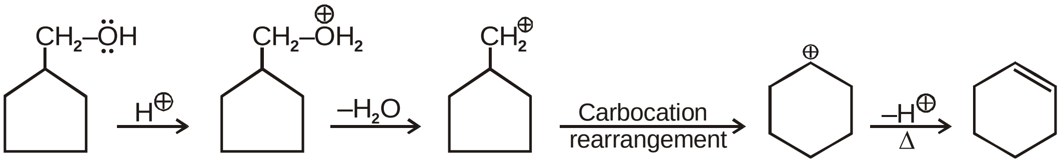
Ans. (b) Ph – CH = CH_2 $\xrightarrow[\text{(ii) } H_2O_2/OH^{\ominus}]{\text{(i) } BH_3\cdot THF}$ Ph – CH_2 = CH_2

Solved Example :

Qus. Write mechanism



Ans.



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 beverages.

(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.

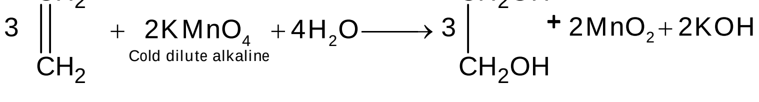
(iv) In the manufacture of picric acid, phenolphthalein, azo dyes.

(v) As a preservative for ink.

Ethylene Glycol : Ethane 1, 2 diol

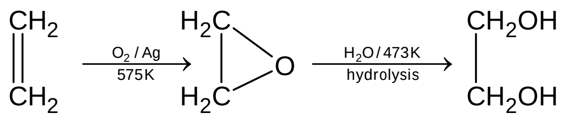
Preparation : Lab preparation by hydroxylation.

(i)



$$3\begin{array}{c}CH_2\\ \| \\ CH_2\end{array} + \underset{\text{Cold dilute alkaline}}{2KMnO_4} + 4H_2O \longrightarrow 3\begin{array}{c}CH_2OH\\ | \\ CH_2OH\end{array} + 2MnO_2 + 2KOH$$

Manufacture :



$$\begin{matrix}CH_2\\ \|\\ CH_2\end{matrix} \xrightarrow[575K]{O_2/Ag} \text{Ethylene epoxide} \xrightarrow[\text{hydrolysis}]{H_2O/473K} \begin{matrix}CH_2OH\\ |\\ CH_2OH\end{matrix}$$

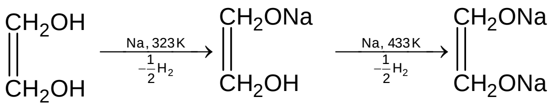
Ethylene epoxide
or oxirane

Physical properties:

It is highly viscous because of the presence of two OH bond it undergoes extensive intermolecular H-bonding. Same reason owes to high solubility in water and high boiling point.

CHEMICAL PROPERTIES :
Reaction with sodium

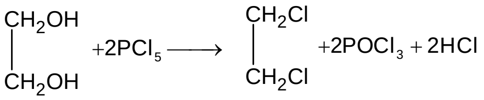
(i)



$$\begin{matrix}CH_2OH\\ \|\\ CH_2OH\end{matrix} \xrightarrow[-\frac{1}{2}H_2]{Na,\ 323K} \begin{matrix}CH_2ONa\\ \|\\ CH_2OH\end{matrix} \xrightarrow[-\frac{1}{2}H_2]{Na,\ 433K} \begin{matrix}CH_2ONa\\ \|\\ CH_2ONa\end{matrix}$$

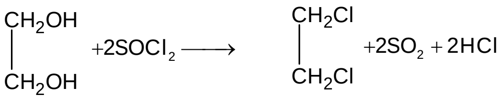
Monosodium glycolate Disodium glycolate

(ii)



$$\begin{matrix}CH_2OH\\ |\\ CH_2OH\end{matrix} + 2PCl_5 \longrightarrow \begin{matrix}CH_2Cl\\ |\\ CH_2Cl\end{matrix} + 2POCl_3 + 2HCl$$

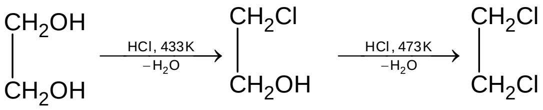
(iii)



$$\begin{matrix}CH_2OH\\ |\\ CH_2OH\end{matrix} + 2SOCl_2 \longrightarrow \begin{matrix}CH_2Cl\\ |\\ CH_2Cl\end{matrix} + 2SO_2 + 2HCl$$

Ethylene dichloride

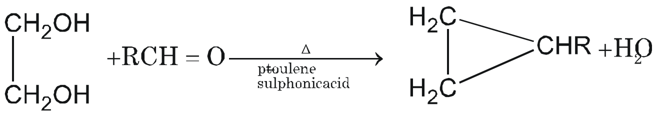
(iv)



$$\begin{matrix}CH_2OH\\ |\\ CH_2OH\end{matrix} \xrightarrow[-H_2O]{HCl,\ 433K} \begin{matrix}CH_2Cl\\ |\\ CH_2OH\end{matrix} \xrightarrow[-H_2O]{HCl,\ 473K} \begin{matrix}CH_2Cl\\ |\\ CH_2Cl\end{matrix}$$

Ethylene chlorohydrin Ethylene dichloride

(v)

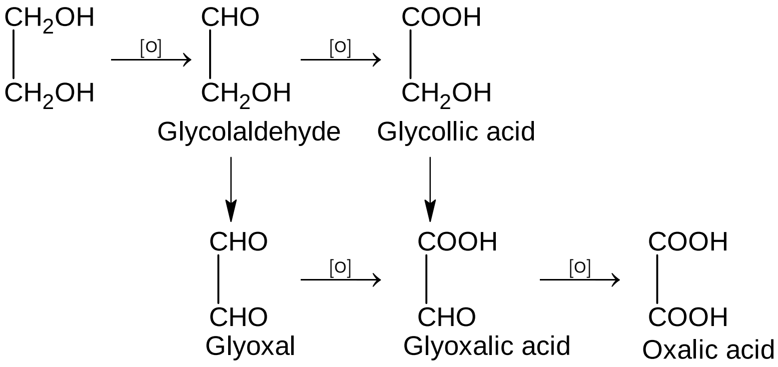


$$\begin{matrix}CH_2OH\\ |\\ CH_2OH\end{matrix} + RCH = O \xrightarrow[\text{p-toulene sulphonicacid}]{\Delta} \text{Cyclic compound} + H_2O$$

Cyclic compound

(vi) **Oxidation :** Ethyelene glycol upon oxidation gives different products with different oxidising agents. For example.

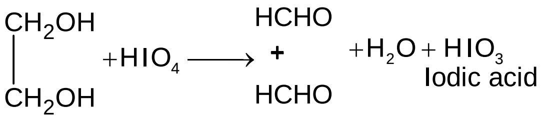
(a)



$$\begin{matrix}CH_2OH\\ |\\ CH_2OH\end{matrix} \xrightarrow{[O]} \begin{matrix}CHO\\ |\\ CH_2OH\end{matrix} \xrightarrow{[O]} \begin{matrix}COOH\\ |\\ CH_2OH\end{matrix}$$

$$\begin{matrix}CHO\\ |\\ CHO\end{matrix} \xrightarrow{[O]} \begin{matrix}COOH\\ |\\ CHO\end{matrix} \xrightarrow{[O]} \begin{matrix}COOH\\ |\\ COOH\end{matrix}$$

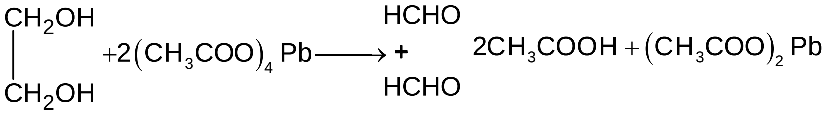
(b) With periodic acid HIO_4 or lead tetra acetate.



$$\begin{matrix}CH_2OH\\ |\\ CH_2OH\end{matrix} + HIO_4 \longrightarrow \begin{matrix}HCHO\\ +\\ HCHO\end{matrix} + H_2O + HIO_3$$

Iodic acid

Also called malapride reaction.



$$\begin{array}{l}CH_2OH\\ \,|\\ CH_2OH\end{array} + 2(CH_3COO)_4Pb \longrightarrow \begin{array}{c}HCHO\\ +\\ HCHO\end{array} \quad 2CH_3COOH + (CH_3COO)_2Pb$$

Solved Example :

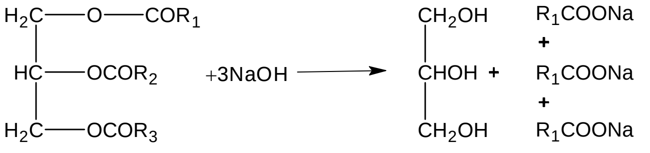
Qus. How would you convert cyclohexane to 1, 6 – hexanediol?

Glycerol (Propane 1, 2, 3 triol)

One of the most important trihydric alcohol.

Preparation:

(i) **By Saponification of oils and fats.**



Sodium salt of fatty acid (soap)

(ii) **From Propylene**

$$CH_3-CH=CH_2 \xrightarrow[-HCl]{Cl_2,\,773K} \underset{\text{Allyl chloride}}{Cl-CH_2-CH=CH_2} \xrightarrow[423K,\,12\text{ atm}]{aq.Na_2CO_3} \underset{\text{Allyl alcohol}}{HO-CH_2-CH=CH_2}$$

$$\xrightarrow[(\text{trans }Cl_2+H_2O)]{HOCl(Cl^+OH^-)} \underset{(\text{glycerol }\beta-\text{monochlorohydrin})}{HOCH_2-CHOH-CH_2Cl} \xrightarrow[-NaCl]{aq.\ NaOH} \underset{\text{glycerol}}{CH_2OH-CHOH-CH_2OH}$$

(iii) **Synthesis from its elements**

$$2C+H_2 \xrightarrow[\text{Berthelets synthesis}]{\text{Electric ore}} CH\equiv CH \xrightarrow[196\text{ K}]{\text{Na in liq. }NH_3} Na^+C^-\equiv CH \xrightarrow[-NaI]{CH_3I}$$

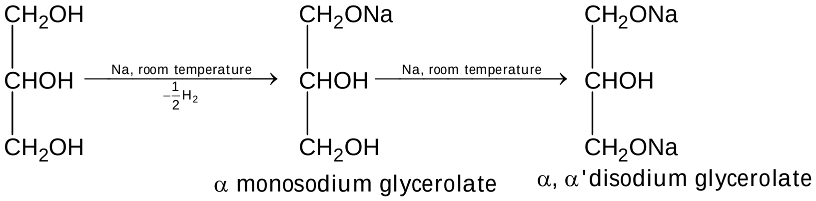
$$\underset{\text{Propyne}}{H_3C-C\equiv CH} \xrightarrow[\text{Lindlar's catalyst}]{H_2/Pd+BaSO_4} \underset{\text{Propylene}}{CH_3-CH=CH_2}$$

Physical Properties :

Highly viscous due to three —OH group due to which it undergoes extensive intermolecular H-bonding.

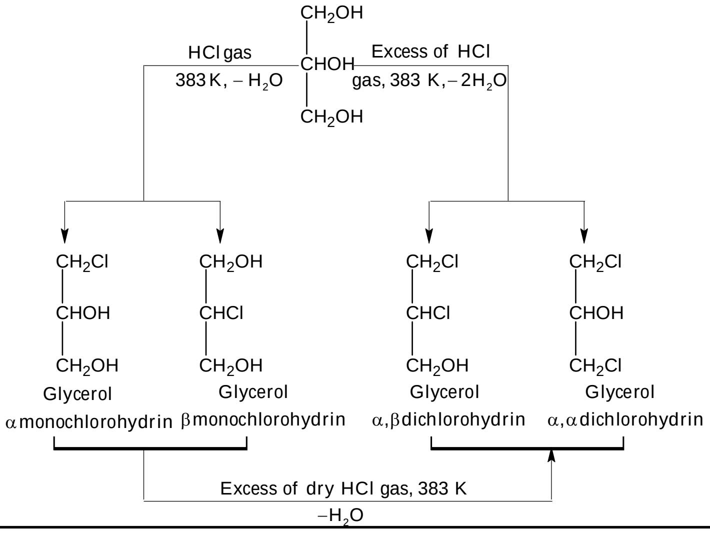
Chemical Properties :

(i) It undergoes reaction of both secondary and primary alcoholic group.



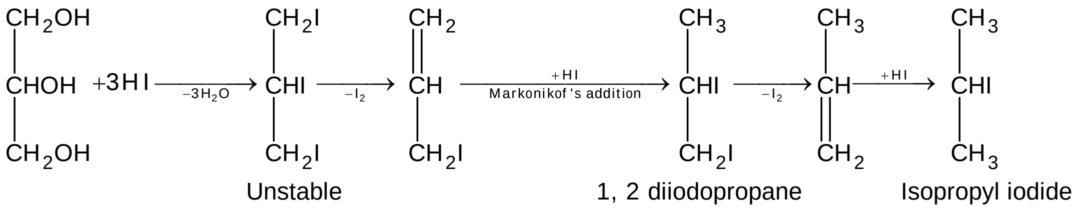
$$\begin{array}{l}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array} \xrightarrow[-\frac{1}{2}H_2]{\text{Na, room temperature}} \underset{\alpha\text{ monosodium glycerolate}}{\begin{array}{l}CH_2ONa\\ |\\ CHOH\\ |\\ CH_2OH\end{array}} \xrightarrow{\text{Na, room temperature}} \underset{\alpha,\alpha'\text{disodium glycerolate}}{\begin{array}{l}CH_2ONa\\ |\\ CHOH\\ |\\ CH_2ONa\end{array}}$$

(ii)

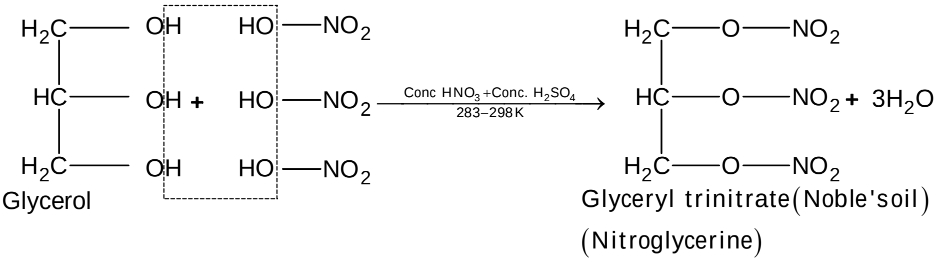


To replace the third hydroxyl group in either of two dichlorohydrins, PCl_5 or PCl_3 is fused.

(iii)

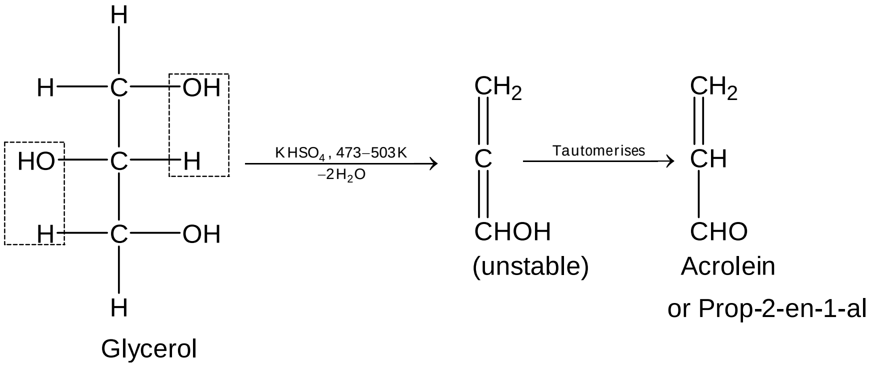


3. Reaction with concentrated nitric acid:

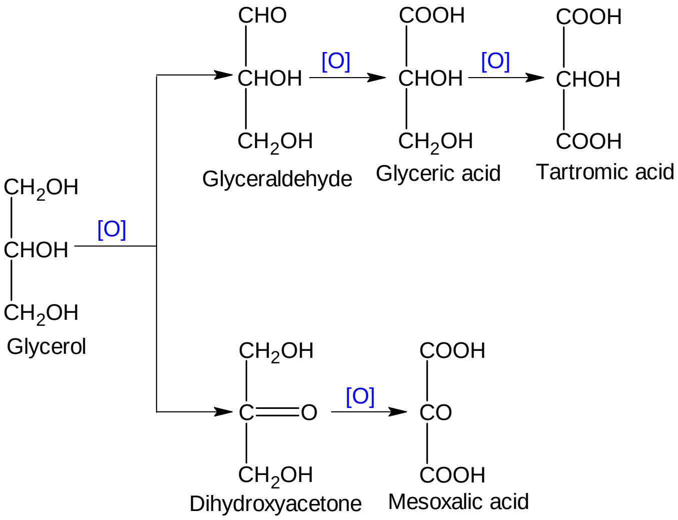


A mixture of glyceryl trinitrate and glyceryl dinitrate absorbed on Kieselguhr is called dynamite.

4. Reaction with $KHSO_4$ – Dehydration.



5. Oxidation.



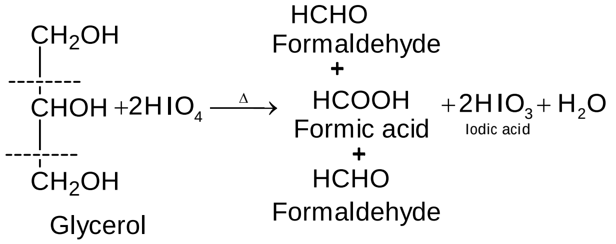
(i) With dil. HNO_3, a mixture of glyceric acid and tartronic acid is produced.

(ii) With conc. HNO_3, mainly glyceric acid is obtained.

(iii) With bismuth nitrate, only mesoxalic acid is formed.

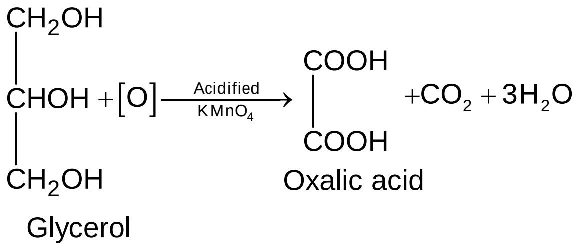
(iv) Mild oxidising agents like bromine water, sodium hypobromite (Br_2/NaOH) and Fenton's reagent (H_2O_2 + $FeSO_4$) give a mixture of glyceraldehyde and dihydroxyacetone. The mixture is called glycerose.

(v) With periodic (HIO_4) acid.



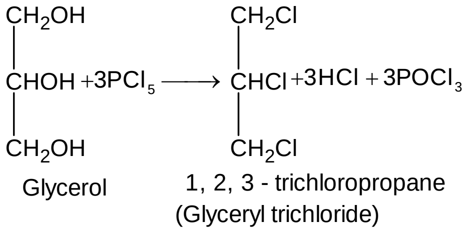
$$\underset{\text{Glycerol}}{\begin{matrix}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{matrix}} + 2HIO_4 \xrightarrow{\Delta} \begin{matrix}\underset{\text{Formaldehyde}}{HCHO}\\ +\\ \underset{\text{Formic acid}}{HCOOH}\\ +\\ \underset{\text{Formaldehyde}}{HCHO}\end{matrix} + \underset{\text{Iodic acid}}{2HIO_3} + H_2O$$

(vi) With acidified potassium permanganate.



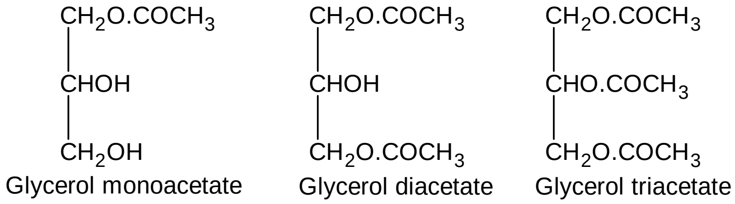
$$\underset{\text{Glycerol}}{\begin{matrix}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{matrix}} + [O] \xrightarrow[KMnO_4]{\text{Acidified}} \underset{\text{Oxalic acid}}{\begin{matrix}COOH\\ |\\ COOH\end{matrix}} + CO_2 + 3H_2O$$

6. **Reaction with phosphorous halides.**



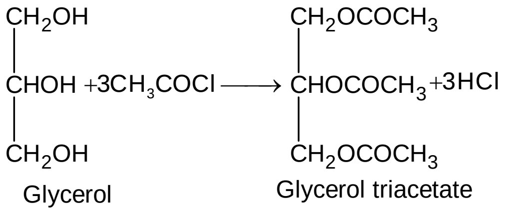
$$\underset{\text{Glycerol}}{\begin{matrix}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{matrix}} + 3PCl_5 \longrightarrow \underset{\substack{\text{1, 2, 3 - trichloropropane}\\ \text{(Glyceryl trichloride)}}}{\begin{matrix}CH_2Cl\\ |\\ CHCl\\ |\\ CH_2Cl\end{matrix}} + 3HCl + 3POCl_3$$

7. **Reaction with monocarboxylic acids.** Glycerol reacts with monocarboxylic acids to form mono-, di- and tri- ester depending upon the amount of the acid used and the temperature of the reaction. An excess of the acid and high temperature favour the formation of tri-esters. For example, with acetic acid, glycerol mono**acetate,** diacetate and triacetate may be formed.



$$\underset{\text{Glycerol monoacetate}}{\begin{matrix}CH_2O.COCH_3\\ |\\ CHOH\\ |\\ CH_2OH\end{matrix}} \qquad \underset{\text{Glycerol diacetate}}{\begin{matrix}CH_2O.COCH_3\\ |\\ CHOH\\ |\\ CH_2O.COCH_3\end{matrix}} \qquad \underset{\text{Glycerol triacetate}}{\begin{matrix}CH_2O.COCH_3\\ |\\ CHO.COCH_3\\ |\\ CH_2O.COCH_3\end{matrix}}$$

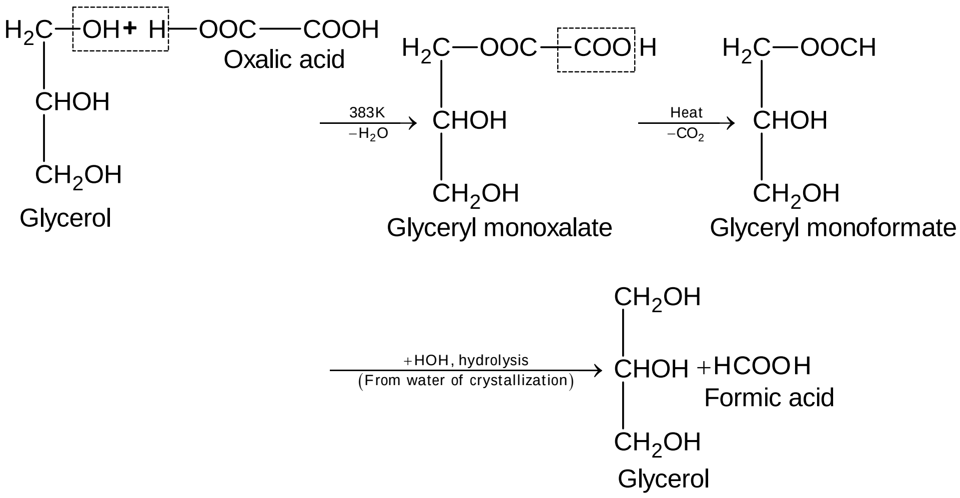
8. **Acetylation.** When treated with acetyl chloride, glycerol forms glycerol triacetate.



$$\underset{\text{Glycerol}}{\begin{matrix}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{matrix}} + 3CH_3COCl \longrightarrow \underset{\text{Glycerol triacetate}}{\begin{matrix}CH_2OCOCH_3\\ |\\ CHOCOCH_3\\ |\\ CH_2OCOCH_3\end{matrix}} + 3HCl$$

9. **Reaction with oxalic acid**

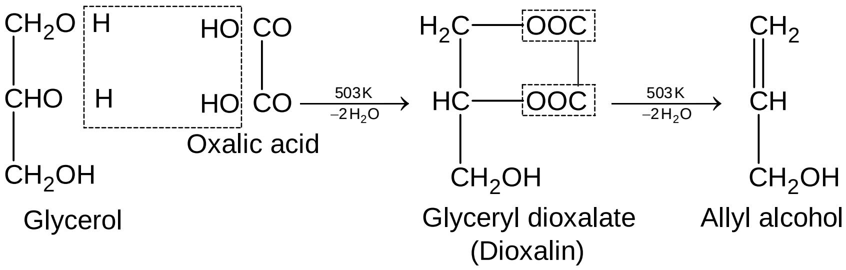
(i)



$$\underset{\text{Glycerol}}{\begin{matrix}H_2C-\boxed{OH + H}-\underset{\text{Oxalic acid}}{OOC-COOH}\\ |\\ CHOH\\ |\\ CH_2OH\end{matrix}} \xrightarrow[-H_2O]{383K} \underset{\text{Glyceryl monoxalate}}{\begin{matrix}H_2C-OOC-\boxed{COO}H\\ |\\ CHOH\\ |\\ CH_2OH\end{matrix}} \xrightarrow[-CO_2]{\text{Heat}} \underset{\text{Glyceryl monoformate}}{\begin{matrix}H_2C-OOCH\\ |\\ CHOH\\ |\\ CH_2OH\end{matrix}}$$

$$\xrightarrow[\text{(From water of crystallization)}]{+HOH,\text{ hydrolysis}} \underset{\text{Glycerol}}{\begin{matrix}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{matrix}} + \underset{\text{Formic acid}}{HCOOH}$$

(ii)



Uses: **Glycerol is used :**

1. In the preparation of nitroglycerine used in making dynamite. Nitroglycerine is also used for treatment of angina pectoris.

2. As an antifreeze in automobile radiators.

3. In medicines like cough syrups lotions etc.

4. In the production of glyptal or alkyl resin (a cross – linked polyester obtained by the condensation polymerization of glycerol and phthalic acid) which is used in the manufacture of paints and lacquers.

5. In making non-drying printing inks, stamp colours, shoes polishes etc.

6. In the manufacture of high class toilet soaps and cosmetics since it does not allow them to dry due to its hydroscopic nature.

7. As a preservative for fruits and other eatables.

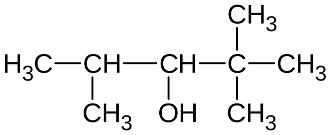
8. As a sweetening agent in beverages and confectionary.

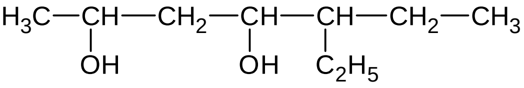
Solved Example :

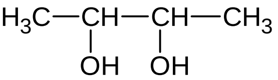
Qus. How does glycerol react with a. HI, b. $(COOH)_2$ and c. conc HNO_3 ?

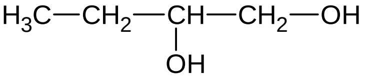
NCERT Level Questions

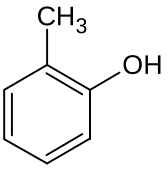
1. Give the common and IUPAC names the following compounds**:**

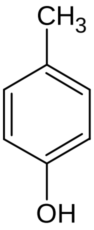
(i) 
$\mathrm{H_3C-\underset{CH_3}{CH}-\underset{OH}{CH}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3}$

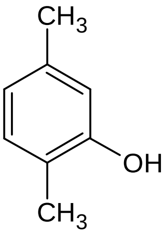
(ii) 
$\mathrm{H_3C-\underset{OH}{CH}-CH_2-\underset{OH}{CH}-\underset{C_2H_5}{CH}-CH_2-CH_3}$

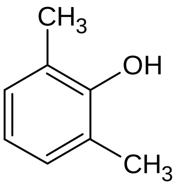
(iii) 
$\mathrm{H_3C-\underset{OH}{CH}-\underset{OH}{CH}-CH_3}$

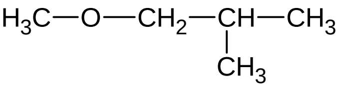
(iv) 
$\mathrm{H_3C-CH_2-\underset{OH}{CH}-CH_2-OH}$

(v) 

(vi) 

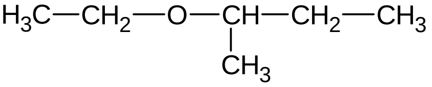
(vii) 

(viii) 

(ix) 
$\mathrm{H_3C-O-CH_2-\underset{CH_3}{CH}-CH_3}$

(x) $\mathrm{H_5C_6-CH_2-C_2H_5}$

(xi) $\mathrm{H_5C_6-CH_2-C_7H_{15}}$(n–)

(xii) 
$\mathrm{H_3C-CH_2-O-\underset{CH_3}{CH}-CH_2-CH_3}$

Sol. **(i)** 2,2,4–Trimethylpentan–3–ol **(ii)** 5–Enthylheptan–2, 4–diol

(iii) Butan–2, 3–diol **(iv)** Propan–1, 2, 3–triol

(v) 2–Methylphenol **(vi)** 4–methylphenol

(vii) 2, 5–Dimethylphenol **(viii)** 2, 6–Dimethylphenol

(ix) 1–Methoxy–2–methylpropane **(x)** Ethoxybenzene

(xi) 1 – Phenoxyheptane **(xii)** 2–Ethoxybutane.

2. Write structures of the compounds whose IUPAC names are as follows**:**

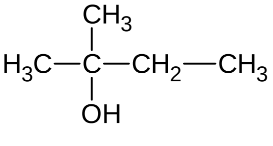
(i) 2–Methylbutane–2–ol **(ii)** 1–Phenylpropan–2–ol

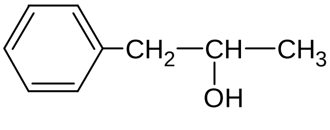
(iii) 3,5–Dimethylhexane–1,3,5–triol **(iv)** 2,3–Diethylphenol

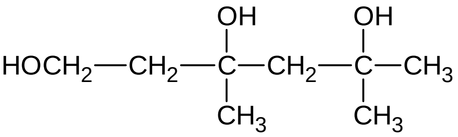
(v) 1–Ethoxypropane **(vi)** 2–Ethoxy–3–Methylpentane

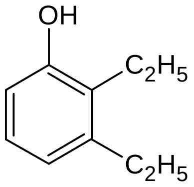
(vii) Cychlohexylmethanol **(viii)** 3–Cyclohexylpentan–3–ol

(ix) Cyclopent–3–en–1–ol **(x)** 3–chloromethylpentan–1–ol

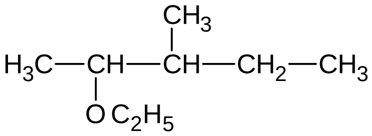
Sol. (i) 
$\mathrm{H_3C-\overset{CH_3}{\underset{OH}{C}}-CH_2-CH_3}$

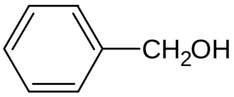
(ii) 

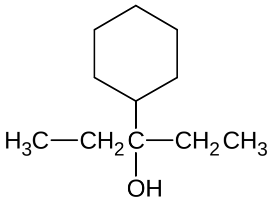
(iii) 
$\mathrm{HOCH_2-CH_2-\overset{OH}{\underset{CH_3}{C}}-CH_2-\overset{OH}{\underset{CH_3}{C}}-CH_3}$

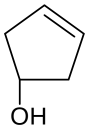
(iv) 

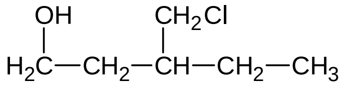
(v) $C_2H_5O-CH_2-CH_2-CH_3$

(vi) 
$H_3C-\underset{OC_2H_5}{CH}-\overset{CH_3}{CH}-CH_2-CH_3$

(vii) 

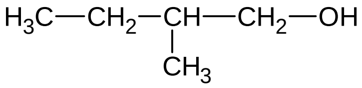
(viii) 

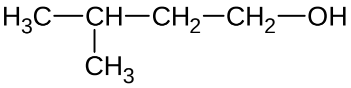
(ix) 

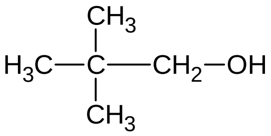
(x) 
$H_2\overset{OH}{C}-CH_2-\overset{CH_2Cl}{CH}-CH_2-CH_3$

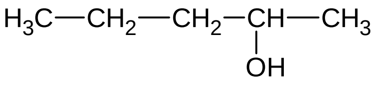
3. Draw the structures of all isomeric alcohols of molecular formula $C_5H_{12}O$ and give their IUPAC names. Classify them as primary, secondary and tertiary alcohols.

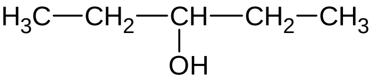
Sol. (a) $CH_3CH_2CH_2CH_2CH_2OH$; Pentan –1–ol (1°)

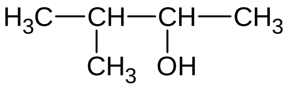
(b) 
$H_3C-CH_2-\underset{CH_3}{CH}-CH_2-OH$ 2-Methylbutan-1-ol (1°)

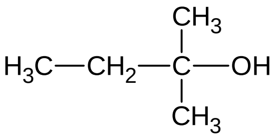
(c) 
$H_3C-\underset{CH_3}{CH}-CH_2-CH_2-OH$ 3-Methylbutane-1-ol (1°)

(d) 
$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-OH$ 2,2-Dimethylpropan-1-ol (1°)

(e) 
$H_3C-CH_2-CH_2-\underset{OH}{CH}-CH_3$ Pentan-2-ol (2°)

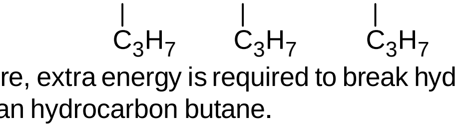
(f) 
$H_3C-CH_2-\underset{OH}{CH}-CH_2-CH_3$ Pentan-3-ol (2°)

(g) 
$H_3C-\underset{CH_3}{CH}-\underset{OH}{CH}-CH_3$ 3-Methylbutan-2-ol (2°)

(h) 
$H_3C-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-OH$ 2-Methylbutan-2-ol (3°)

4. Explain why is propanol higher boiling point than that of the hydrocarbons, butane ?

Sol. Propanol undergoes intermolecular H-bonding because of the presence of –OH group. On the other hand, butane does not.


$$------\overset{\delta+}{H}-\underset{C_3H_7}{\overset{\delta-}{O}}-----\overset{\delta+}{H}-\underset{C_3H_7}{\overset{\delta-}{O}}------\overset{\delta+}{H}-\underset{C_3H_7}{\overset{\delta-}{O}}------$$

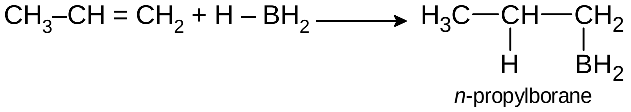
Therefore, extra energy is required to break hydrogen bonds. For this reason, propanol has a higher boiling point than hydrocarbon butane.

5. Alcohols are comparatively more soluble in water than the hydrocarbons of comparable molecular masses. Explain this fact.

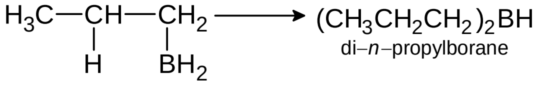
Sol. Alcohols are more soluble in water because of intermolecular hydrogen bonding between alcohol and water molecules.

6. What is meant by hydroboration-oxidation reaction ? Illustrate it with an example.

Sol. **Hydroboration.** Diborane (B_2H_6) reacts with alkenes to yield alkylboranes, R_3B. These are oxidized to alcohols on reaction with H_2O_2 is presence of an alkali.



$$CH_3\text{–}CH = CH_2 + H - BH_2 \longrightarrow \underset{n\text{-propylborane}}{H_3C-\underset{H}{CH}-\underset{BH_2}{CH_2}}$$



$$H_3C-\underset{H}{CH}-\underset{BH_2}{CH_2} \longrightarrow \underset{\text{di–}n\text{–propylborane}}{(CH_3CH_2CH_2)_2BH}$$

$$(CH_3CH_2CH_2)_2BH + CH = CH_2 \longrightarrow \underset{\text{tri–}n\text{–propylborane}}{(CH_3CH_2CH_2)_3B}$$

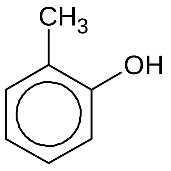
or $$6CH_3CH = CH_2 + \underset{\text{diborane}}{B_2H_6} \longrightarrow \underset{\text{Tri–}n\text{–propylborane}}{2(CH_3CH_2CH_2)_3B}$$

$$(CH_3CH_2CH_2)_3B \xrightarrow{3H_2O_2\,/\,OH^-} \underset{\text{Propane–1–ol}}{2CH_3CH_2CH_2OH} + B(OH)_3$$

In it the addition to BH_3 occurs is anti–Markovnikov's addition. During oxidation of trialkylobrane, boron is replaced by OH group.

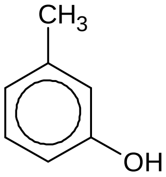
7. Give the structures and IUPAC names of monohydric phenols of molecular formula C_7H_8O.

Sol. (i)



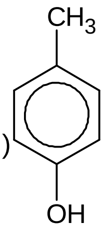
; 2-Methylphenol

(ii)



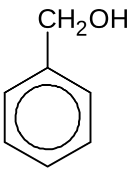
; 3-Methylphenol

(iii)



; 4-Methylphenol

(iv)



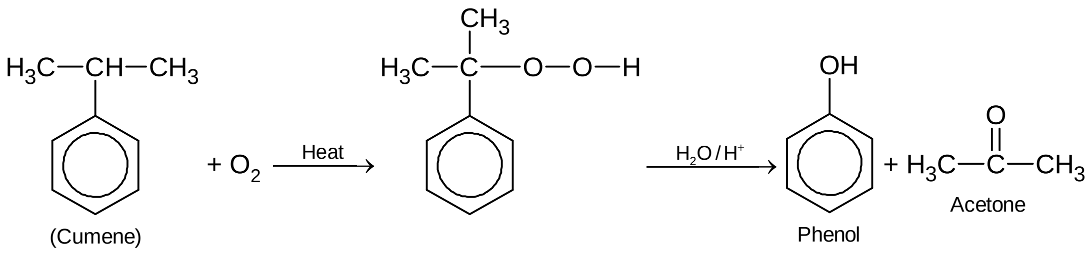
; Benzylalcohol

8. While separating a mixture of ortho and para nitrophenols by steam distillation, name the isomer which is steam volatile. Give reason.

Sol. *o – nitrophenol* is *steam volatile* due to intramolecular hydrogen bonding while *p* – nitrophenol is less volatile due to intermolecular hydrogen bonding which causes the association of molecules.

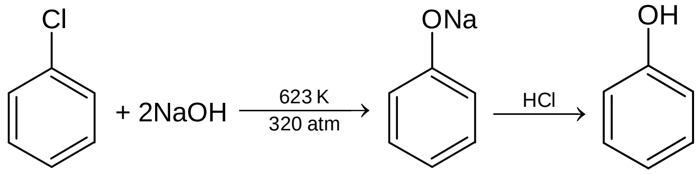
9. Give the equation of reaction of preparation of phenol from cumene.

Sol.



10. Write chemical reaction for the prepration of phenol from chlorobenzene.

Sol. Chlorobenzene is fused with NaOH (at 623 K and 320 atm pressure) to produce sodium phenoxide, which gives phenol on acidification. (Dow's process)



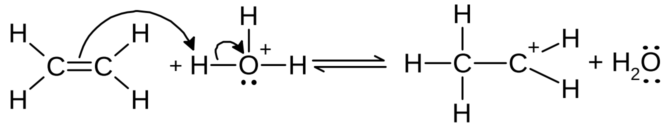
Chlorobenzene Sodium phenoxide Phenol

11. Write the mechanism for hydration of ethene to yield ethanol.

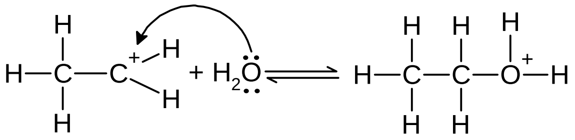
Sol. The mechanism of hydration of ethene to form ethanol involves three steps.

Step 1: Protonation of ethene to form carbocation by electrophilic attack of H_3O^+:

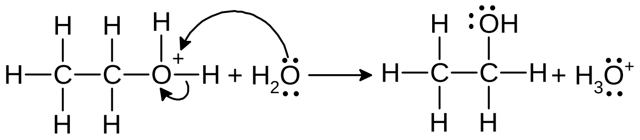
$H_2O + H^+ \longrightarrow H_3O^+$



Step 2: Nucleophilic attack of water on carbocation:

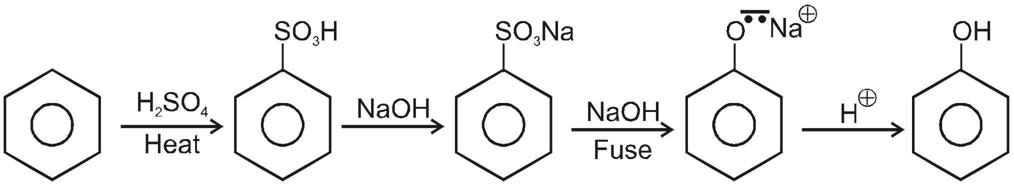


Step 3: Deprotonation to form ethanol:



12. You are given benzene, conc. H_2SO_4 and NaOH. Write the equations for the preparation of phenol using these reagents.

Sol.



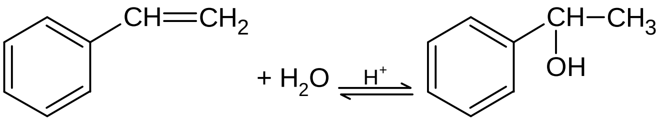
13. Show how will you synthesise :

(i) 1-phenylethanol from a suitable alkene.

(ii) cyclohexylmethanol using an alkyl halide by S_N2 reaction.

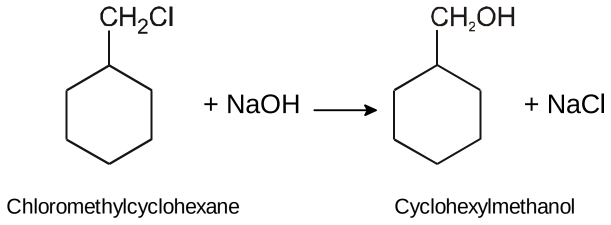
(iii) pentan-1-ol using a suitable alkyl halide ?

Sol. (i) By acid-catalyzed hydration of ethylbenzene (styrene), 1-phenylethanol can be synthesized.



Phenylethene 1-Phenylethanol

(ii) When chloromethylcyclohexane is treated with sodium hydroxide, cyclohexylmethanol is obtained.

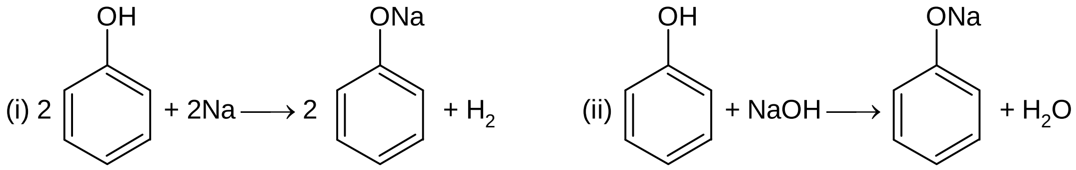


(iii) When 1-chloropentane is treated with NaOH, pentan-1-ol is produced.

$$\underset{\text{1-Chloropentane}}{CH_3CH_2CH_2CH_2CH_2Cl} + NaOH \longrightarrow \underset{\text{Pantan-1-ol}}{CH_3CH_2CH_2CH_2CH_2OH}$$

14. Give two reactions that show the acidic nature of phenol. Compare its acidity with that of ethanol.

Sol.



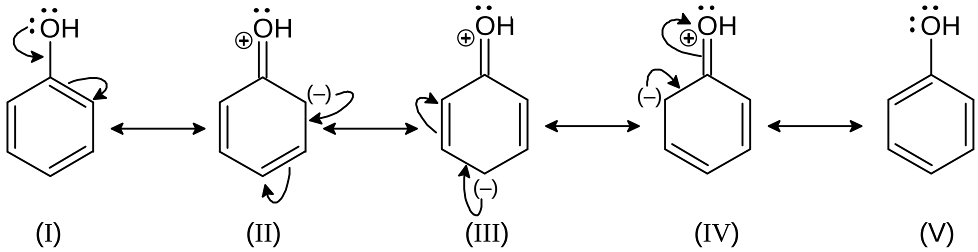
It is more acidic than ethanol (which is due to stabilization of phenoxide ion by resonance).

15. Explain why is ortho **–** nitrophenol more acidic than ortho – methoxyphenol?

Sol. Orthonitrophenol is more acidic as compared to orthomethoxyphenol because the nitro ($–NO_2$) group is an *electron withdrawing group* and due to its presence the positive charge on oxygen atom of phenol increases and so it becomes more acidic. On the other hand methoxy ($–OCH_3$) group is *electron releasing* and due to its presence the positive charge on oxygen atom of phenol decreases acid it becomes less acidic (*i.e.* O – H bond with not break easily).

16. Explain how does the **–**OH group attached to a carbon of benzene ring activates it towards electrophilic substitution?

Sol. Various resonance structure of phenol are



Since there is negative charge at *o*– and *p*–position, therefore –OH group activates ring towards electrophilic substitution reaction.

17. Give the equations of the following reactions:

(i) Reaction of propene with mercuric acetate followed by hydrolysis**.**

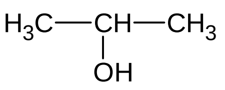
(ii) Oxidation of propan–1–ol with alkaline $KMnO_4$ solution**.**

(iii) Reaction of bromine in CS_2 with phenol**.**

(iv) Action of dilute HNO_3 with phenol**.**

(v) Treating phenol with chloroform in presence of aqueous NaOH at 343 K**.**

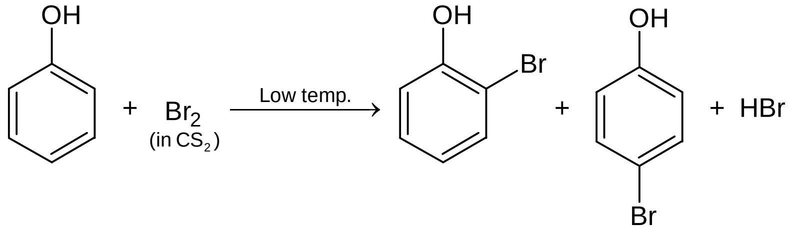
Sol. (i) $CH_3CH = CH_2 \xrightarrow[H_2O,NaBH_4]{Hg(OAc)_2}$



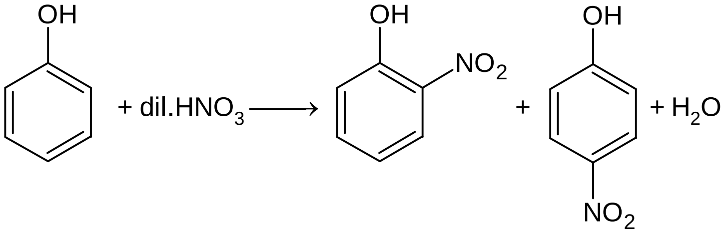
$$H_3C—\underset{\underset{OH}{|}}{CH}—CH_3$$

(ii) $CH_3CH_2CH_2OH \xrightarrow[KOH]{KMnO_4} CH_3CH_2COOH$

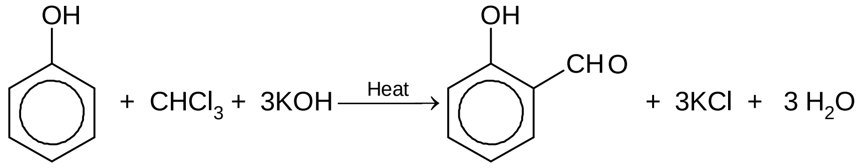
(iii)



(iv)



(v)



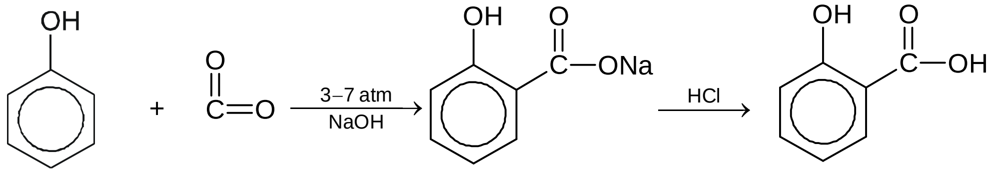
Phenol Chloroform (Salicyldehyde)

18. Write short notes on**:**

(i) Kolbe reaction **(ii)** Reimer–Tiemann reaction**.**

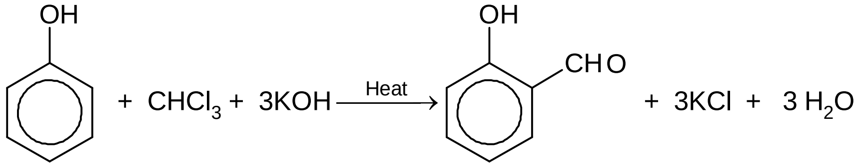
(iii) Williamson ether synthesis **(iv)** Unsymmetrical ether.

Sol. **(i) Kolbe's Reaction.** When phenol is reacted with CO_2 in presence of NaOH at high pressure, sodium salicylate is formed which on hydrolysis yields salicylic acid.



Sod. phenoxide Carbondioxide Sod. salicylate Salicylic acid

(ii) Reimer–Tiemann Reaction



Phenol Chloroform (Salicyldehyde)

(iii) Williamson ether synthesis : When sodium salt of alcohol reacts with alkyl halide to give ether. It is called Williamson's synthesis. It is used to prepare unsymmetrical ether.

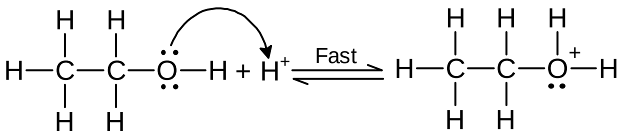
$$C_2H_5ONa + CH_3I \longrightarrow \underset{\text{Methoxyethane}}{C_2H_5OCH_3} + NaI$$

(iv) Unsymmetrical ether : If the alkyl or aryl groups attached to the oxygen atom are called unsymmetrical ethers. For example, ethyl methyl ether, methyl phenyl ether, 4-Chlorophenyl-4-nitrophenyl ether, etc.

19. Write the mechanism of acid dehydration of ethanol to yield ethen.

Sol. The mechanism of acid dehydration of ethanol to yield ethene involves the following three steps:

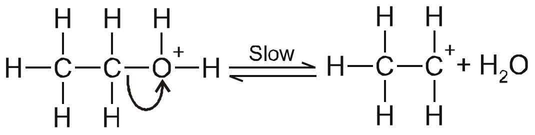
Step 1: Protonation of ethanol to form ethyl oxonium ion:



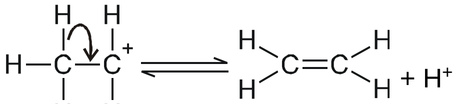
Ethanol

Protonated ethanol
(Ethyl oxonium ion)

Step 2: Formation of carbocation (rate determining step):



Step 3: Elimination of a proton to form ethene:



Ethene

The acid consumed in step 1 is released in Step 3. After the formation of ethene, it is removed to shift the equilibrium in a forward direction.

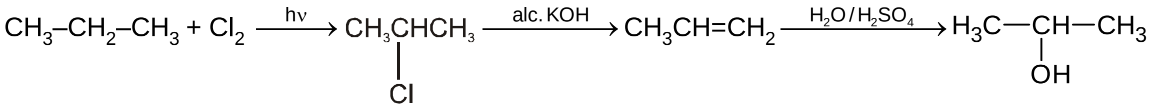
20. How are the following conversions carried out?

(i) Propane → Propan–2–ol

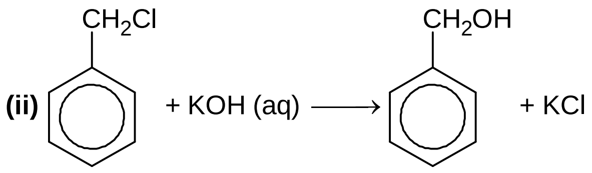
(ii) Benzyl chloride → Benzyl alcohol

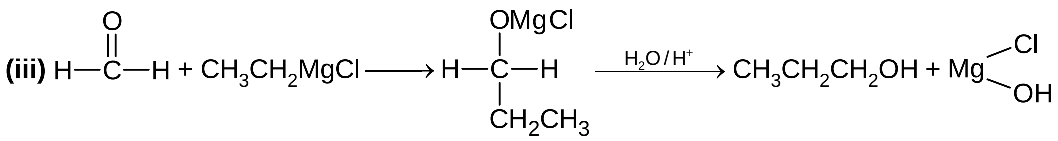
(iii) Ethyl magnesium chloride → Propan–1–ol

(iv) Methyl magnesium bromide → 2–Methylpropan–2–ol**.**

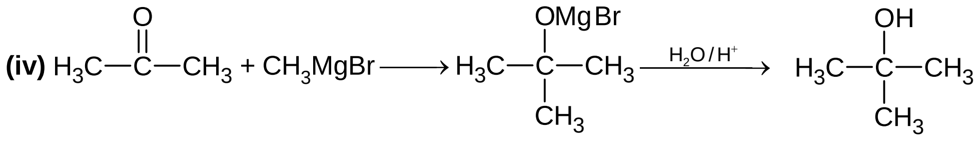
Sol. 

$$\text{(i) } CH_3–CH_2–CH_3 + Cl_2 \xrightarrow{h\nu} CH_3\underset{\substack{|\\ Cl}}{C}HCH_3 \xrightarrow{alc.\,KOH} CH_3CH{=}CH_2 \xrightarrow{H_2O/H_2SO_4} H_3C—\underset{\substack{|\\ OH}}{C}H—CH_3$$





$$\text{(iii) } H—\overset{\substack{O\\ \|}}{C}—H + CH_3CH_2MgCl \longrightarrow H—\underset{\substack{|\\ CH_2CH_3}}{\overset{\substack{OMgCl\\ |}}{C}}—H \xrightarrow{H_2O/H^+} CH_3CH_2CH_2OH + Mg\begin{smallmatrix}Cl\\ OH\end{smallmatrix}$$



$$\text{(iv) } H_3C—\overset{\substack{O\\ \|}}{C}—CH_3 + CH_3MgBr \longrightarrow H_3C—\underset{\substack{|\\ CH_3}}{\overset{\substack{OMgBr\\ |}}{C}}—CH_3 \xrightarrow{H_2O/H^+} H_3C—\underset{\substack{|\\ CH_3}}{\overset{\substack{OH\\ |}}{C}}—CH_3$$

2-Methypropen-2-ol

21. Name the reagents used in the following reactions**:**

(i) Oxidation of a primary alcohol to carboxylic acid.

(ii) Oxidation of a primary alcohol to an aldehyde.

(iii) Bromination of phenol to 2,4,6–tribromophenol.

(iv) Benzyl alcohol to benzoic acid.

(v) Dehydration of propan–2–ol to propene.

(vi) Butan–2–one to butan–2–ol.

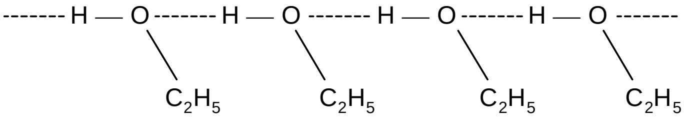
Sol. **(i)** Alkaline $KMnO_4$ ($KMnO_4$ / KOH) **(ii)** Cu / 573 K *i.e.* Hot reduced copper

(iii) Bromine water[Br_2(aq)] **(iv)** Acidified $KMnO_4$ [$KMnO_4$ / H_2SO_4]

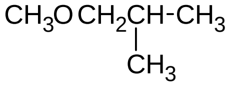
(v) Conc. H_2SO_4 **(vi)** $LiAlH_4$

22. Give reason for the higher boiling point of ethanol in comparison to methoxymethane.

Sol. Ethanol undergoes intermolecular H-bonding due to the presence of OH group, resulting in the association of molecules. Extra energy is required to break these hydrogen bonds. On the other hand, methoxymethane does not undergo H-bonding. Hence, the boiling point of ethanol is higher than that of methoxymethane.



23. Give IUPAC names of the following ethers**:**

(i) 

$CH_3OCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H\text{-}CH_3$

(ii) $CH_3\,OCH_2CH_2Cl$

(iii) $O_2N – C_6H_4 – OCH_3$ (*p*) **(iv)** $CH_3 – CH_2 – CH_2 – OCH_3$

Sol. **(i)** 2–Methyl–1–methoxypropane **(ii)** 2–Chloro–1–methoxyethane

(iii) 4–Nitroanisole **(iv)** 1–Methoxypropane

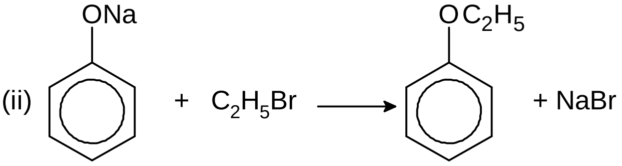
24. Write the names of reagents and equations for the preparation of the following ethers by Williamson synthesis**:**

(i) 1–Propoxypropane **(ii)** Ethoxybenzene

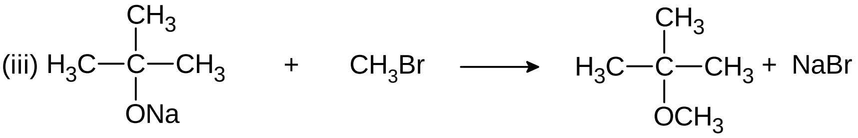
(iii) 2–Methyl–2–methoxypropane **(iv)** 1–Methoxyethane.

Sol. (i) $CH_3CH_2CH_2Br + CH_3CH_2CH_2ONa \rightarrow CH_3CH_2CH_2OCH_2CH_2CH_2 + NaBr$

1–Bromopropane Sod. Propoxide

(ii) 

Sod. phenoxide Bromoethane

(iii) 

$$H_3C—\underset{\displaystyle ONa}{\overset{\displaystyle CH_3}{C}}—CH_3 + CH_3Br \longrightarrow H_3C—\underset{\displaystyle OCH_3}{\overset{\displaystyle CH_3}{C}}—CH_3 + NaBr$$

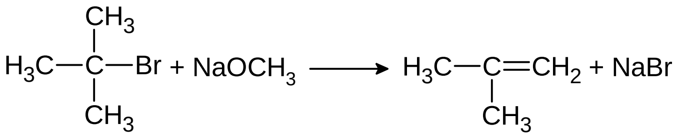
Sodium-2-Methyl-2-propoxide Bromoethane 2-Methoxy-2-methylpropane

(iv) $CH_3Br + CH_3CH_2ONa \longrightarrow CH_3OCH_2CH_3 + NaBr$

Bromoethane Sod. ethoxide

25. Illustrate with examples the limitations of Williamson Synthesis for the preparation of certain types of ethers.

Sol. It is not possible to prepare di – tertiary butyl ether by Williamsons synthesis because tertiary halides undergo elimination reactions instead of substitution reaction and so an alkene is produced

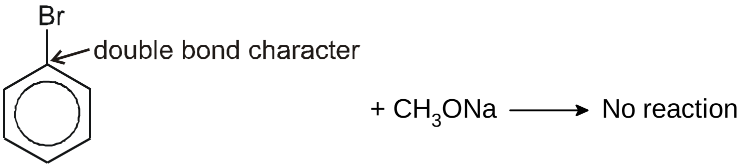


$$H_3C-C(CH_3)_2-Br + NaOCH_3 \longrightarrow H_3C-C(CH_3)=CH_2 + NaBr$$

(alkene)

It is due to the fact that alkoxides are not only nucleophiles but they are also strong bases. They react will alkyl halides forming alkenes.

Anisole cannot be prepared by the action of bromobenzene with sodium methoxide.



This is because of the fact that aryl halides are much less reactive towards nucelophilic substitution reactions as compared to alkyl halides.

26. How is 1-propoxypropane synthesized from propan-1-ol ? Write mechanism for this reaction.

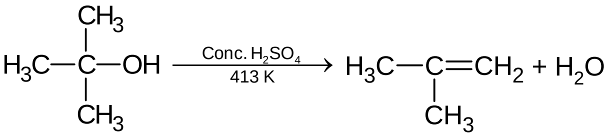
Sol. 1-propoxypropane can be prepared by heating propan-1-ol with Conc. H_2SO_4 at 413 K

$$CH_3CH_2CH_2OH \; + \; HOCH_3CH_2CH_3 \xrightarrow[413\ K]{Conc.\ H_2SO_4} CH_3CH_2CH_2{-}O{-}CH_2CH_2CH_3$$

Propan-1-ol 1-Propoxypropane

27. Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. Give reason.

Sol. It is not a suitable method because on dehydration a secondary or tertiary alcohol forms alkenes easily.



$$H_3C-C(CH_3)_2-OH \xrightarrow[413\ K]{Conc.\ H_2SO_4} H_3C-C(CH_3)=CH_2 + H_2O$$

(alkene)

28. Write the equation of the reaction of hydrogen iodide with

(i) 1 – Propoxyproane **(ii)** methoxybenzene and **(iii)** Benzyl ethyl ether**.**

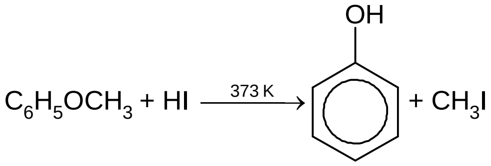
Sol. (i) $CH_3CH_2CH_2OCH_2CH_2CH_3 + HI \xrightarrow{373K} CH_3CH_2CH_2OH + CH_3CH_2CH_2I$

In presence of excess of HI, the reaction goes further

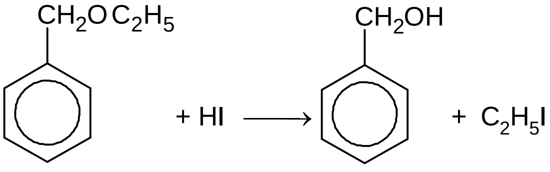
$CH_3CH_2CH_2OH + HI \rightarrow CH_3CH_2CH_2I + H_2O$

In such a case 2 moles of $CH_3CH_2CH_2I$ are formed.

(ii)



(iii)



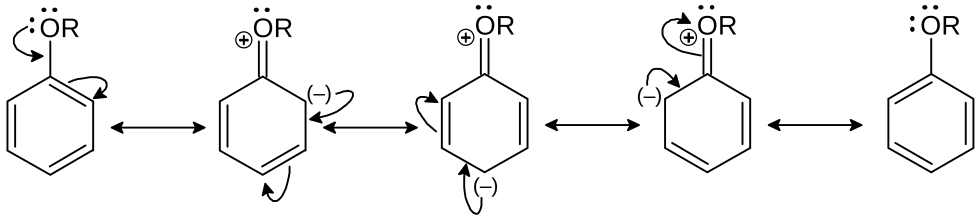
Benzylethylether

29. Explain the fact that in aryl alkyl ethers :

(i) the alkoxy group activates the benzene ring towards electrphilic substitution, and

(ii) it directs the incoming substituents to ortho and para positions in benzene ring.

Sol. Various resonating structure of aryl alkyl ethers are**:**

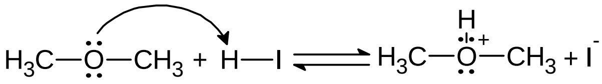


Since there is negative charge at *o*– and *p*–positions, therefore the –OR groups is activating towards electrophilic substitution. Since the attack of electrophile will be at *o*– or *p*–position so –OR group is *ortho*–, *para*– directing group.

30. Write the mechanism of the reaction of HI with methoxymethane.

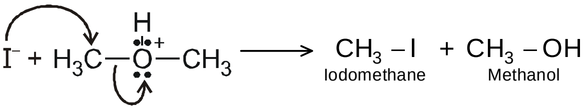
Sol. The mechanism of the reaction of HI with methoxymethane involves the following steps:

Step1: Protonation of methoxymethane:



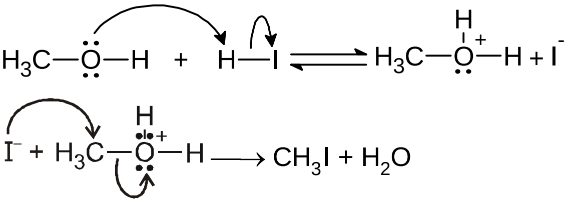
$$H_3C-\ddot{O}-CH_3 + H-I \rightleftharpoons H_3C-\overset{H}{\overset{|}{\underset{\cdot\cdot}{O}^+}}-CH_3 + I^-$$

Step2: Nucleophilic attack of $I^{?:}$



$$I^- + H_3C-\overset{H}{\overset{|}{\underset{\cdot\cdot}{O}^+}}-CH_3 \longrightarrow \underset{\text{Iodomethane}}{CH_3-I} + \underset{\text{Methanol}}{CH_3-OH}$$

Step3: When HI is in excess and the reaction is carried out at a high temperature, the methanol formed in the second step reacts with another HI molecule and gets converted to methyl iodide



$$H_3C-\ddot{O}-H + H-I \rightleftharpoons H_3C-\overset{H}{\overset{|}{\underset{\cdot\cdot}{O}^+}}-H + I^-$$

$$I^- + H_3C-\overset{H}{\overset{|}{\underset{\cdot\cdot}{O}^+}}-H \longrightarrow CH_3I + H_2O$$

31. Write equations for the following reactions**:**

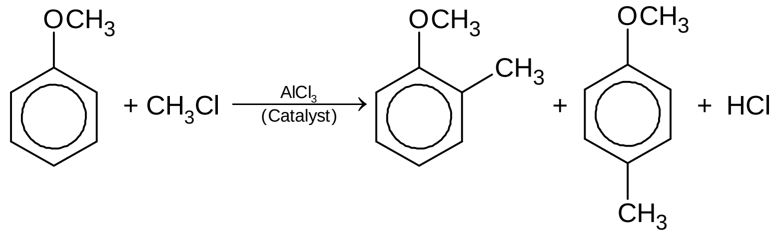
(i) Friedel Crafts reaction – alkylation in anisole.

(ii) Nitration on anisole.

(iii) Bromination of anisole in ethanoic acid medium.

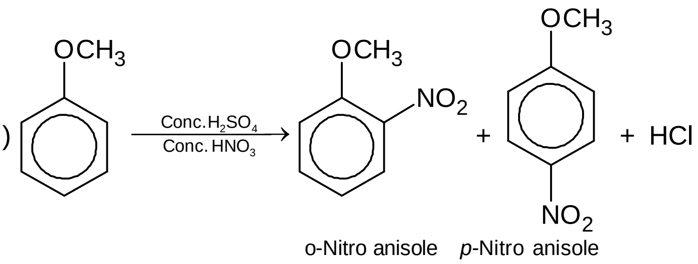
(iv) Friedel Crafts acetylation of anisole**.**

Sol. (i)

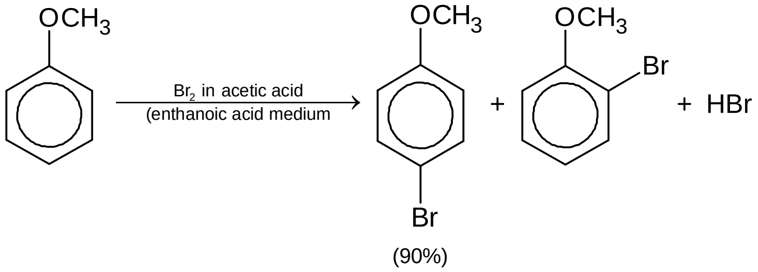


o-Methyl anisole *p*-Methyl anisole

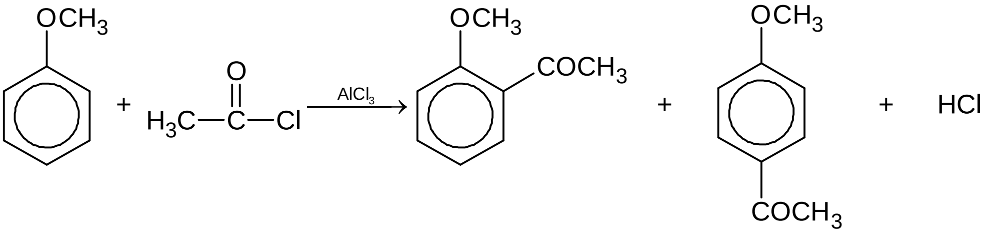
(ii)



o-Nitro anisole *p*-Nitro anisole

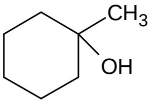
(iii) 

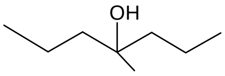
In this case *p* – Bromoanisole is the major product.

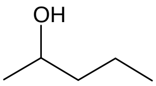
(iv) 

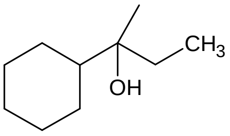
o-Methyl acetophenone *p*-Methoxy acetophenone

32. Show would you synthesise the following alcohols from appropriate alkenes ?

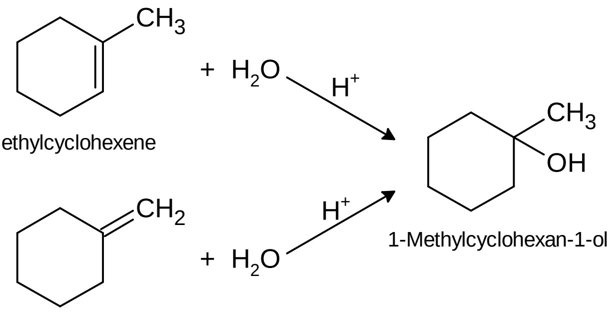
(i) 

(ii) 

(iii) 

(iv) 

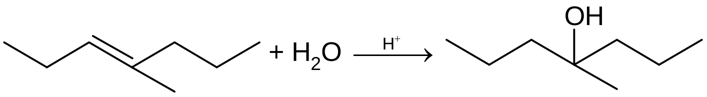
Sol. The given alcohols can be synthesized by applying Markovnikov's rule of acid-catalyzed hydration of appropriate alkenes.

(i) 

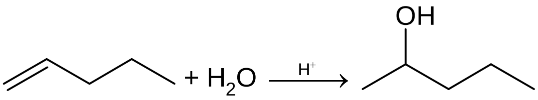
1-Methylcyclohexene

1-Methylcyclohexan-1-ol

1-Methylcyclohexene

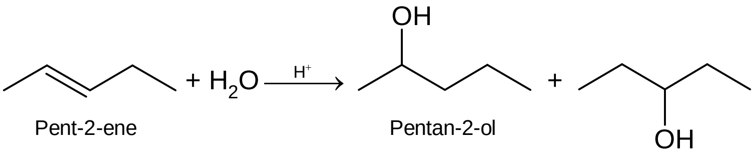
(ii) 

4-Methylhept-3-ene 4-Methylheptan-4-ol

(iii) 

Pent-1-ene Pentan-2-ol

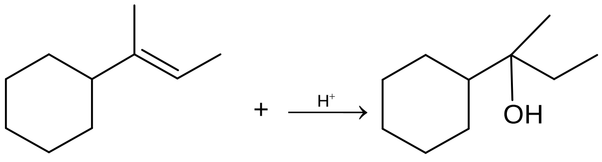
Acid-catalyzed hydration of pent-2-ene also produces pentan-2-ol but along with pentan-3-ol.



Pent-2-ene Pentan-2-ol Pentan-2-ene

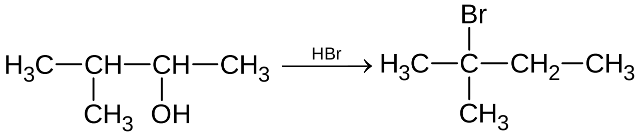
Thus, the first reaction is preferred over the second one to get pentan-2-ol.

(iv)



2-Cyclohexylbut-2-ene 2-Cyclohexylbutan-2-ol

33. When 3-methylbutan-2-ol is treated with HBr. The following reaction takes place :

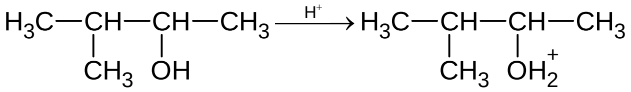


$$H_3C-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{HBr} H_3C-\overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_3$$

Give a mechanism for this reaction.

Sol. The mechanism of the given reaction involves the following steps:

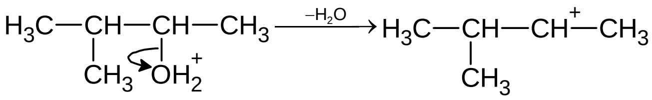
Step 1: Protonation



$$H_3C-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{H^+} H_3C-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{\overset{+}{O}H_2}{|}}{CH}-CH_3$$

3-Methylbutan-2-ol

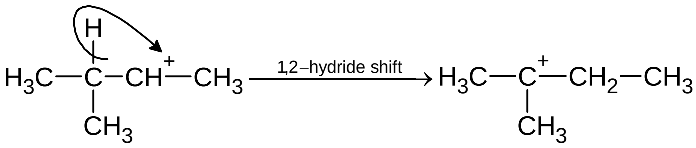
Step 2: Formation of 2° carbocation by the elimination of a water molecule



$$H_3C-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{\overset{+}{O}H_2}{|}}{CH}-CH_3 \xrightarrow{-H_2O} H_3C-\underset{\underset{CH_3}{|}}{CH}-\overset{+}{CH}-CH_3$$

2º Carbocation

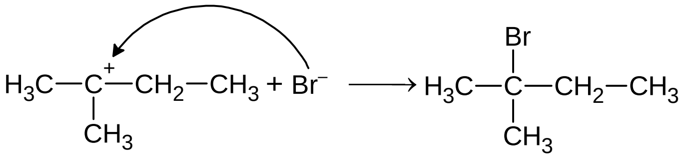
Step 3: Re-arrangement by the hydride-ion shift



$$H_3C-\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{C}}-\overset{+}{CH}-CH_3 \xrightarrow{1,2-\text{hydride shift}} H_3C-\overset{+}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_3$$

(Less stable) 3º Carbocation (more stable)

Step 4: Nucleophilic attack



$$H_3C-\overset{+}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_3 + Br^- \longrightarrow H_3C-\overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_3$$

2-Bromo-2-methylbutane

Board Level Questions

1. Why is it that phenol is acidic and hexanol is neutral towards a solution of NaOH? **[2 Marks 2001]**

Sol. The phenoxide ion phenol undergoes resonance stabilisation and thus phenol loses H^+ ion to show acidic character.

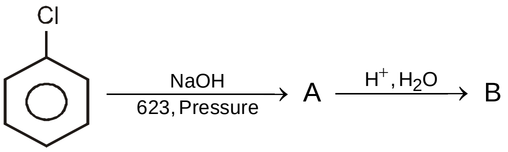
$$C_6H_5OH \longrightarrow \underset{\text{Resonance stabilised}}{C_6H_5O^-} + H^+$$

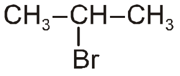
On the other hand the alkoxide ion shows no such resonance stabilisation.

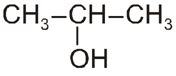
2. Identify A and B in each of the following sequences : **[3 Marks 2001]**

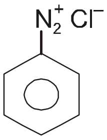
(i) $CH_3–CH=CH_2 \xrightarrow{HBr} A \xrightarrow{aq.\,KOH} B$

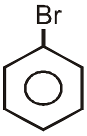
(ii) $C_6H_5NH_2 \xrightarrow[HCl]{NaNO_2} A \xrightarrow{CuBr} B$

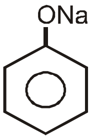
(iii)


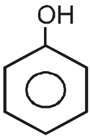
Sol. **(i)** A is

$CH_3–\underset{\displaystyle Br}{\underset{|}{CH}}–CH_3$

B is

$CH_3–\underset{\displaystyle OH}{\underset{|}{CH}}–CH_3$

(ii) A is


B is


(iii) A is


B is


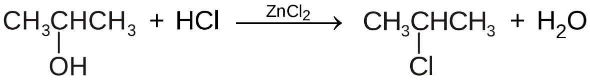
3. Arrange the following sets of compounds in order of their increasing boiling points :
pentan-1-ol, n-butane, pentanal, ethoxyethane. **[1 Marks 2002]**

Sol. n-Butane, ethoxyethane, pentanal and pentan-1-ol

4. Write one distinction test for Ethyl alcohol and 2-propanol : **[2 Marks 2002]**

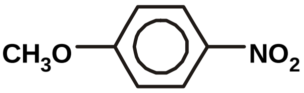
Sol. Treat the compound with Lucas reagent (conc. HCl + anhy. $ZnCl_2$) 2-propanol gives turbidity in 5 min whereas ethanol gives no turbidity at room temperature.

$$CH_3CH_2OH + HCl \xrightarrow{ZnCl_2} \text{No reaction}$$


$$CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_3 + HCl \xrightarrow{ZnCl_2} CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3 + H_2O$$

Turbidity appear
in 5 min

5. Write the IUPAC names of the following compounds :



Sol. 4-Nitro-1-methoxybenzene

6. Write the reaction and state the condition for each of the following conversion : **[3 Marks 2002]**

(i) Ethene to ethanol (ii) Chlorobenzene to phenol

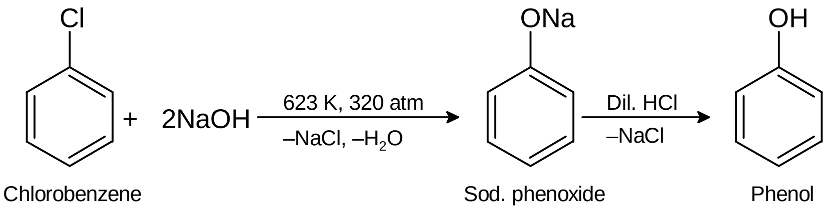
(iii) Ethanal to 2-propanol

(a) Write the reactions and their conditions only for the commercial preparation of phenol from cumene.

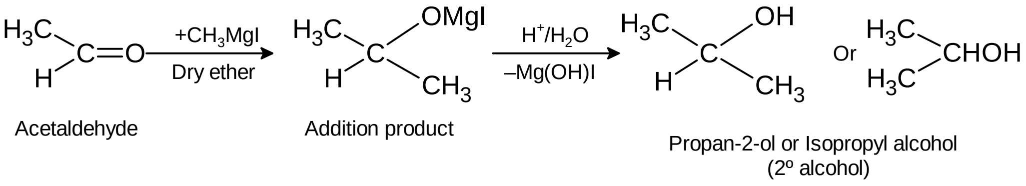
Sol. (a) (i) $H_2C{=}CH_2 + H_2O \xrightarrow{H^+} CH_3CH_2OH$

ethanol

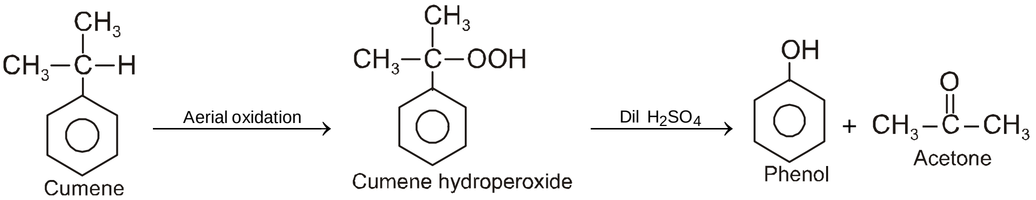
(ii)



(iii)



(b) Phenol is prepared commercially from cumene by its aerial oxidation and then treatment with aq. acid.



7. How would you distinguish ethanol and phenol? **[1 Marks 2004]**

Sol. Phenol gives violet colour complex with $FeCl_3$ solution, while no colourisation is obtained with ethanol. Ethanol gives iodoform test while phenol does not.

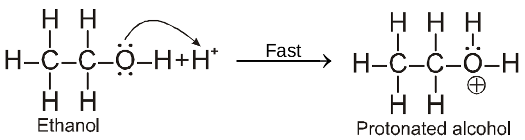
8. What happens when ethanol is heated with concentrated sulphuric acid at 453 K? Explain the mechanism of this reaction. **[2 Marks 2004]**

Sol. Ethanol undergoes dehydration by heating it with concentrated H_2SO_4 at 453 K.

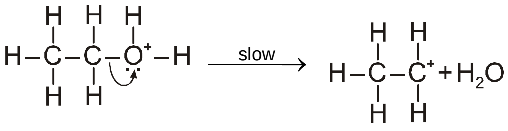
$$C_2H_5OH \xrightarrow[453\,K]{H_2SO_4} CH_2{=}CH_2 + H_2O$$

Mechanism : The dehydration of ethanol involves the following steps :

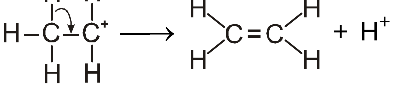
(i) Formation of protonated alcohol :



(ii) Formation of carbocation



(iii) Formation of ethene

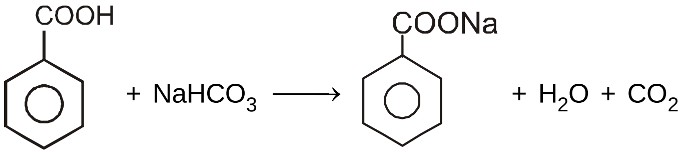


9. Describe simple chemical tests to distinguish between the following pairs of compounds :

(i) Phenol and Benzoic acid (ii) Diethyl ether and Propanol **[2 Marks 2004]**

Sol. **(i)** Add sodium bicarbonate to each compound.

With benzoic acid, CO_2 gas is evolved.



Phenol does not form CO_2

(ii) Add PCl_5 to each compound.

Diethyl ether does not react in cold but form ethyl chloride on warming.

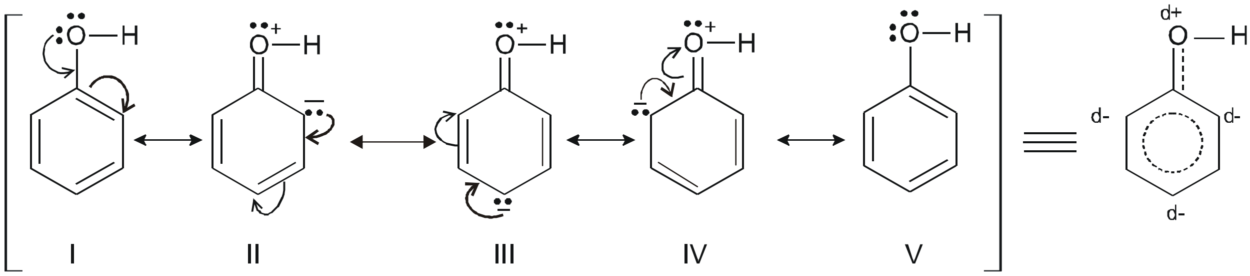
$$C_2H_5–O–C_2H_5 + PCl_5 \longrightarrow 2C_2H_5Cl + POCl_3$$

Propanol forms propyl chloride in cold.

$$CH_3CH_2CH_2OH + PCl_5 \longrightarrow CH_3CH_2Cl + POCl_3 + HCl$$

10. Explain how an OH group attached to a carbon in the bezene ring activates benzene towards electrophilic substitution. **[2 Marks 2005]**

Sol. The OH^- group is highly activating group. It directs the incoming groups to ortho and para positions in the ring because these positions become electron rich due to the electronic and mesomeric effects caused by the OH^- group as shown below :



11. Give reasons for the following : **[2 Marks 2006]**

(a) Ortho-nitrophenol is more acidic than ortho-methoxyphenol.

(b) Glycerol is used in cosmetics.

Sol. (a) In ortho-nitrophenol, the nitro($–NO_2$) group withdraws electrons from the benzene ring by inductive as well as resonance effects. It increases the stability of phenoxide ion.

In ortho-methoxyphenol, the electron donating methoxy group intensifies the negative charge on the phenoxide ion. The stability of phenoxide ion decreases. Hence nitrophenol is more acidic than o-methoxy phenol.

(b) Glycerol is used in cosmetics becuase it is hygroscopic in nature.

12. How may the following conversions be carried out:

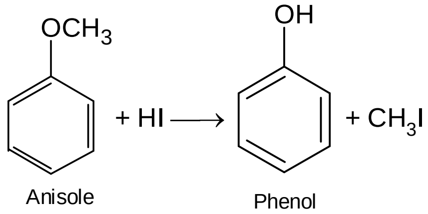
(i) Propene to propan-2-ol

(ii) Anisole to phenol (Write the reaction only) **[3 Marks 2007]**

Sol. (i) Propene to Propan-2-ol

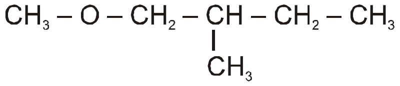
$$\underset{\text{Propene}}{CH_3-CH=CH_2} + H_2O \xrightarrow{H_2SO_4} H_3C—\underset{\underset{OH}{|}}{CH}—CH_3$$

Propan-2-ol

(ii) 

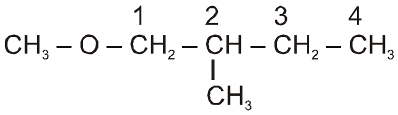
Anisole Phenol

13. Write the IUPAC name of the following compound : **[1 Marks 2008]**



$CH_3-O-CH_2-CH(CH_3)-CH_2-CH_3$

Sol.



$\overset{}{CH_3}-O-\overset{1}{CH_2}-\overset{2}{CH}(CH_3)-\overset{3}{CH_2}-\overset{4}{CH_3}$

3-Methyl-1-Methoxy butane.

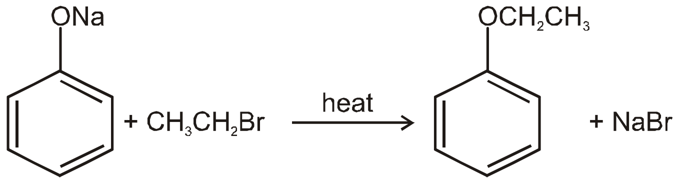
14. Name the reagents and write the chamical equations for the preparation of the following compounds by Williamson's synthesis : **[3 Marks 2008]**

(i) Ethoxybenzene

(ii) 2-Methy1-2-methoxypropane

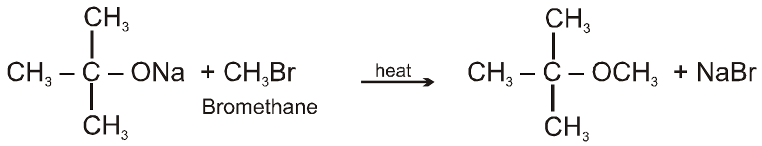
(b) Why do phenols not give the protonation reaction readily?

Sol. (a) (i)



Sod. phenoxide Bromoethane Ethoxybenzene

(ii)



$(CH_3)_2C(CH_3)-ONa + CH_3Br \xrightarrow{heat} (CH_3)_2C(CH_3)-OCH_3 + NaBr$

Sodium 2-methyl-2-propoxide 2-methyl-2-methoxypropane

(b) In phenols, the lone pairs of electrons on the oxygen atom are delocalised over the benzene ring due to resonance and hence are not easily avilable for protonation.

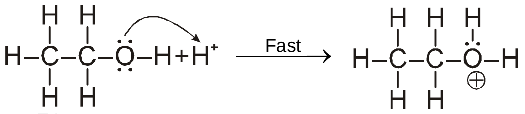
15. Explain the mechanism of acid dehydration of ethanol to yield ethene. **[2 Marks 2009]**

Sol. Dehydration of alcohol : Ethanol undergoes dehydration by heating it with concentrated H_2SO_4 at 453 K.

$$C_2H_5OH \xrightarrow[453\,K]{H_2SO_4} CH_2{=}CH_2 + H_2O$$

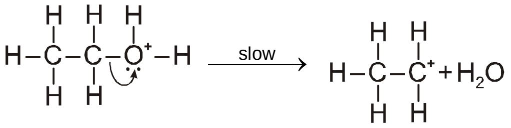
Mechanism : The dehydration of ethanol involves the following steps :

(i) Formation of protonated alcohol :

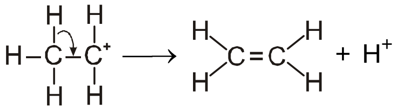


Ethanol Protonated alcohol

(ii) Formation of carbocation



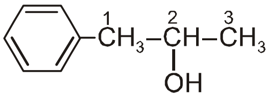
(iii) Formation of ethene



16. Write the structure of the molecule of compound whose IUPAC name is 1-phenylpropan-2-ol.

[1 Marks 2010]

Sol.

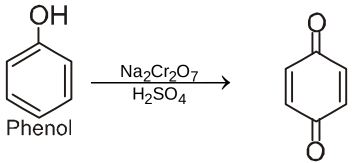


1-phenylpropan-2-ol

17. How would you convert the following : **[3 Marks 2010]**

(i) Phenol to benzoquinone (ii) Propanone to 2-methylpropan-2-ol (iii) Propene to propan-2-ol

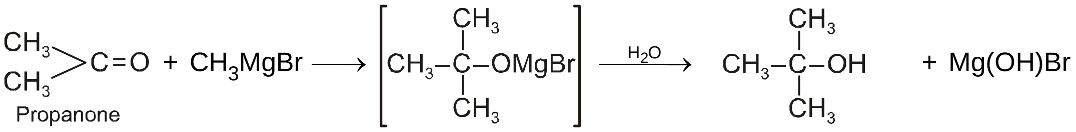
Sol. **(i)**



Phenol

benzoquinone

(ii)

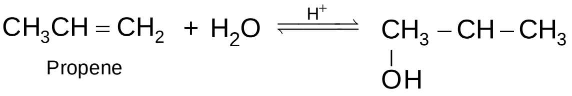


$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O + CH_3MgBr \longrightarrow \left[CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OMgBr\right] \xrightarrow{H_2O} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH + Mg(OH)Br$$

Propanone

2-methyl propan-2-ol

(iii)



$$CH_3CH=CH_2 + H_2O \overset{H^+}{\rightleftharpoons} CH_3-\underset{OH}{CH}-CH_3$$

Propene

propan-2-ol

18. How would you convert ethanol to ethene ? **[1 Marks 2011]**

Sol. When dehydration of ethanol is carried out at higher temperature (443 K), ethene is formed. The following chemical reaction takes place.

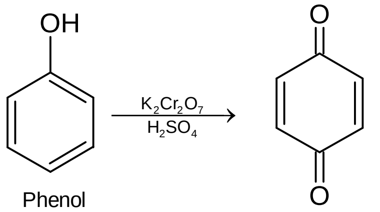
$$CH_3CH_2OH \xrightarrow[443K]{H_2SO_4} CH_2 = CH_2$$

19. How would you obtain the following: **[5 Marks 2011]**

(i) Benzoquinone from phenol (ii) 2-methyl propan-2-ol from methyl-magnesium bromide

(iii) Propane-2-ol from propene

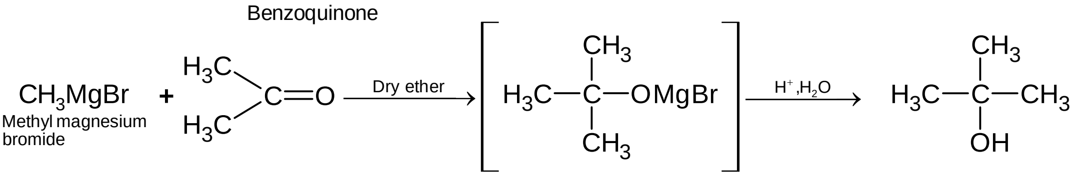
Sol. **(i)**



Phenol

Benzoquinone

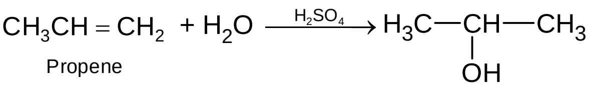
(ii)



$$\underset{\text{Methyl magnesium bromide}}{CH_3MgBr} + \begin{matrix}H_3C\\H_3C\end{matrix}\!\!>C=O \xrightarrow{\text{Dry ether}} \left[H_3C-\overset{CH_3}{\underset{CH_3}{C}}-OMgBr\right] \xrightarrow{H^+,H_2O} H_3C-\overset{CH_3}{\underset{OH}{C}}-CH_3$$

2-Methyl propan-2-ol

(iii)



$$CH_3CH=CH_2 + H_2O \xrightarrow{H_2SO_4} H_3C-\underset{OH}{CH}-CH_3$$

Propene

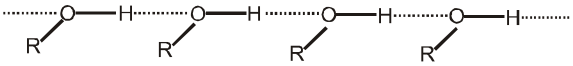
Propan-2-ol

20. Explain the following behaviours :

(i) Alcohols are more soluble in water than the hydrocarbons of comparable molecular masses.

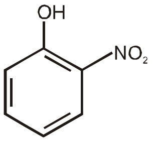
(ii) Ortho-nitrophenol is more acidic than ortho-methoxyphenol. **[2 Marks 2012]**

Sol. Alcohols undergo intermolecular H-bonding while hydrocarbons do not.

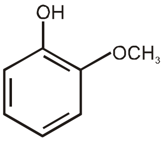


Hence, they are more soluble in water than the hydrocarbons of comparable molecular masses.

(ii)



o-Nitrophenol



o-Methoxyphenol

The nitro-group is an electron-withdrawing group. The presence of this group in the ortho position decreases the electron density in the O – H bond. As a result, it is easier to lose a proton. Also, the *o*-nitrophenoxide ion formed after the loss of protons is stabilized by resonance. Hence, *ortho* nitrophenol is a stronger acid. On the other hand, methoxy group is an electron-releasing group. Thus, it increases the electron density in the O – H bond and hence, the proton cannot be given out easily. For this reason, ortho-nitrophenol is more acidic than ortho-methoxy phenol.

21. (a) Write a suitable chemical equation to complete each of the following transformations: **[5 Marks 2012]**

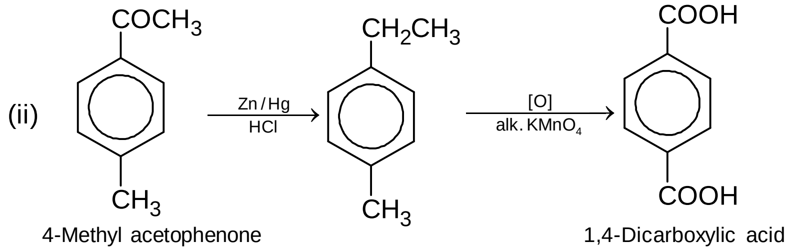
(i) Butan-1-ol to butanoic acid (ii) 4-methylacetophenone to benzene-1, 4-dicarboxylic acid

(b) An organic compound with molecular formula C9H10O forms 2,4-DNP derivative, oxidation it gives 1, 2-benzenedicarboxylic acid. Identify the compound.

Sol. (a)

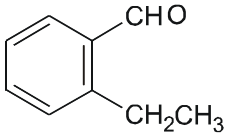
(i) $$\underset{\text{Butanol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow[\text{(ii) Dil. } H_2SO_4]{\text{(i) } K_2Cr_2O_7 / H_2SO_4} \underset{\text{Butanoic Acid}}{CH_3CH_2CH_2COOH}$$

(ii)



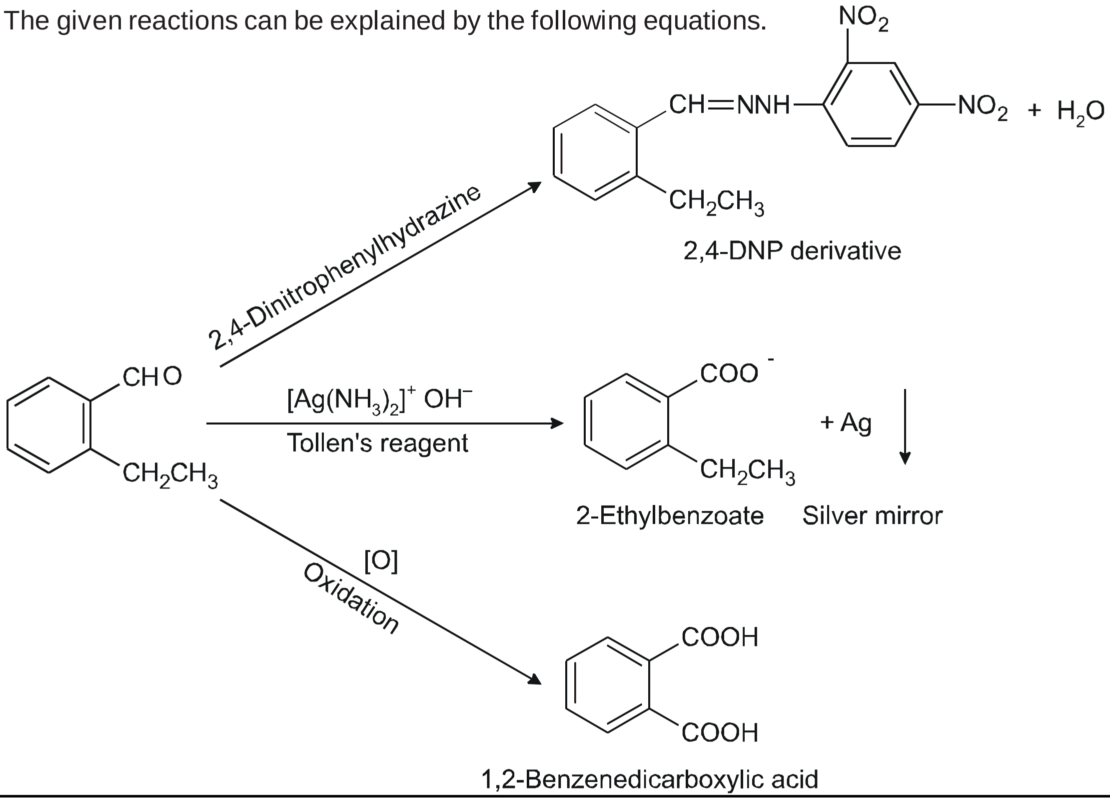
(b) It is given that the compound (with molecular formula $C_9H_{10}O$) forms 2, 4-DNP derivative and reduce Tollen's reagent. Therefore, the given compound must be an aldehyde.

Again, the compound undergoes Cannizzaro reaction and on oxidation gives 1, 2-benzenedi carboxylic acid. Therefore, the –CHO group is directly attached to a benzene ring and this benzaldehyde is ortho-ubstituted. Hence, the compound is 2.



2-Ethylbenzaldehyde

The given reactions can be explained by the following equations.



Home Test

1. n-propyl alcohol and isopropyl alcohol can be chemically distinguished by which reagent :
(A) PCl_5 (B) Reduction
(C) Oxidation with Potassium dichromate (D) Ozonolysis

2. Williamson's synthesis is used for the preparation of
(A) Alchols (B) Ketones (C) Ethers (D) Aldehydes

3. Which one of the following gases is liberated when ethyl alcohol is heated with methyl magnesium iodide?
(A) Methane (B) Ethane (C) Carbon dioxide (D) Propane

4. Phenol can be converted to o-hydroxybenzaldehyde by
(A) Kolbe's reaction (B) Reimer-Tiemann reaction
(C) Wurtz reaction (D) Sandmeyer's reaction

5. Phenol can be distinguished from ethanol by the following reagents except
(A) Sodium (B) $NaOH/I_2$ (C) Neutral $FeCl_3$ (D) Br_2/H_2O

6. The best method to prepare cyclohexene from cyclohexanol is by using
(A) HBr (B) Conc. H_3PO_4 (C) Conc. HCl + $ZnCl_2$ (D) Conc. HCl

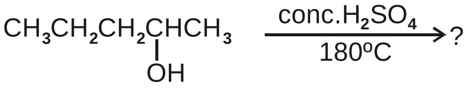
7. Which of the following compounds would be most soluble in water ?
(A) $CH_3CH_3CH_2CH_2CH_3$ (B) $CH_3CH_2CH_2CH_2CH_2OH$
(C) $CH_3CH_2CH_2CH_2OH$ (D) $CH_2(OH)CH_2CH_2CH_2OH$

8. What product is formed in

$$CH_3CH_2CH = CH_2 \xrightarrow[H_2SO_4]{H_2O} ?$$

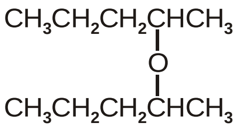
(A) 2-butanol (B) Equal amounts of 1-butanol and 2-butanol
(C) $CH_3CH_2CH(OH)CH_2OH$ (D) 1-butanol

9. What product is formed in



$$CH_3CH_2CH_2\underset{OH}{\underset{|}{C}}HCH_3 \xrightarrow[180^oC]{conc.H_2SO_4} ?$$

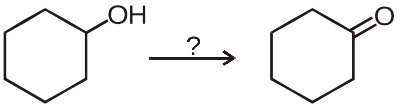
(A) Predominantly 2-pentene (B) Equal amounts of 1-pentene and 2-pentene

(C)


$$\begin{array}{c} CH_3CH_2CH_2CHCH_3 \\ | \\ O \\ | \\ CH_3CH_2CH_2CHCH_3 \end{array}$$

(D) predominantly 1-pentene

10. What reagent(s) would you use to carry out the following conversion ?

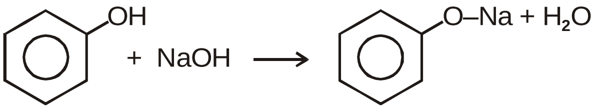


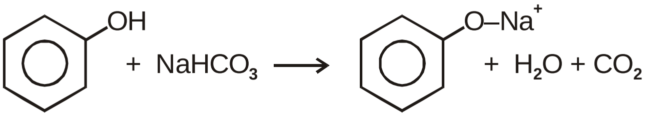
(A) Concentrated sulfuric acid at a temperature of 140 ºC
(B) Hydrogen gas and a nickel catalyst
(C) Sodium dichromate and sulfuric acid
(D) Concentrated sulfuric acid at a temperature of 180 ºC

11. Which of the following reactions will take place that is, which of the products shown will actually form ?

(A) $CH_3CH_2CH_2CH_2OH + NaHCO_3 \longrightarrow CH_3CH_2CH_2CH_2O^- Na^+ + H_2O + CO_2$

(B) $CH_3CH_2CH_2CH_2OH + NaOH \longrightarrow CH_3CH_2CH_2CH_2O^- Na^+ + H_2O$

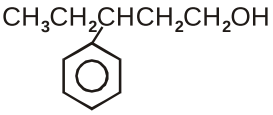
(C) 

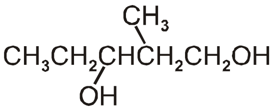
(D) 

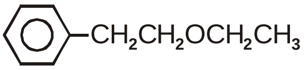
12. The boiling point of diethyl ether is nearly the same as that of

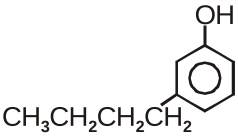
(A) Butyl alcohol (B) Dimethyl ether (C) Pentane (D) 1-pentanol

13. Which of the following is a phenol ?

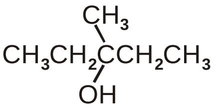
(A) 

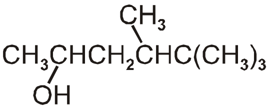
(B) 
$CH_3CH_2\underset{OH}{CH}\overset{CH_3}{CH}CH_2CH_2OH$

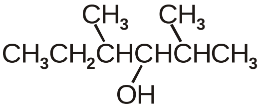
(C) 

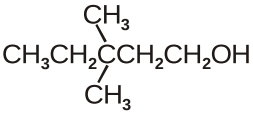
(D) 

14. Which of the following alcohols would be classified as atertiary (3^o) alcohol ?

(A) 
$CH_3CH_2\overset{CH_3}{\underset{OH}{C}}CH_2CH_3$

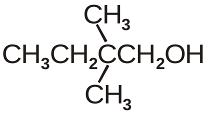
(B) 
$CH_3\underset{OH}{CH}CH_2\overset{CH_3}{CH}C(CH_3)_3$

(C) 
$CH_3CH_2\overset{CH_3}{CH}\underset{OH}{CH}\overset{CH_3}{CH}CH_3$

(D) 
$CH_3CH_2\overset{CH_3}{\underset{CH_3}{C}}CH_2CH_2OH$

15. Which of the following alcohols would be the least soluble in water ?

(A) $CH_3CH_2CH_2CH_2CH_2CH_2CH_2OH$ (B) $CH_3CH_2CH_2CH_2CH_2OH$

(C) 
$CH_3CH_2\overset{CH_3}{\underset{CH_3}{C}}CH_2OH$

(D) $CH_3CH_2CH_2OH$

16. A student needs to prepare 2-methylcyclohexanol. He combines methylcyclohexene, water, and a platinum catalyst. Will the reaction be successful ? Why or why not ?

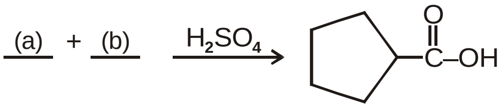
(A) The reaction will be successful because an alkene is readily hydrated to form an alcohol.

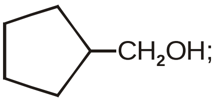
(B) The reaction will be successful because platinum allows the –OH group to add to the less substituted carbon of the double bond.

(C) Very little, if any, 2-methylcyclohexanol would form under these conditions because dilute sulfuric acid, not platinum, is needed as a catalyst.

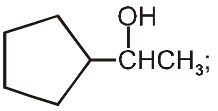
(D) Very little, if any, 2-methylcyclohexanol would form under these conditions because the –OH preferentially binds to the same carbon to which the methyl group is attached. In addition, a different catalyst is needed.

17. Complete the following reaction :

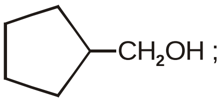


(A) 

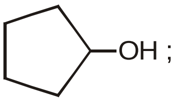
(b) O_2

(B) 

(b) CrO_3

(C) 

(b) $K_2Cr_2O_7$

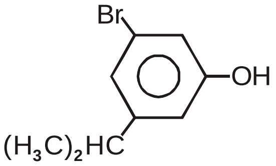
(D) 

(b) $K_2Cr_2O_7$

18. Glycerol is not used in which of the following formulations ?

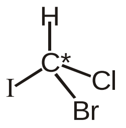
(A) The formulation of plasticclays to prevent dehydration
(B) The formlation of some medicines
(C) The formulation of antifreeze
(D) The formulation of hand lotion

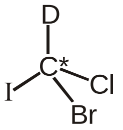
19. The correct name for the compound shown is :

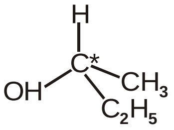


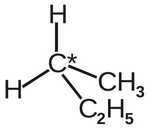
(A) 1-isopropyl-3-bromo-5-hydroxybenzene
(B) 3-bromo-5-propylphenol
(C) 3-bromo-5-isopropylphenol
(D) 1-bromo-3-hydroxy-5-isopropylbenzene

20. In which of the following molecules carbon atom marked with asterisk (*) is asymmetric ?

(i) 

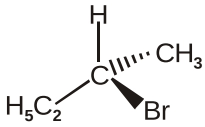
(ii) 

(iii) 

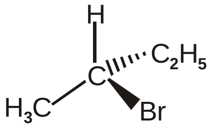
(iv) 

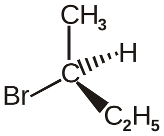
(A) (a), (b), (c), (d)
(B) (a), (b), (c)
(C) (b), (c), (d)
(D) (a), (c), (d)

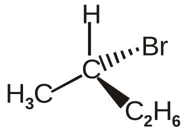
21. Which of the following structures is enantiomeric with the molecule (A) given below :

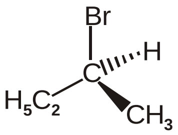


(A)

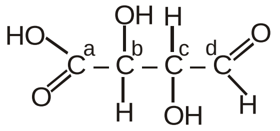
(A) 

(B) 

(C) 

(D) 

22. Which of the carbon atoms present in the molecule given below are asymmetric ?



(A) a, b, c, d
(B) b, c
(C) a, d
(D) a, b, c

23. Write down the structure and IUPAC name for neo-pentylbromide.

24. How many alcohols with molecular formula $C_4H_{10}O$ are chiral in nature?

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

25. What is the correct order of reactivity of alcohols in the following reaction ?

$$R-OH + HCl \xrightarrow{ZnCl_2} R-Cl + H_2O$$

(A) 1° > 2° > 3° (B) 1° < 2° > 3° (C) 3° > 2° > 1° (D) 3° > 1° > 2°

26. CH_3CH_2OH can be converted into CH_3CHO by ______________.

(A) catalytic hydrogenation (B) treatment with $LiAlH_4$

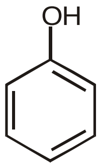
(C) treatment with pyridinium chlorochromate (D) treatment with $KMnO_4$

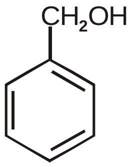
27. The process of converting alkyl halides into alcohols involves_____________.

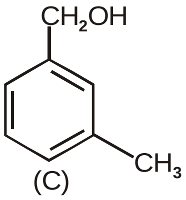
(A) addition reaction (B) substitution reaction

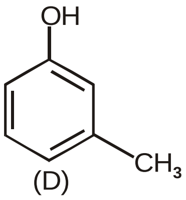
(C) dehydrohalogenation reaction (D) rearrangement reaction

28. Which of the following compounds is aromatic alcohol ?


(A)


(B)

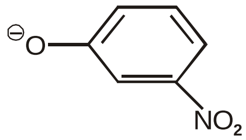

(C)


(D)

(A) A, B, C, D (B) A, D (C) B, C (D) A

29. Which of the following species can act as the strongest base?

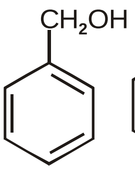
(A) $^{\ominus}OH$ (B) $^{\ominus}OR$ (C) $^{\ominus}OC_6H_5$ (D)

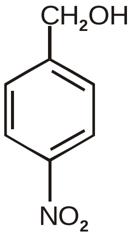


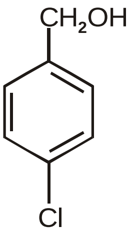
30. Which of the following compounds will react with sodium hydroxide solution in water?

(A) C_6H_5OH (B) $C_6H_5CH_2OH$ (C) $(CH_3)_3$ COH (D) C_2H_5OH

31. Mark the correct increasing order of reactivity of the following compounds with HBr/HCl.


(a)


(b)


(c)

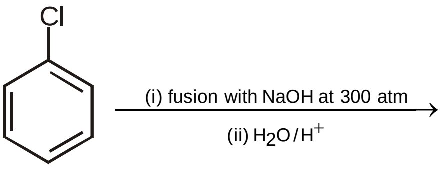
(A) a < b < c (B) b < a < c (C) b < c < a (D) c < b < a

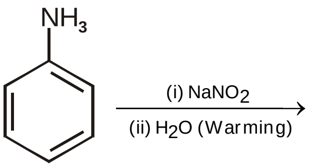
32. Which of the following are used to convert RCHO into RCH_2OH ?

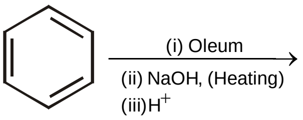
(A) H_2/Pd (B) $LiAlH_4$

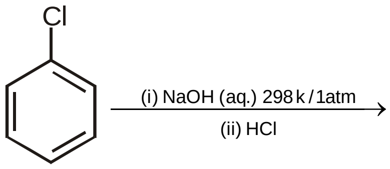
(C) $NaBH_4$ (D) Reaction with RMgX followed by hydrolysis

33. Which of the following reactions will yield phenol ?

(A)


(B)


(C)


(D)


34. Which of the following reagents can be used to oxidise primary alcohols to aldehydes?

(A) CrO_3 in anhydrous medium.
(B) $KMnO_4$ in acidic medium.
(C) Pyridinium chlorochromate.
(D) Heat in the presence of Cu at 573K.

35. Phenol can be distinguished from ethanol by the reactions with _________.

(*A) Br_2/water
(B) Na
(C) Neutral $FeCl_3$
(D) All the above

V. Assertion and Reason Type

Note : In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

36. **Assertion :** Addition reaction of water to but-1-ene in acidic medium yields butan-1-ol

Reason : Addition of water in acidic medium proceeds through the formation of primary carbocation.

(A) Assertion and reason both are correct and reason is correct explanation of assertion.
(B) Assertion and reason both are wrong statements.
(C) Assertion is correct but reason is wrong statement.
(D) Assertion is wrong but reason is correct statement.
(E) Assertion and reason both are correct statements but reason is not correct explanation of assertion.

37. **Assertion :** *p*-nitrophenol is more acidic than phenol.

Reason : Nitro group helps in the stabilisation of the phenoxide ion by dispersal of negative charge due to resonance.

(A) Assertion and reason both are correct and reason is correct explanation of assertion.
(B) Assertion and reason both are wrong statements.
(C) Assertion is correct but reason is wrong statement.
(D) Assertion is wrong but reason is correct statement.
(E) Assertion and reason both are correct statements but reason is not correct explanation of assertion.

38. **Assertion :** Boiling points of alcohols and ethers are high.

Reason : They can form intermolecular hydrogen-bonding.

(A) Assertion and reason both are correct and reason is correct explanation of assertion.
(B) Assertion and reason both are wrong statements.
(C) Assertion is correct but reason is wrong statement.
(D) Assertion is wrong but reason is correct statement.
(E) Assertion and reason both are correct statements but reason is not correct explanation of assertion.

39. **Assertion :** Like bromination of benzene, bromination of phenol is also carried out in the presence of Lewis acid.

Reason : Lewis acid polarises the bromine molecule.

(A) Assertion and reason both are correct and reason is correct explanation of assertion.

(B) Assertion and reason both are wrong statements.

(C) Assertion is correct but reason is wrong statement.

(D) Assertion is wrong but reason is correct statement.

(E) Assertion and reason both are correct statements but reason is not correct explanation of assertion.

40. **Assertion :** *o*-Nitrophenol is less soluble in water than the *m*- and *p*-isomers.

Reason : *m*- and *p*- Nitrophenols exist as associated molecules.

(A) Assertion and reason both are correct and reason is correct explanation of assertion.

(B) Assertion and reason both are wrong statements.

(C) Assertion is correct but reason is wrong statement.

(D) Assertion is wrong but reason is correct statement.

(E) Assertion and reason both are correct statements but reason is not correct explanation of assertion.

41. **Assertion :** Phenol forms 2, 4, 6 – tribromophenol on treatment with Br_2 in carbon disulphide at 273K.

Reason : Bromine polarises in carbon disulphide.

(A) Assertion and reason both are correct and reason is correct explanation of assertion.

(B) Assertion and reason both are wrong statements.

(C) Assertion is correct but reason is wrong statement.

(D) Assertion is wrong but reason is correct statement.

(E) Assertion and reason both are correct statements but reason is not correct explanation of assertion.