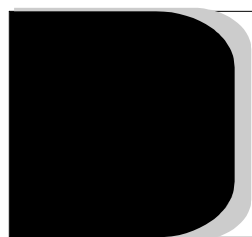




CLASSROOM STUDY
PACKAGE

CHEMISTRY

Alcohol Ether Phenol



JEE EXPERT

CONTENTS

S. NO.	Page No.
1. ALCOHOL	1 - 27
2. ETHER	28 - 34
3. PHENOL	35 - 49
4. EXERCISE -I	50 - 65
5. EXERCISE -II	66 - 70
6. EXERCISE -III	71 - 76
7. ANSWER KEY	77 - 77

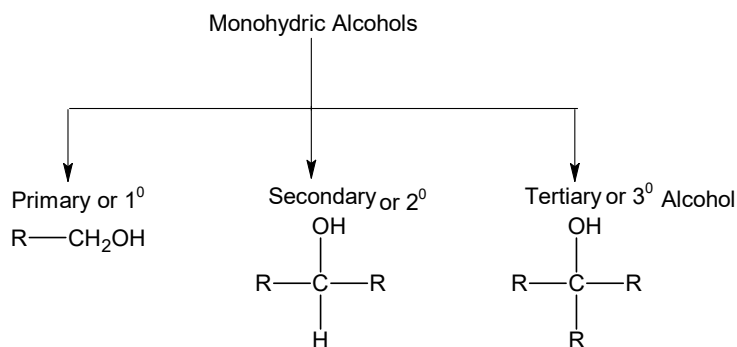
ALCOHOL, ETHER & PHENOL

INTRODUCTION :

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

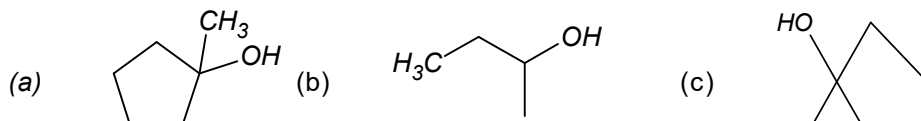
The substitution of a hydrogen atom in a hydrocarbon by an alkoxy or aryloxy group ($R-O/Ar-O$) yields another class of compounds known as '**Ethers**', for example, CH_3OCH_3 (dimethyl ether) or by substituting the hydrogen atom of hydroxyl group of an alcohol or phenol by an alkyl or aryl group.

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



Solved Example :

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



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

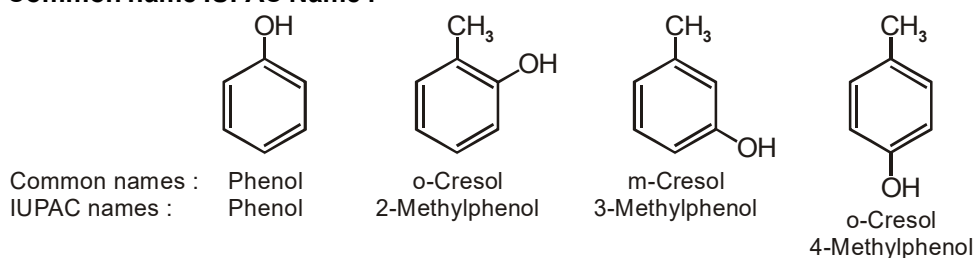
ALCOHOLS :

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
$\begin{array}{c} CH_3-CH-CH_3 \\ \\ OH \end{array}$	Isopropyl alcohol	Propan-2-ol
$CH_3-CH_2-CH_2-CH_2-OH$	n-Butyl alcohol	Butan-1-ol
$\begin{array}{c} CH_3-CH-CH_2-CH_3 \\ \\ OH \end{array}$	sec-Butyl alcohol	Butan-2-ol
$\begin{array}{c} CH_3-CH-CH_2-CH_3 \\ \\ OH \end{array}$	Isobutyl alcohol	2-Methylpropan-1-ol
$\begin{array}{c} CH_3 \\ \\ CH_3-C-OH \\ \\ CH_3 \end{array}$	tert-Butyl alcohol	2-Methylpropan-2-ol
$\begin{array}{c} CH_2-CH-CH_2 \\ \quad \quad \\ OH \quad OH \quad OH \end{array}$	Glycerol	Propan-1,2,3-triol

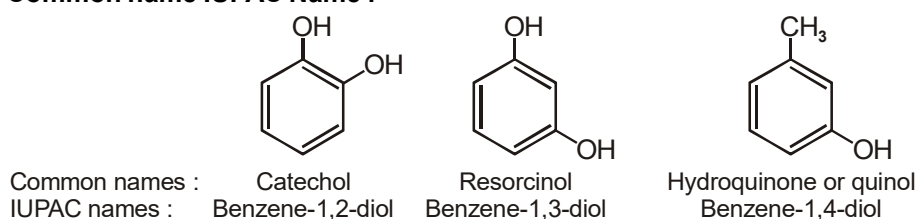
- (b) **Phenols** : The simplest hydroxy derivative of benzene is phenol. It is its common name and also an accepted IUPAC name.

Common name IUPAC Name :



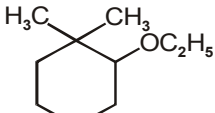
Dihydroxy derivatives of benzene are known as 1,2-, 1, 3-and 1, 4-benzenediol.

Common name IUPAC Name :



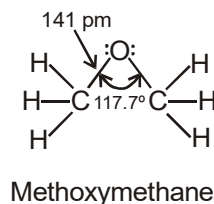
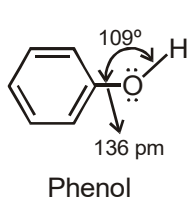
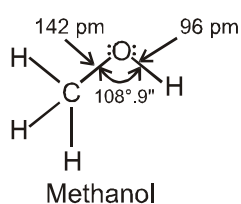
- (c) **Ethers** : Common names of ethers are derived from the names of alkyl/aryl groups written as separate words in alphabetical order and adding the word 'ether' at the end. For example, $\text{CH}_3\text{OC}_2\text{H}_5$ is ethylmethyl ether.

Table : Common and IUPAC names of some Ethers :

Compound	Common name	IUPAC name
CH_3OCH_3	Dimethyl ether	Methoxymethane
$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	Diethyl ether	Ethoxyethane
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3$	Methyl n-propyl ether	1-Methoxypropane
$\text{C}_6\text{H}_5\text{OCH}_3$	Methylphenyl ether (Anisole)	Methoxybenzene (Anisole)
$\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_3$	Ethylphenyl ether (Phenetole)	Ethoxybenzene
$\text{C}_6\text{H}_5\text{O}(\text{CH}_2)_6\text{CH}_3$	Heptylphenyl ether	1-Phenoxyheptane
$\text{CH}_3\text{O}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$	methyl isopropyl ether	2-Methoxypropane
$\text{C}_6\text{H}_5-\text{O}-\text{CH}_2-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$	Phenylisopentyl ether	3-Methylbutoxybenzene
$\text{CH}_3-\text{O}-\text{CH}_2-\text{CH}_2-\text{OCH}_3$	—	1,2-Dimethoxyethane
	—	2-Ethoxy-1,1-dimethylcyclohexane

Structures of functional groups :

In alcohols, the oxygen of the $-\text{OH}$ 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.



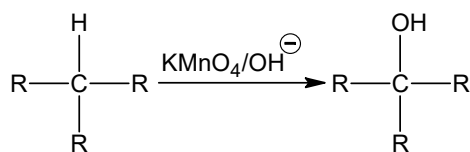
Structures of methanol, phenol and methoxymethane

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

PREPARATION OF ALCOHOLS

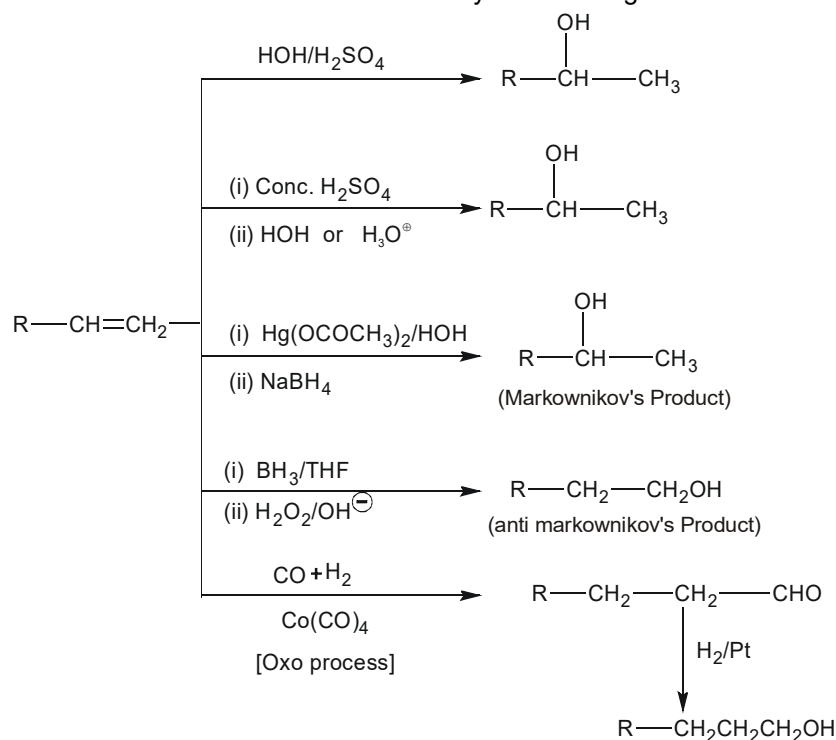
1. From Alkanes :

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



2. From Alkenes :

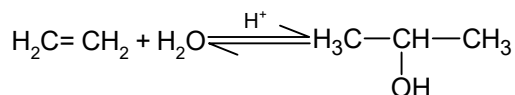
Alkenes can be converted into alcohol by the following reactions:



From alkenes :

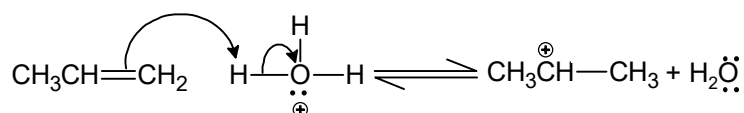
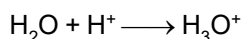
A wide variety of electrophilic additions involve similar mechanisms. First, a strong electrophile attracts the loosely held electrons from the π -bond of an alkene. The electrophile forms a sigma bond to one of the carbons of the (former) double bond, while the other carbon becomes a carbocation. The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

By acid-catalysed hydration :

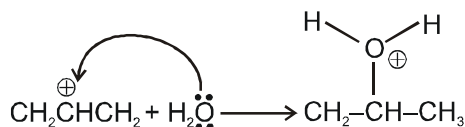


Mechanism:

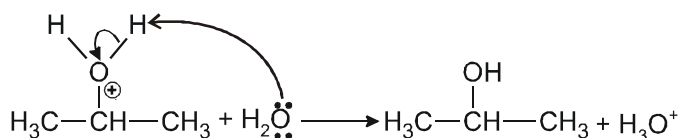
Step 1 - Protonation of alkene by electrophilic attack of H_3O^+ to form carbocation



Step 2 - Nucleophilic attack of water on the carbocation

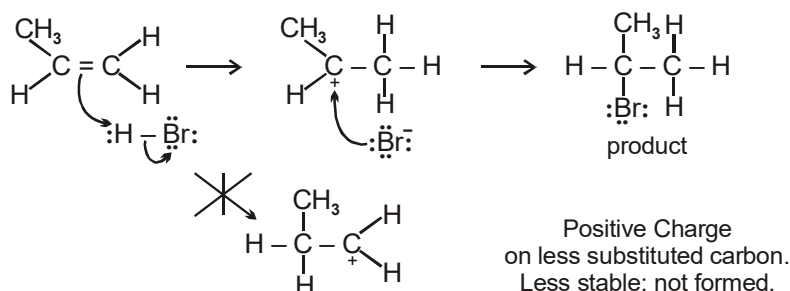


Step 3 - Deprotonation to form alcohol



Example :

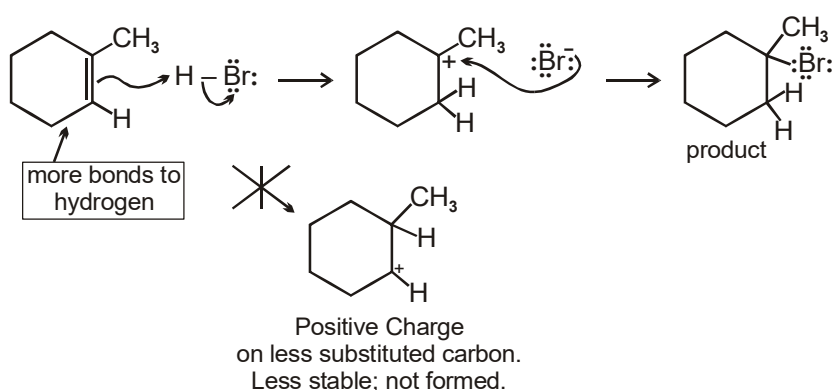
The ionic addition of HBr to propene shows protonation of the less substituted carbon to give the more substituted carbocation. Reaction with bromide ion completes the addition.



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

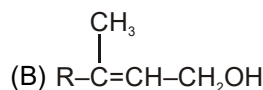
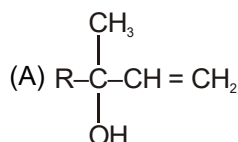
MARKOVNIKOV'S RULE : The addition of a proton acid to the double bond of an alkene result in a product with the acid proton bonded to the carbon atom that already holds the greater number of hydrogen atoms. This is the original statement of Markovnikov's rule. Reactions that follow this rule are said 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 electrophile adds in such a way as to generate the most stable intermediate.

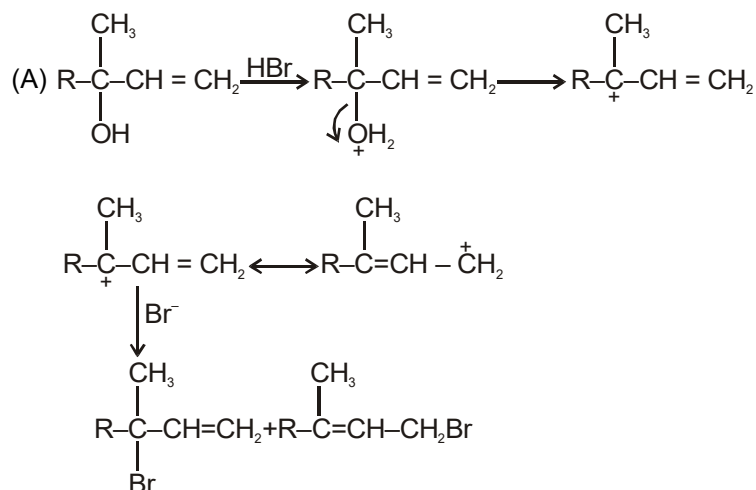


Solved Example :

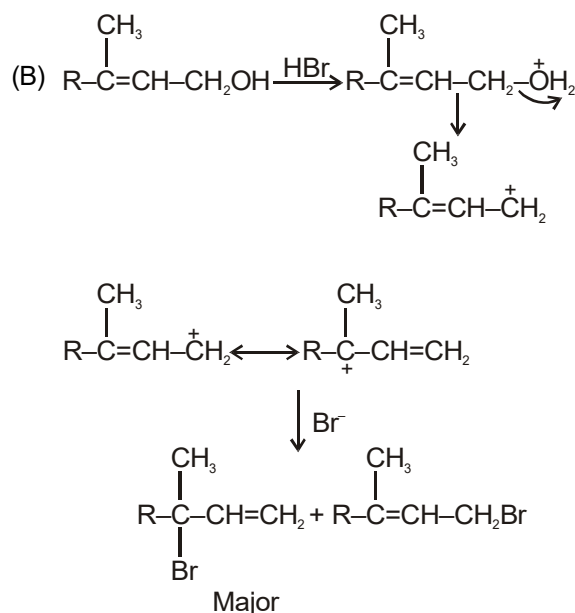
Qus. The following two alcohols give the same bromo compound when treated with HBr. Explain.



Ans. The reaction in each case proceeds according to S_N1 mechanism. The course of the reaction is shown here. More stable cation will give major product.



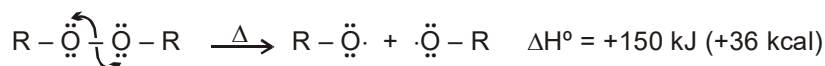
Major



Major

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

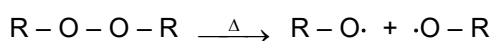
In 1933, M. S. Kharasch and F.W. Mayo showed that anti-Markovnikov products result from addition of HBr (but not HCl or HI) in the presence of peroxides. Peroxides give rise to free radicals that act as catalysts to accelerate the addition, causing it to occur by a different mechanism. The oxygen-oxygen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



Alkoxy radicals ($\text{R}-\text{O}\cdot$) catalyze the anti-Markovnikov addition of HBr. The mechanism of this free-radical chain reaction is shown next.

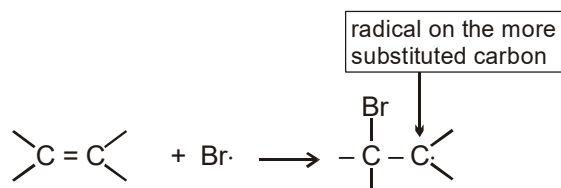
Free-Radical Addition of HBr to Alkenes :

Initiation : Radicals are formed

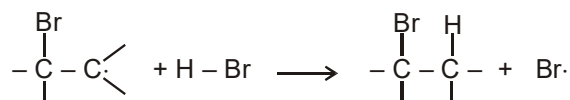


Propagation : A radical reacts to generate another radical.

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



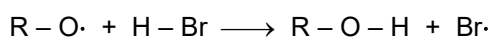
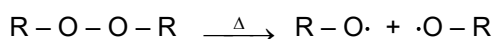
Step-II : The alkyl radical abstracts a hydrogen atom from HBr to generate the product and a bromine radical.



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

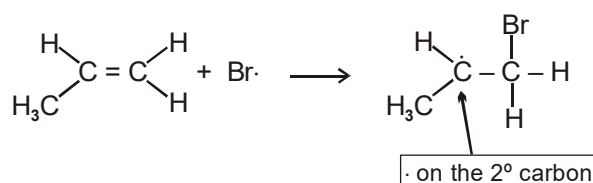
Example : Free-radical addition of HBr to propene.

Initiation : Radicals are formed.

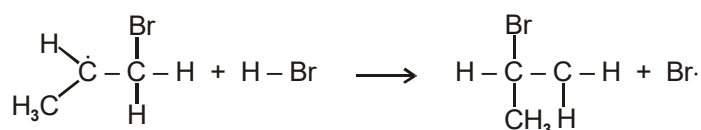


Propagation : A radical reacts to generate another radical.

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.



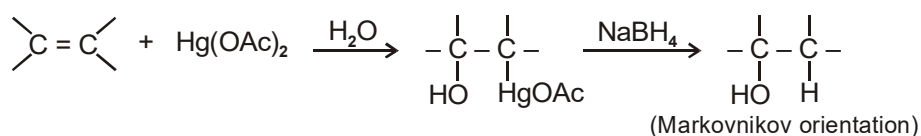
The bromine radical generated in Step 2 goes on to react in Step 1, continuing the chain.

Hydration by Oxymercuration Demercuration (OMDM) :

Many alkanes do not easily undergo hydration in aqueous acid.

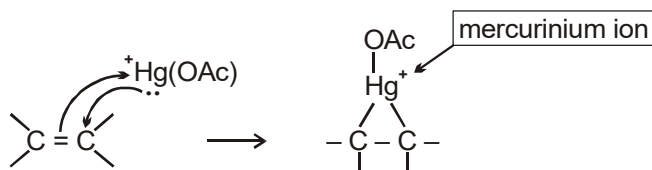
Oxymercuration-demercuration is another method for converting alkenes to alcohols with Markovnikov orientation.

Oxymercuration-Demercuration :

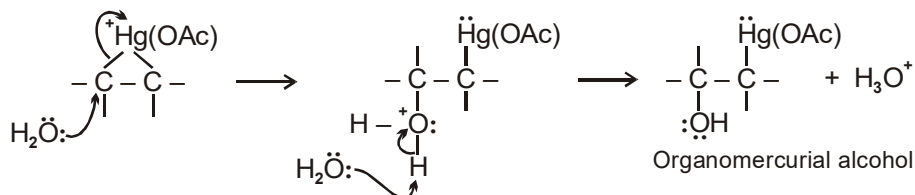


Oxymercuration of an Alkene :

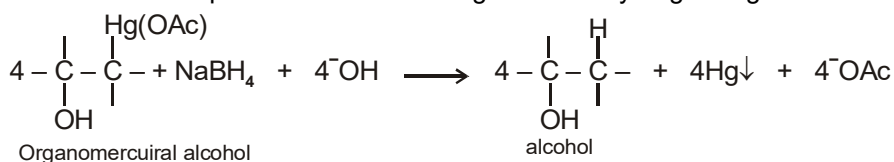
Step-I : Electrophilic attack forms a mercurinium ion.



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

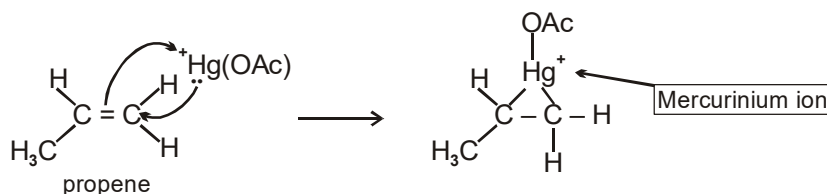


Demercuration replaces the mercuric fragment with hydrogen to give the alcohol.

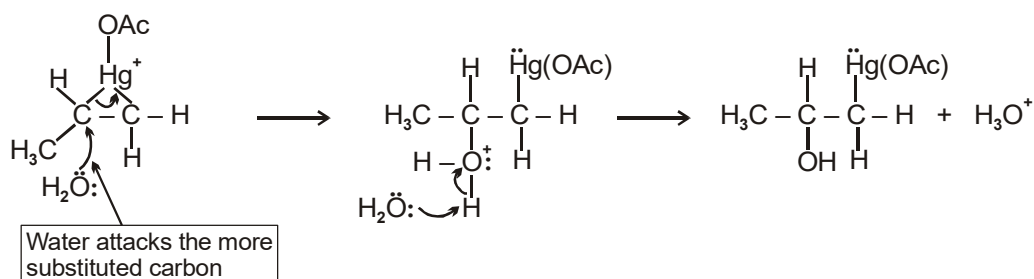


Example : Oxymercuration-demercuration of propene.

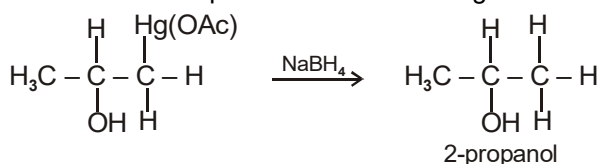
Step-1 : Electrophilic attack forms a mercurinium ion.



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



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

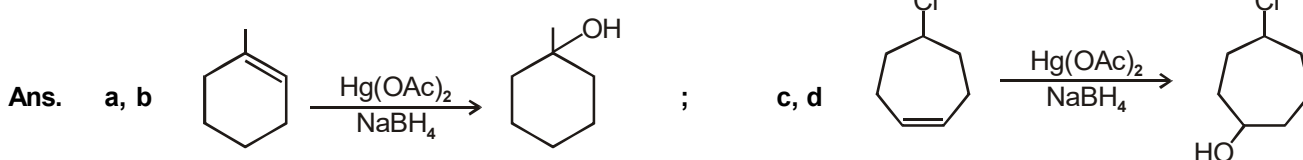


Solved Example :

Qus. Predict the major products of the following reactions.

- (a) 1-methylcyclohexene + aqueous $\text{Hg}(\text{OAc})_2$
(c) 4-chlorocycloheptene + $\text{Hg}(\text{OAc})_2$ in CH_3OH

- (b) The product from part (a), treated with NaBH_4
(d) The product from part (c), treated with NaBH_4



Solved Example :

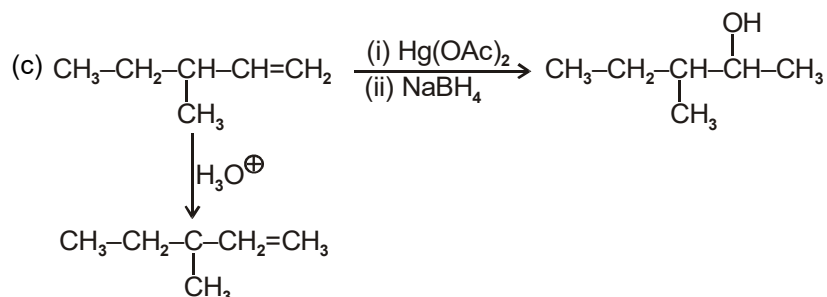
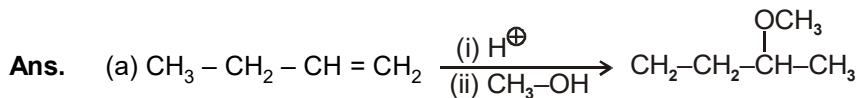
Qus. Show how you would accomplish the following synthetic conversions.

(a) 1-butene \rightarrow 2-methoxybutane

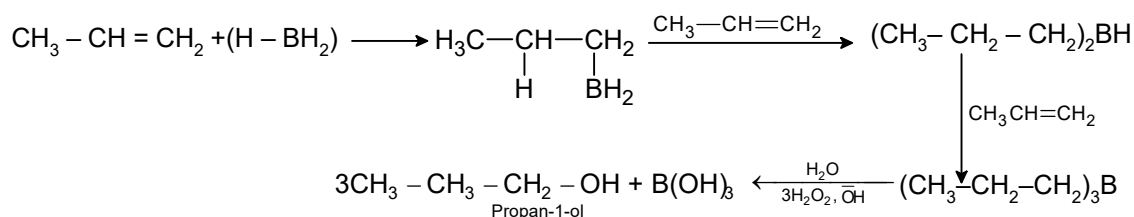
(b) 1-iodo-2-methylcyclopentane \rightarrow 1-methylcyclopentanol

(c) 3-methyl-1-pentene \rightarrow 3-methyl-2-pentanol

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



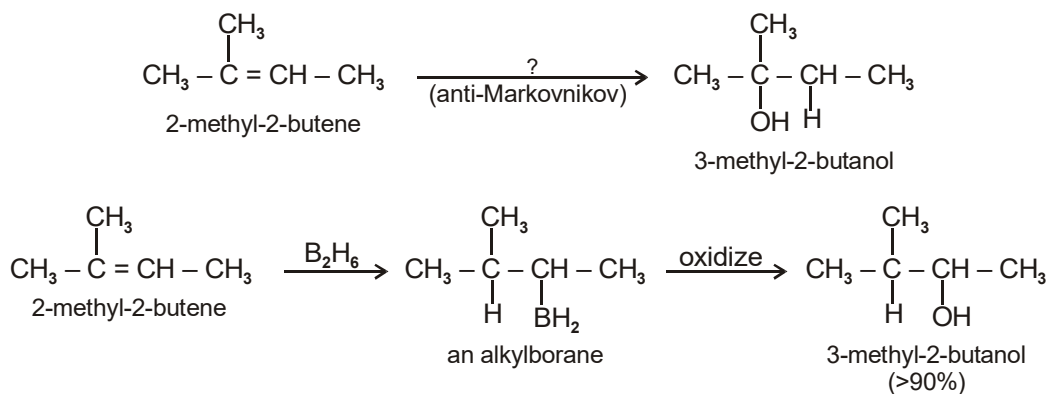
Hydration by hydroboration-oxidation (HBO) :



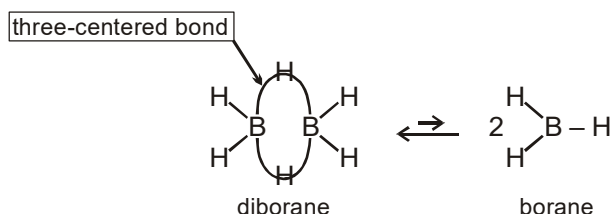
The product so formed looks as if it were formed by the addition of water to the alkene in a way opposite to Markovnikov's rule.

Hydroboration of Alkenes :

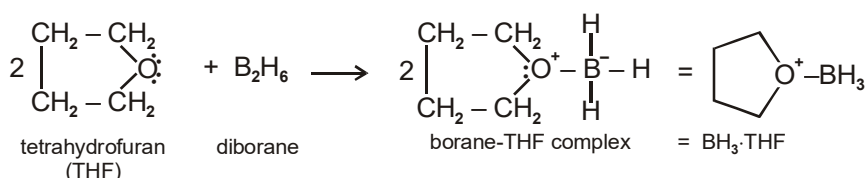
We have seen two methods for hydrating an alkene with Markovnikov orientation. What if we need to convert an alkene to the anti-Markovnikov alcohol? For example, the following transformation cannot be accomplished using the hydration procedures covered thus far.



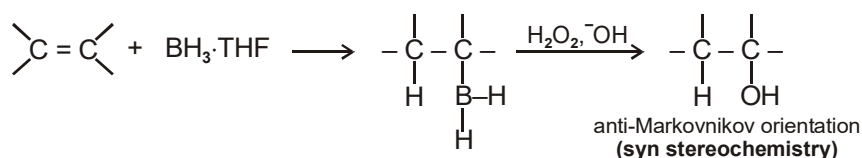
Diborane (B_2H_6) is a dimer composed of two molecules of borane (BH_3). The bonding in diborane is unconventional, using three-centered (banana-shaped) bonds with protons in the middle of them. Diborane is in equilibrium with a small amount of borane (BH_3), a strong Lewis acid with only six valence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



Diborane 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.

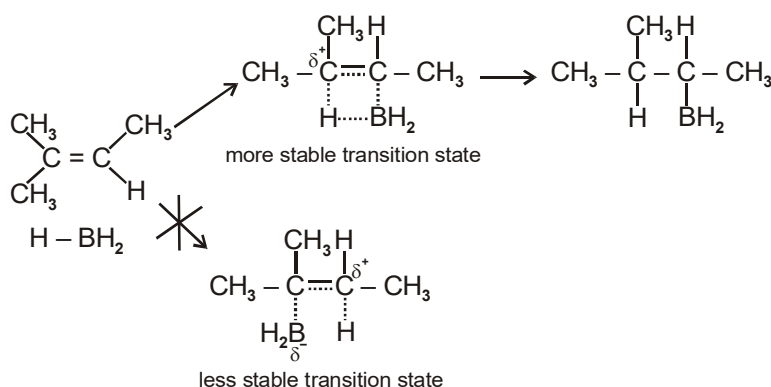


Hydroboration-oxidation :



Mechanism : Hydroboration of an Alkene :

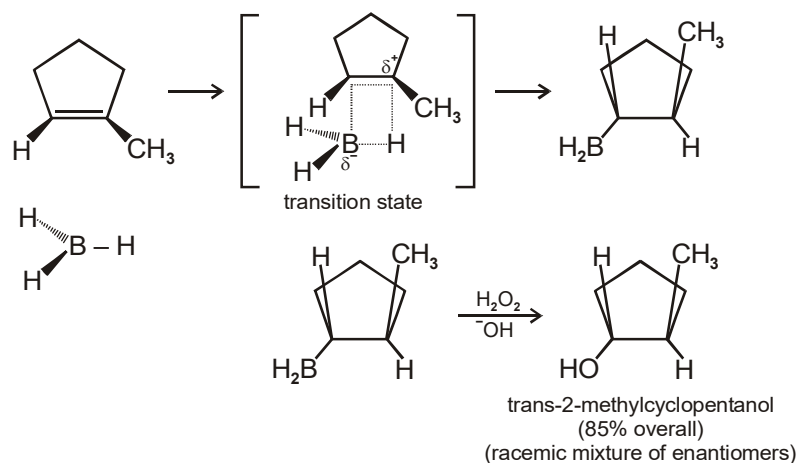
Borane adds to the double bond in a single step. Boron adds to the less hindered, less substituted carbon, and hydrogen adds to the more substituted carbon.



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.)

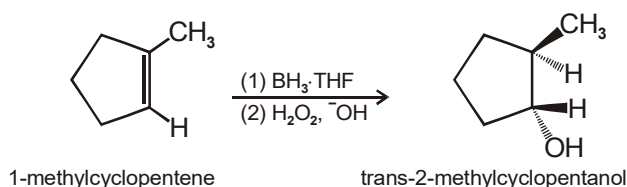
The stereochemistry of the hydroboration-oxidation of 1-methylcyclopentene is shown next. Boron and hydrogen add to the same face of the double bond (syn) to form a trialkylborane. Oxidation of the trialkylborane replaces boron with a hydroxyl group in the same stereochemical position. The product is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



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.

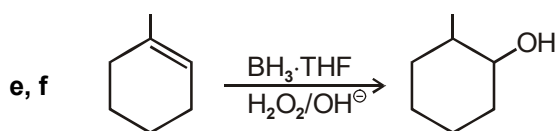
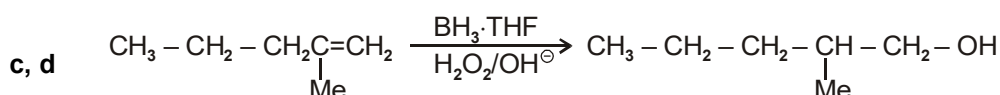
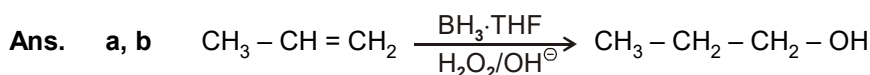


The 2-methylcyclopentanol that results from this synthesis is the pure trans isomer.

Solved Example :

Qus. Predict the major products of the following reactions.

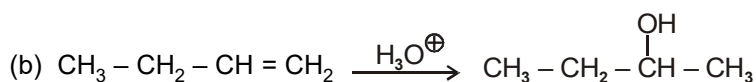
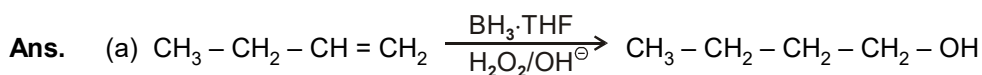
- | | |
|--|--|
| (a) propene + $\text{BH}_3 \cdot \text{THF}$ | (b) The product from part (a) + $\text{H}_2\text{O}_2/\text{OH}^-$ |
| (c) 2-methyl-2-pentene + $\text{BH}_3 \cdot \text{THF}$ | (d) The product from part (c) + $\text{H}_2\text{O}_2/\text{OH}^-$ |
| (e) 1-methylcyclohexene + $\text{BH}_3 \cdot \text{THF}$ | (f) The product from part (e) + $\text{H}_2\text{O}_2/\text{OH}^-$ |



Solved Example :

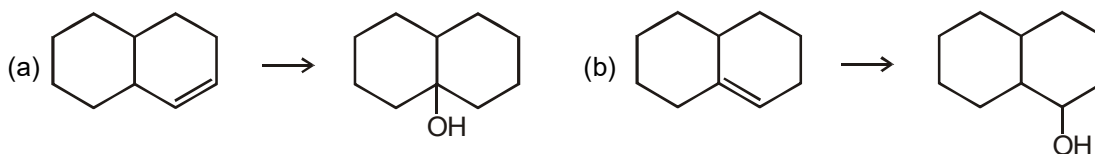
Qus. Show how you would accomplish the following synthetic conversions.

- (a) 1-butene \rightarrow 1-butanol
(b) 1-butene \rightarrow 2-butanol



Solved Example :

Qus. Show how you would accomplish the following transformations.



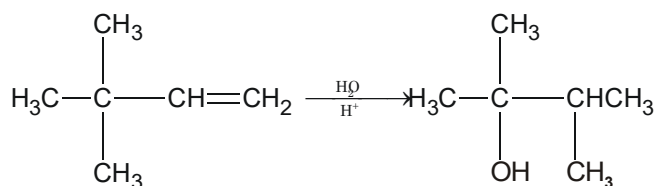
(c) 1-methylcycloheptanol \rightarrow 2-methylcycloheptanol

Ans. (a) by H_3O^+

(b) by HBO

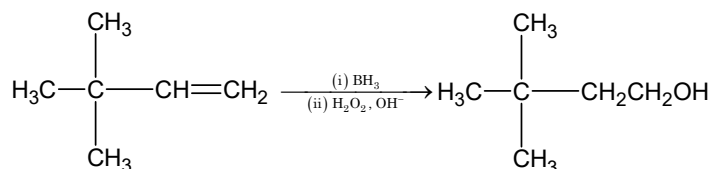
Hydration, hydroboration and oxymercuration – demercuration of alkenes.

Hydration :



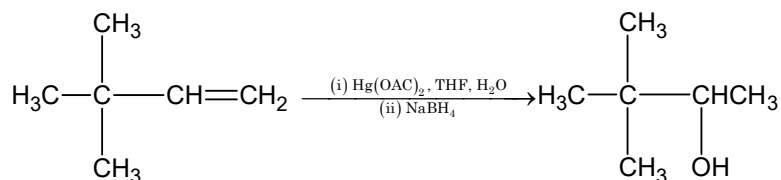
According to Markovnikov's rule, rearrangement possible

Hydroboration :



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

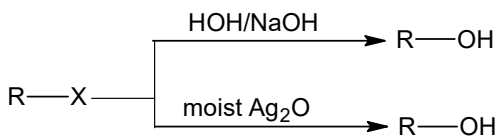
Oxymercuration – demercuration :



According to Markovnikov's rule but rearrangement not possible

3. From alkyl halides

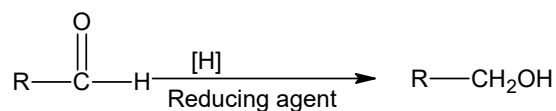
Alkyl halides give alcohol with KOH/NaOH or with moist Ag_2O .



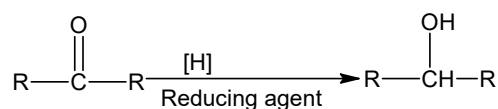
4. Reduction of aldehydes and ketones

(a) **Reduction by reducing agents**

(i) Aldehyde gives primary alcohol

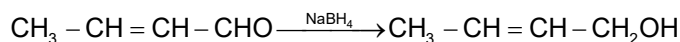


(ii) Ketone gives secondary alcohol

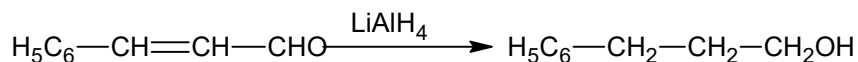


Reducing agents

- (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



- 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.

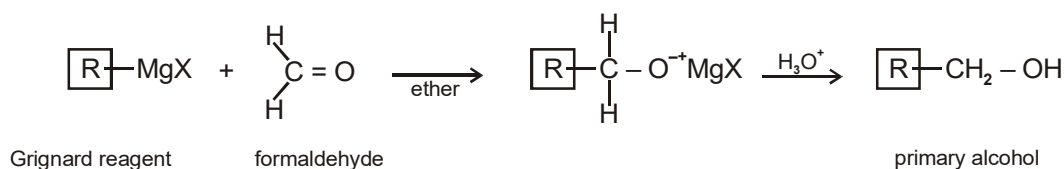


(b) Reduction by Grignard reagents

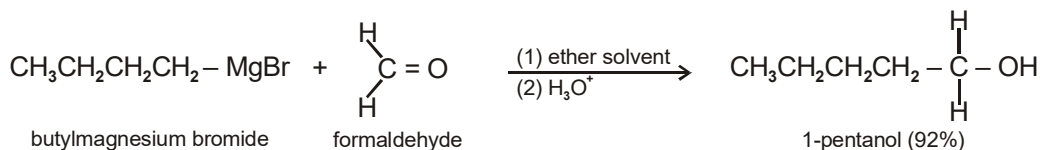
Addition followed by hydrolysis

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.

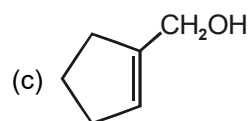
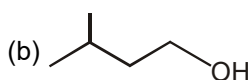
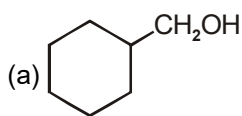


For example,

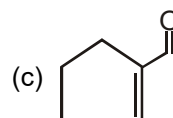
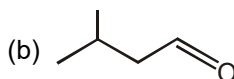
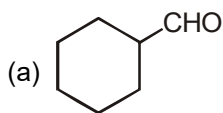


Solved Example :

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

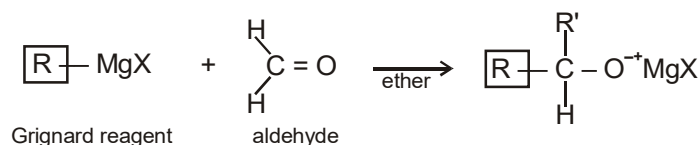


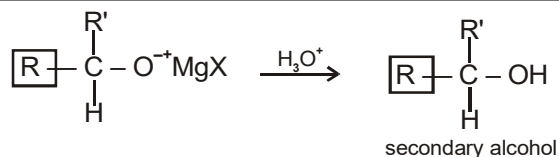
Ans. By reaction of CH_3MgBr with



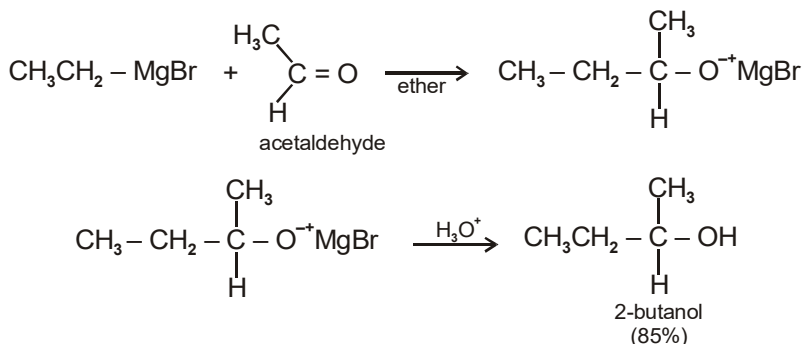
Addition to Aldehydes : Formation of Secondary Alcohols :

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



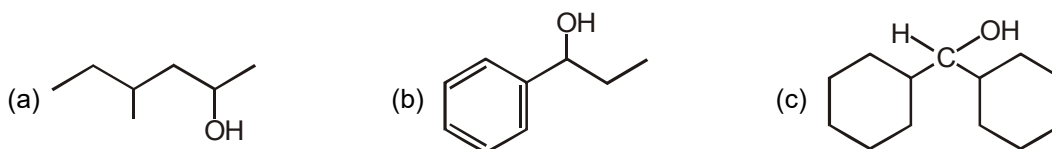


The two alkyl groups of the secondary alcohol are the alkyl group from the Grignard reagent and the alkyl group that was bonded to the carbonyl group of the aldehyde.



Solved Example :

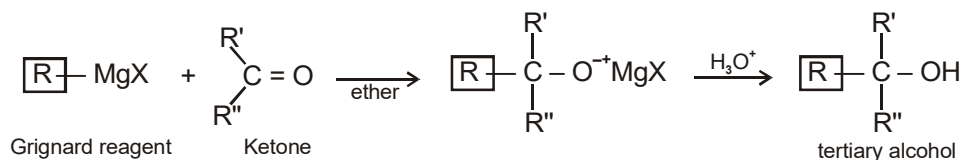
Qus. Show two ways you could synthesize each of the following alcohols by adding an appropriate Grignard reagent to an aldehyde.



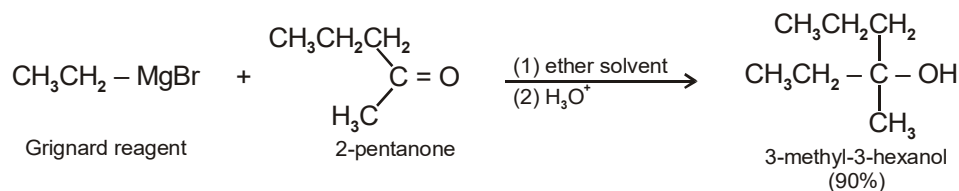
Ans. A secondary alcohol has two groups on the carbinol carbon atom. Consider two possible reactions, with either group added as the Grignard reagent.

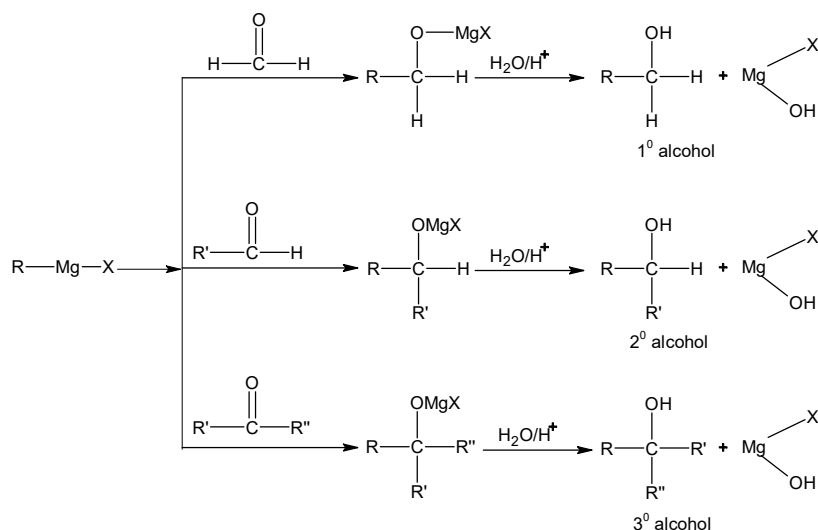
Addition to Ketones : Formation of Tertiary Alcohols :

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.



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

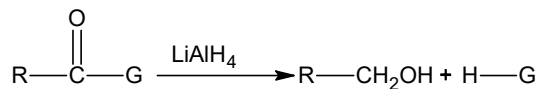




- Methanol can not be prepared by this method.

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

(a) Reduction by LiAlH_4

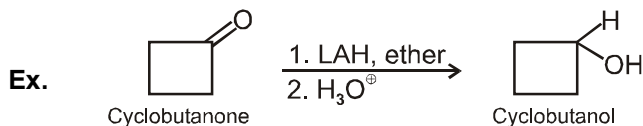


$\text{G} = \text{OH}$ (acid)

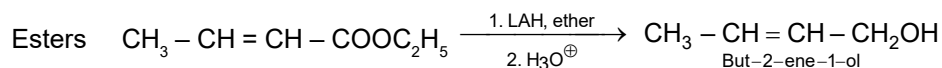
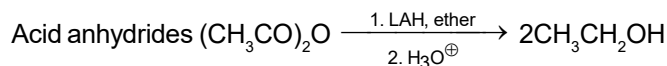
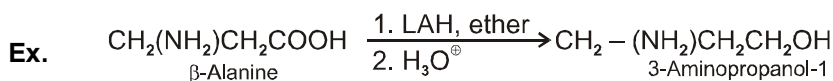
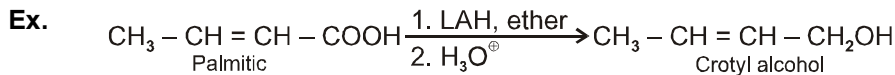
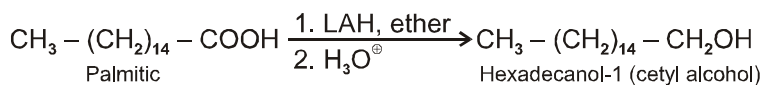
$\text{G} = \text{Cl}$ (acid chloride)

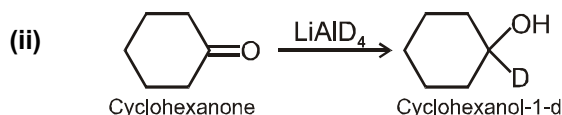
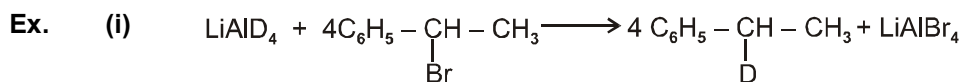
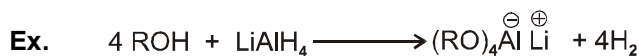
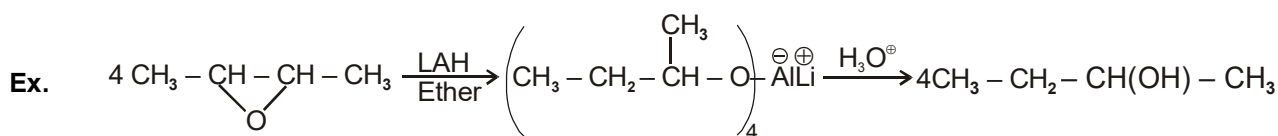
$\text{G} = \text{OR}'$ (ester)

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



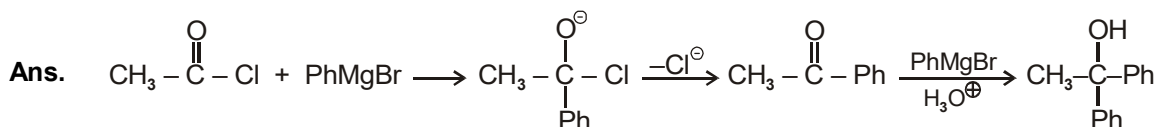
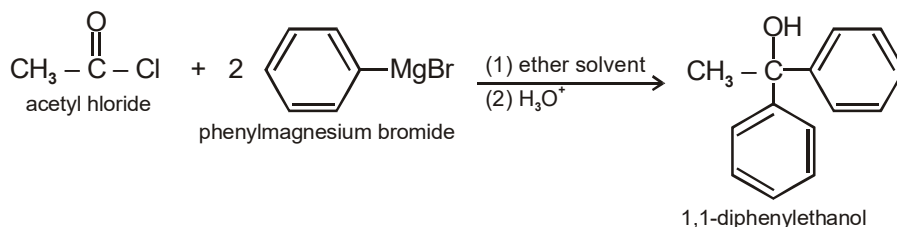
Ex. Acids





Solved Example :

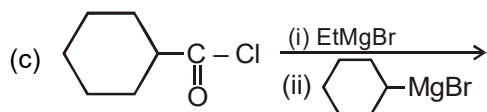
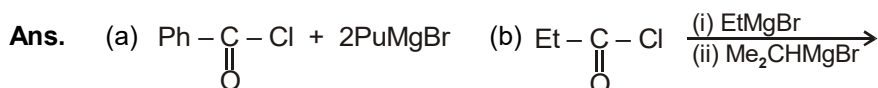
Qus. Propose a mechanism for the reaction of acetyl chloride with phenylmagnesium bromide to give 1,1-diphenylethanol.



Solved Example :

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

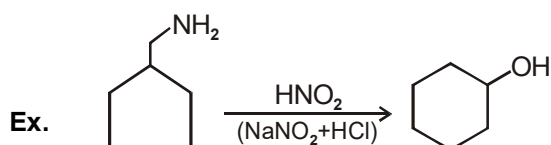
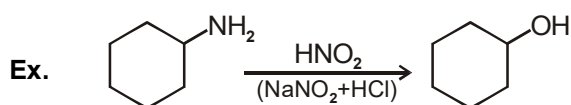
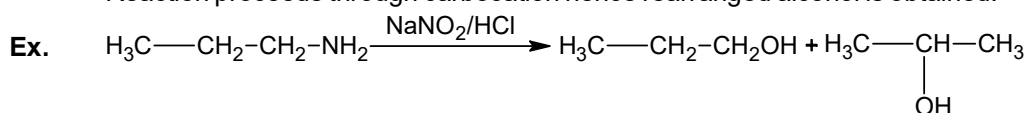
(a) $\text{Ph}_3\text{C} - \text{OH}$ (b) 3-ethyl-2-methyl-3-pentanol (c) dicyclohexylphenylmethanol



6. From aliphatic primary amines :

It react with nitrous acid to give alcohol.

- Nature of alcohol depends on the nature of carbon having $-\text{NH}_2$ group.
- Reaction proceeds through carbocation hence rearranged alcohol is obtained.



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 :

Solved Example :

[16]

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.

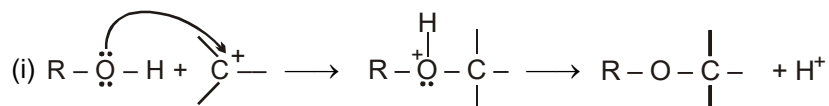
CHEMICAL PROPERTIES & ALCOHOL:

Chemical properties of alcohols can be discussed under following categories :

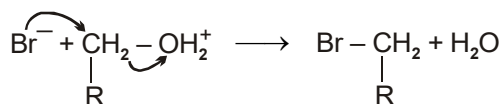
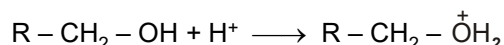
- (A) Reaction involving breaking of oxygen – hydrogen bond.
(B) Reaction involving breaking of carbon – oxygen bond.
(C) Oxidation of alcohols.
(D) Dehydrogenation of alcohols.
(E) Some miscellaneous reactions of monohydric alcohol.

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

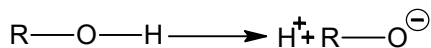
Alcohols as nucleophiles :



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

Protonated alcohols as electrophiles :

- (a) Alcohols are acidic in nature because hydrogen is present on electro negative oxygen atom.
(b) Alcohol is weaker acid

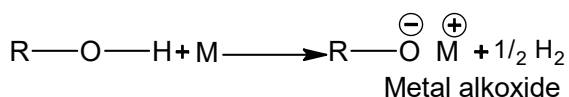


acidity \propto stability of acid anions.

Acidity of $1^\circ > 2^\circ > 3^\circ$

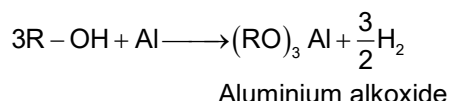
Alcohols give following reactions due to breaking of oxygen – hydrogen bond.

(i) Reaction with metal

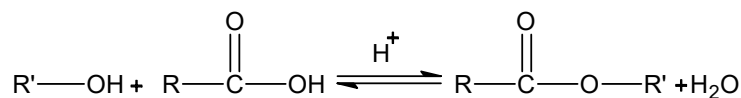


M = 1st group metal.

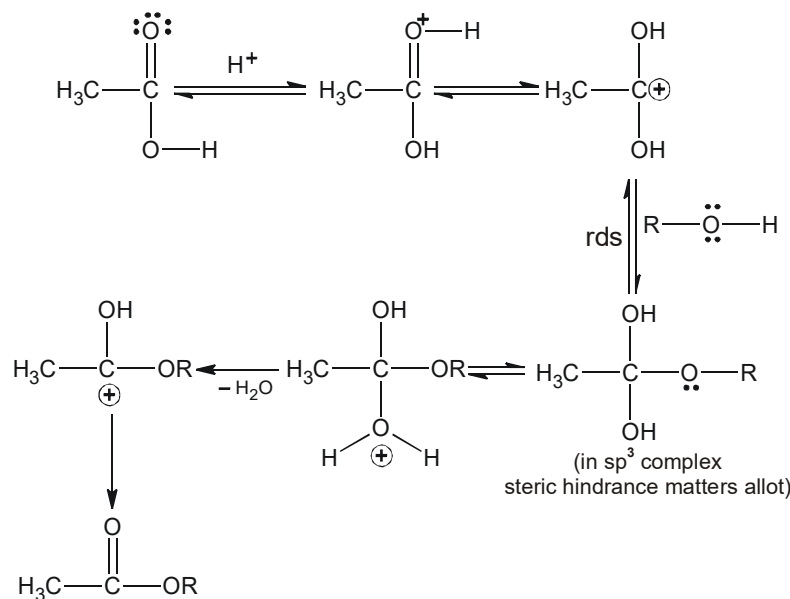
M = Al, Mg, Zn



(ii) **Esterification (With carboxylic acid)**



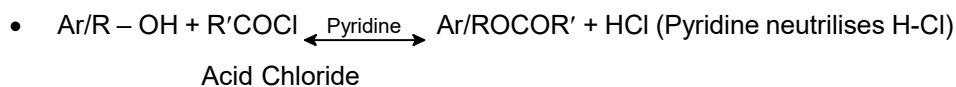
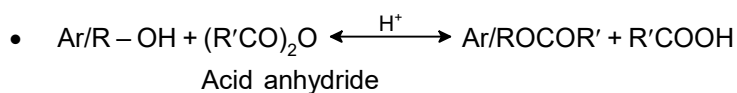
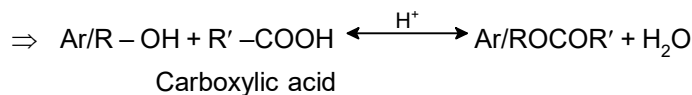
It is reversible acid catalysed reaction. It follows SN_1 mechanism.



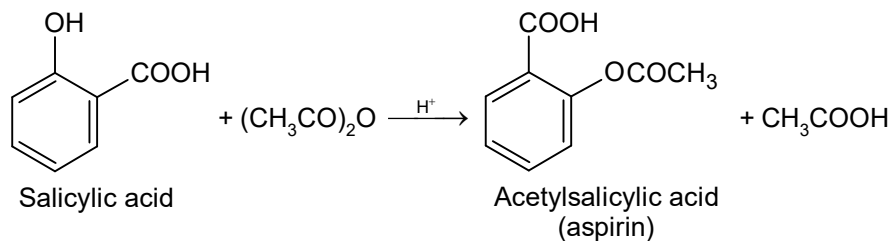
Increasing the size of alkyl group on alcohol part decreases the nucleophilic character because steric hindrance increases.

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

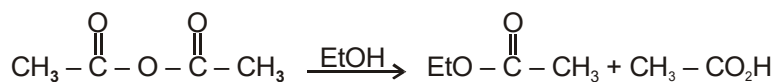
Order of reactivity of alcohols $CH_3OH > 1^\circ \text{ alcohol} > 2^\circ \text{ alcohol} > 3^\circ \text{ alcohol}$



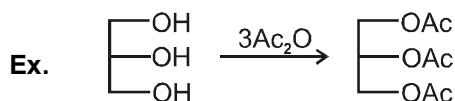
Example - Acetylation of salicylic acid



Acylation of Alcohol :

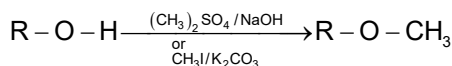


(MOL.WEIGHT OF ALCOHOL INCREASED BY 42 amu OR BY C₂H₂O)



(MOL.WEIGHT OF ALCOHOL INCREASED BY 126 amu)

(iv) Alkylation of Alcohol

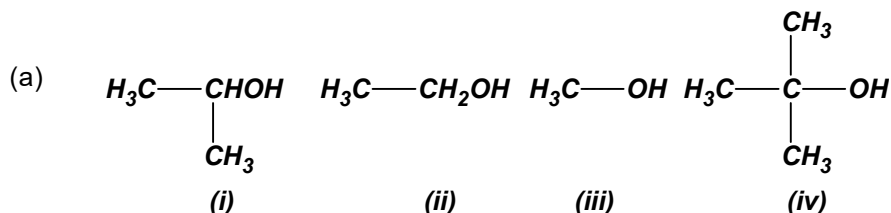


Methylation is mainly used for determination of hydroxyl groups in an unknown compound.

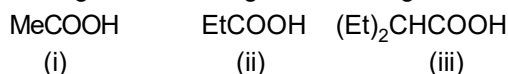
$$\text{No. of hydroxyl groups} = \frac{\text{Molecular weight of methylated ether produced} - \text{molecular weight of reactant}}{14}$$

Solved Example :

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



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

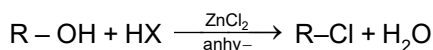


Ans. (a) (iii) > (ii) > (i) > (iv) (b) (i) > (ii) > (iii)

(B) Reaction involving breaking of carbon – oxygen bond

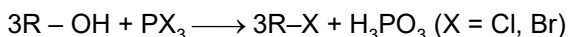
Order of reactivity of alcohol. 3° > 2° > 1°

Reaction with hydrogen halides :



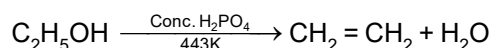
- Lucas test [test with Lucas reagent (conc. HCl and ZnCl₂)] -Used for distinguishing the three classes of alcohols.

Reaction with phosphorus trihalides :

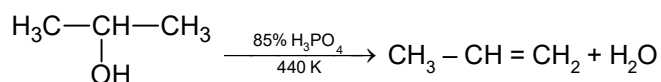


Dehydration:

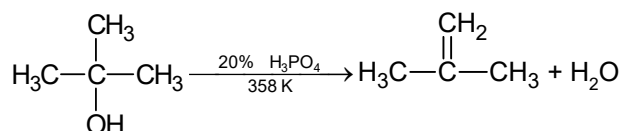
From 1° alcohol



From 2° alcohol



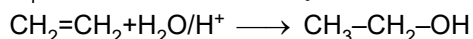
From 3° alcohol



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

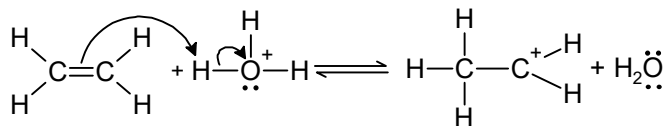
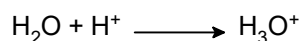
Mechanism in presence of acidic medium :

E₁ mechanism : follow saytzeff's rule.

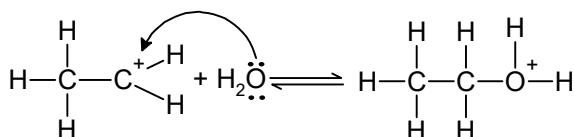


The mechanism of hydration of ethene to form ethanol involves three steps.

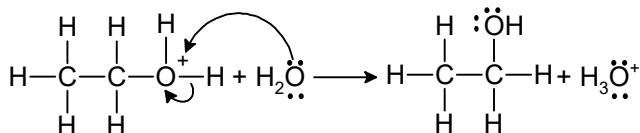
Step 1: Protonation of ethene to form carbocation by electrophilic attack of H₃O⁺:



Step 2: Nucleophilic attack of water on carbocation:

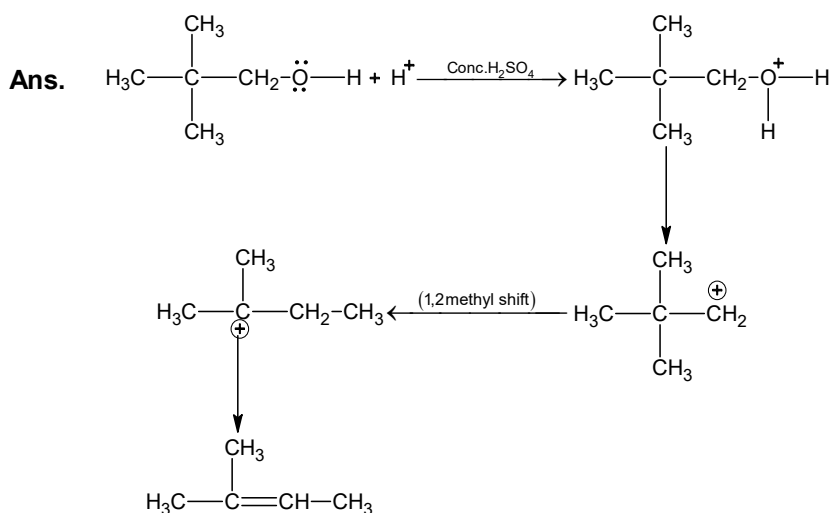


Step 3: Deprotonation to form ethanol:



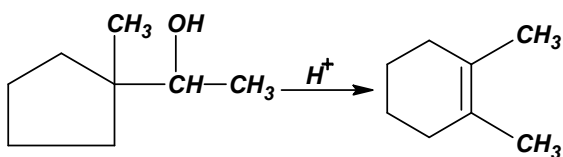
Solved Example :

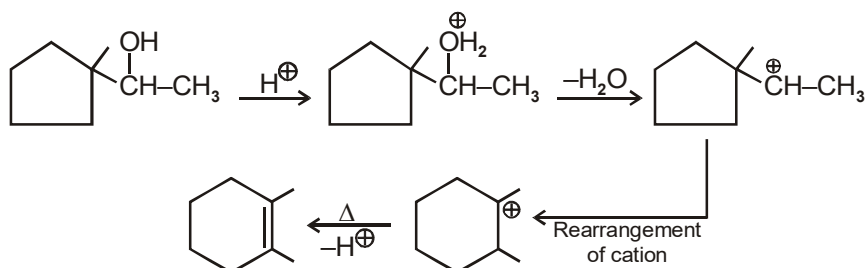
Qus. Write the product with mechanism when neopentyl alcohol reacts with H₃O⁺ ?



Solved Example :

Qus. Write mechanism

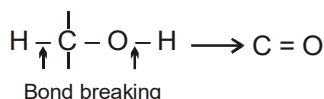




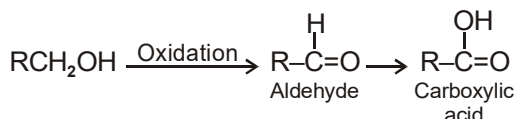
Ans.

(C) Oxidation of alcohol :

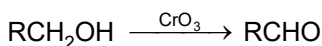
Oxidation of alcohols involves the formation of a carbon-oxygen double bond with cleavage of an O–H and C–H bonds.



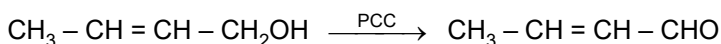
Such a cleavage and formation of bonds occur in oxidation reactions. These are also known as **dehydrogenation** reactions as these involve loss of dihydrogen from an alcohol molecule. Depending on the oxidising agent used, a primary alcohol is oxidised to an aldehyde which in turn is oxidised to a carboxylic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



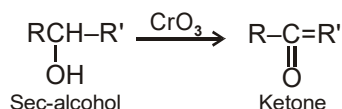
Strong oxidising agents such as acidified potassium permanganate are used for getting carboxylic acids from alcohols directly. CrO_3 in anhydrous medium is used as the oxidising agent for the isolation of aldehydes.



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.

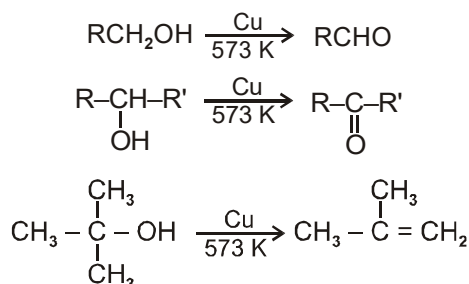


Secondary alcohols are oxidised to ketones by chromic anhydride (CrO_3).

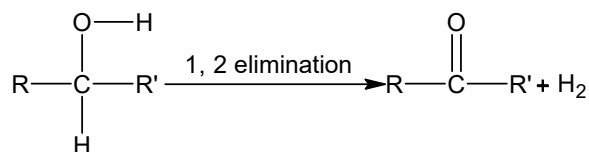


Tertiary alcohols do not undergo oxidation reaction. Under strong reaction conditions such as strong oxidising agents (KMnO_4) and elevated temperatures, cleavage of various C – C bonds takes place and a mixture of carboxylic acids containing lesser number of carbon atoms is formed.

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).



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.

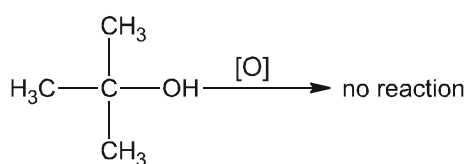
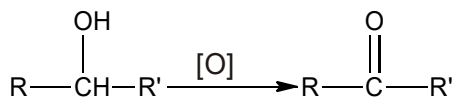
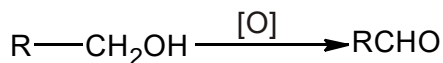


So oxidation of alcohol \propto numbers of α - hydrogen atom.

(a) With mild oxidising agents :

Like

- (i) X_2
- (ii) Fenton reagent $[\text{FeSO}_4/\text{H}_2\text{O}_2]$
- (iii) Jones reagent / CH_3COCH_3 $[\text{CrO}_3/\text{dil. H}_2\text{SO}_4]$
- (iv) $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$ cold

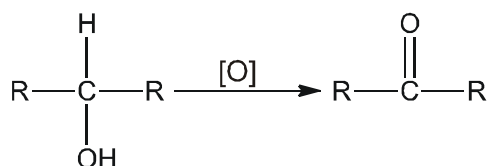
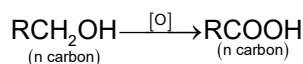


Note : PCC (Pyridinium chloro chromate) is a selective reagent which converts 1° alc to aldehyde.

(b) With strong oxidising agent

Oxidising agents are

- (i) $\text{KMnO}_4 / \text{OH}^- / \Delta$
- (ii) $\text{KMnO}_4 / \text{H}^+ / \Delta$
- (iii) $\text{K}_2\text{Cr}_2\text{O}_7 / \text{H}^+ / \Delta$
- (iv) Conc. HNO_3 / Δ



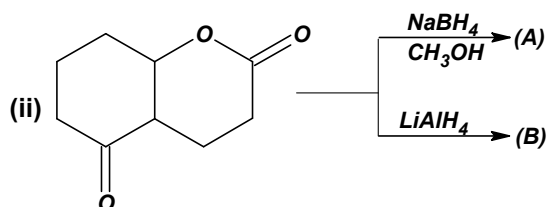
Reduction :



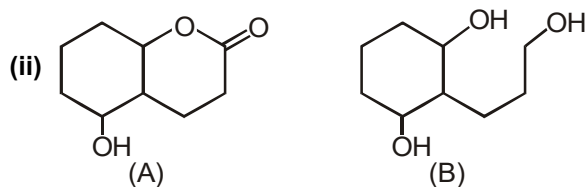
Solved Example :

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

- (a) $\text{CH}_3-\text{CH}_2-\text{CHOHCH}_3$
- (b) $\text{PhCH}_2\text{CHOHCH}_3$
- (c) PhCHOHCH_3
- (d) $\text{CH}_3\text{CH}_2\text{OH}$
- (e) $\text{CH}_3\text{COCH}_2-\text{COOC}_2\text{H}_5$



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

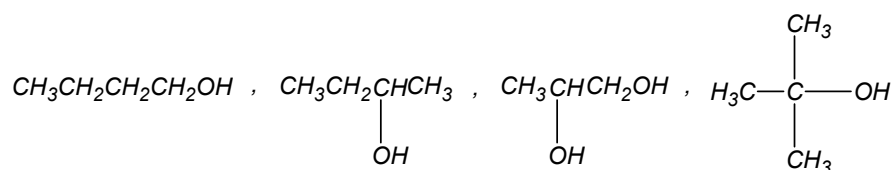


Distinguishing 1°, 2°, 3° alcohol

Test	1° alc	2° alc	3° alc
(I) Lucas test [ZnCl ₂ + HCl] 5 – 10 min.	No reaction at room temperature	White turbidity after 5-15 min. $RCH(OH)R + HCl$ $\downarrow ZnCl_2$ $R-\underset{\substack{ \\ Cl}}{CH}-R + H_2O$	White turbidity instantaneously $R_3C-OH + HCl$ $\downarrow ZnCl_2$ R_3C-Cl
(II) Victor Meyer test (P/I ₂ , AgNO ₂ , HNO ₂ , NaOH)	Red colour	Blue colour	Colourless
	RCH_2OH $\downarrow P/I_2$ RCH_2I $\downarrow AgNO_2$ RCH_2NO_2 $\downarrow HONO$ $R-\overset{\substack{NO_2 \\ }}{C}=\overset{\substack{NOH \\ }}{C}$ Nitrollic acid $\downarrow NaOH$ $R-\overset{\substack{NO_2 \\ }}{C}=\overset{\substack{NO^-Na^+ \\ }}{C}$ Sodium nitrolate (red)	$R-\underset{\substack{ \\ R}}{CHOH}$ $\downarrow P/I_2$ $R-\underset{\substack{ \\ R}}{CHI}$ $\downarrow AgNO_2$ $R-\underset{\substack{ \\ R}}{CHNO_2}$ $\downarrow HNO_2$ $R-\underset{\substack{ \\ R}}{C}-NO_2$ \downarrow $R-\underset{\substack{ \\ N=O}}{C}-NO_2$ (Pseudo nitrole) $\downarrow NaOH$ Blue	R_3C-OH $\downarrow P/I_2$ R_3C-I $\downarrow AgNO_2$ R_3C-NO_2 $\downarrow HNO_2$ No reaction (colourless)

Solved Example :

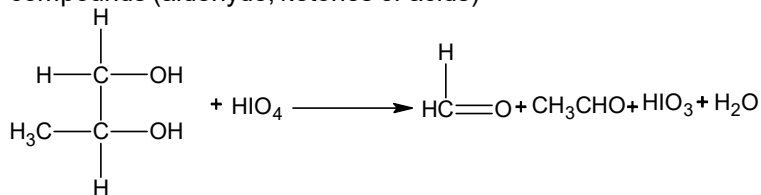
Qus. Which of the following alcohols would react fastest with Lucas reagent?



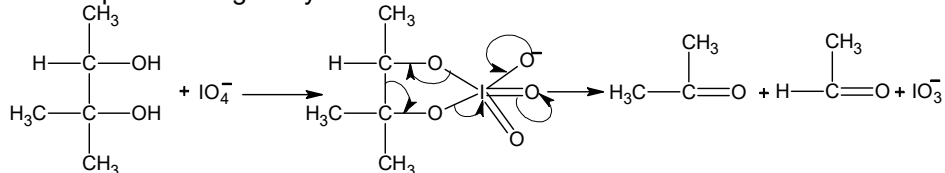
Ans. $(CH_3)_3COH$, it being a tertiary alcohol.

PERIODATE OXIDATION :

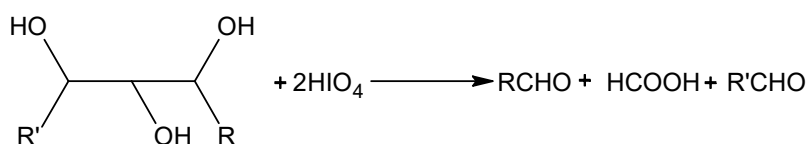
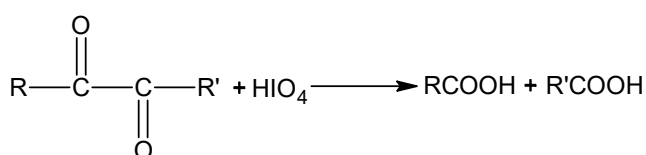
Compounds that have hydroxyl group on adjacent atoms undergo oxidation cleavage when they are treated with aq. Periodic acid (HIO_4). The reaction breaks carbon carbon bonds and produced carbonyl compounds (aldehyde, ketones or acids)



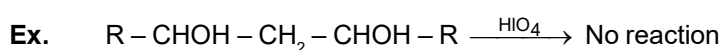
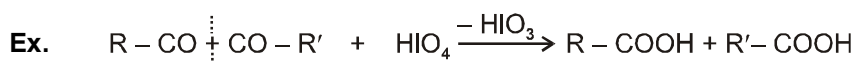
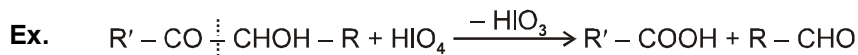
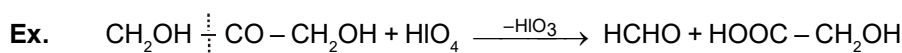
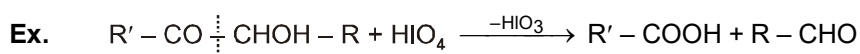
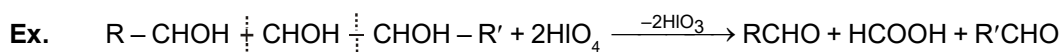
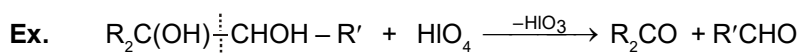
It takes place through a cyclic intermediate.

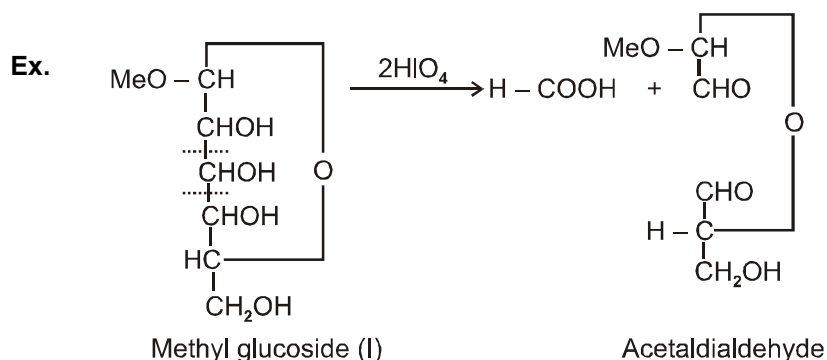
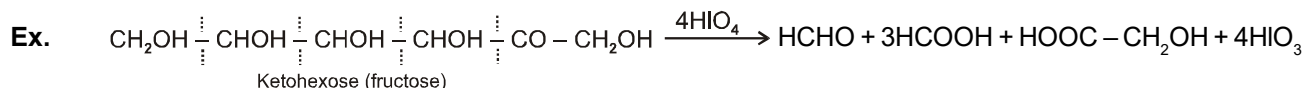
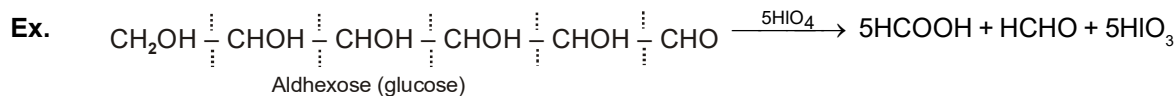
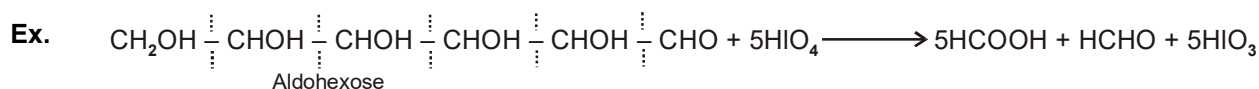
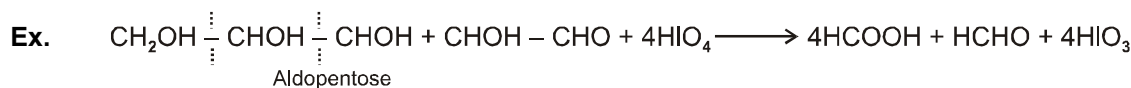


Other examples



This oxidation is useful in determination of structure.





Migratory preference of the group

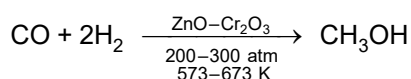
Migration depends on the stability of Transition state.

In general migration of $\text{C}_6\text{H}_5 > \text{alkyl}$

Methanol and ethanol are among the two commercially important alcohols :

1. Methanol :

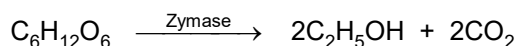
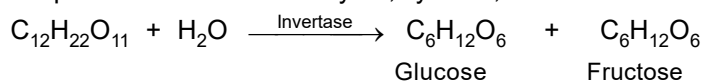
Methanol, CH_3OH , also known as 'wood spirit', was produced by destructive distillation of wood. Today, most of the methanol is produced by catalytic hydrogenation of carbon monoxide at high pressure and temperature and in the presence of $\text{ZnO} - \text{Cr}_2\text{O}_3$ catalyst.



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 :

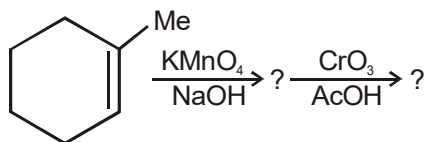
Ethanol, $\text{C}_2\text{H}_5\text{OH}$, is obtained commercially by fermentation, the oldest method is from sugars. The sugar in molasses, sugarcane or fruits such as grapes is converted to glucose and fructose, (both of which have the formula $\text{C}_6\text{H}_{12}\text{O}_6$), in the presence of an enzyme, invertase. Glucose and fructose undergo fermentation in the presence of another enzyme, zymase, which is found in yeast.



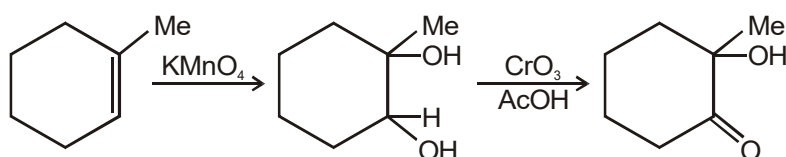
In wine making, grapes are the source of sugars and yeast. As grapes ripen, the quantity of sugar increases and yeast grows on the outer skin. When grapes are crushed, sugar and the enzyme come in contact and fermentation starts. Fermentation takes place in anaerobic conditions i.e. in absence of air.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

Solved Example :

Qus. Complete the following equation and comment.



Ans. The course of the reaction is shown here.



Alkaline permanganate converts a double bond to a cis-diol. In the present case, this dihydroxylation produces a secondary and tertiary alcoholic group. Now, CrO_3/AcOH is a comparatively weaker oxidizing group and can oxidize the secondary alcoholic group but cannot oxidize the tertiary alcoholic group. This is why the final product is a α -hydroxy carbonyl compound like acyloin.

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 is the 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 (ethylmethyl ether)

$CH_3-O-C_6H_5$ Methoxy benzene (Anisole)

There are various types of cyclic ethers also.



Oxirane
(Epoxide)



Oxetane
(Oxacyclo butane)

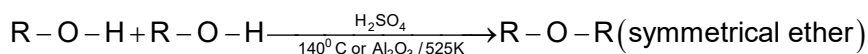


Tetra hydro furan
(Oxacyclo pentane)

PREPARATION OF ETHERS :

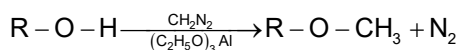
(i) From 1° alcohol

- (a) With H_2SO_4



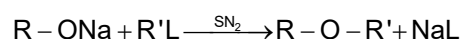
Order of dehydration $1^\circ > 2^\circ > 3^\circ$ alcohol

- (b) With diazomethane



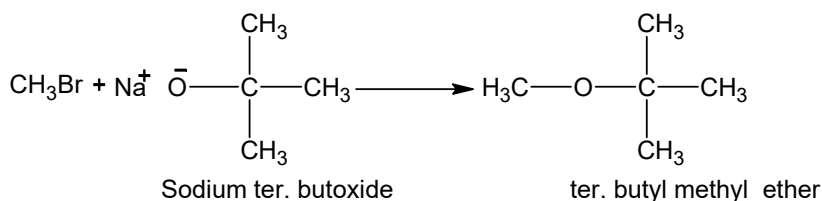
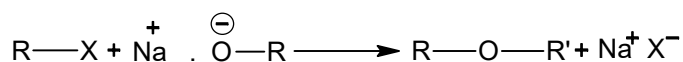
Williamson's synthesis

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



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

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



Solved Example :

Qus. Suggest some types of ethers that cannot be synthesized by the typical Williamson ether synthesis.

Ans. These are as follows :

(A) $\text{HR}_2\text{C}-\text{O}-\text{CR}_3$, one group is secondary and the other is tertiary.

(B) $\text{R}_3\text{C}-\text{O}-\text{CR}_3$, both the groups are tertiary.

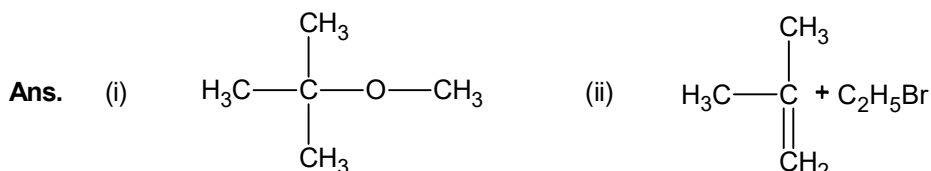
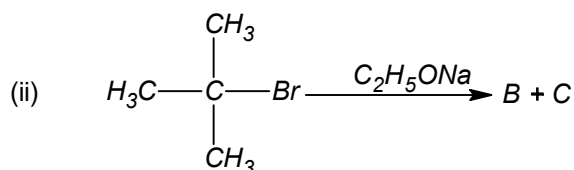
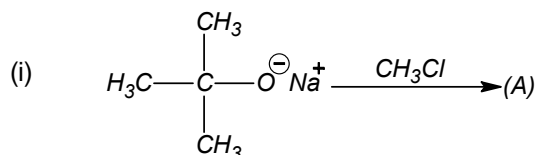
(C) $\text{Ar}-\text{O}-\text{Ar}$

(D) $\text{RCH}=\text{CH}-\text{O}-\text{CH}=\text{CHR}'$, vinyl halides do not undergo nucleophilic displacement reaction ($\text{S}_{\text{N}}2$).

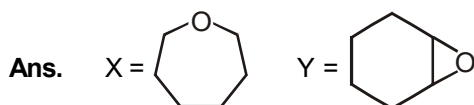
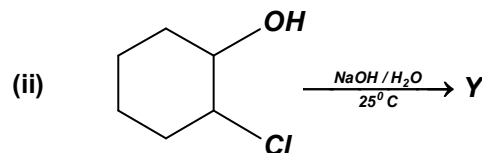
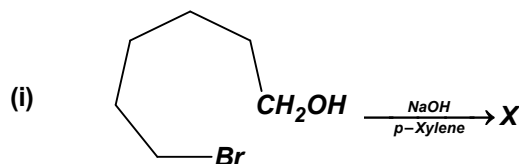
(E) $\text{R}_3\text{CCH}_2-\text{O}-\text{CH}_2\text{CR}'_3$, neopentyl type halides are inert to $\text{S}_{\text{N}}2$ reactions.

Solved Example :

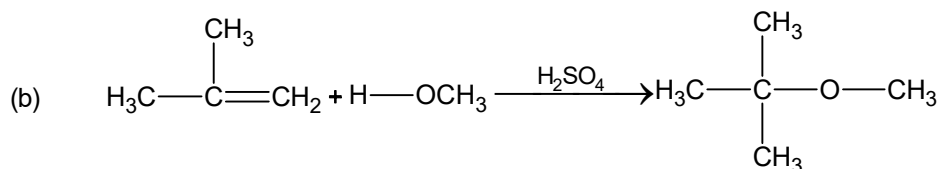
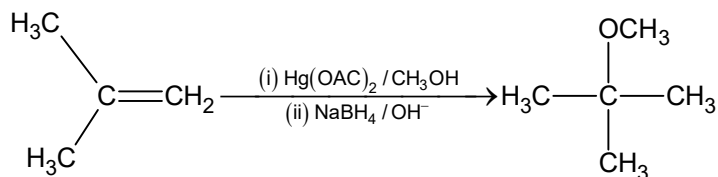
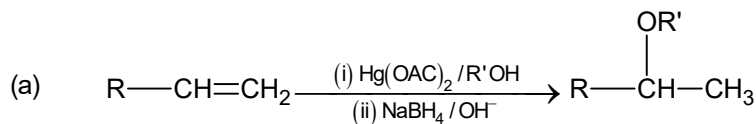
Qus. Write the product

**Solved Example :**

Qus. Find product

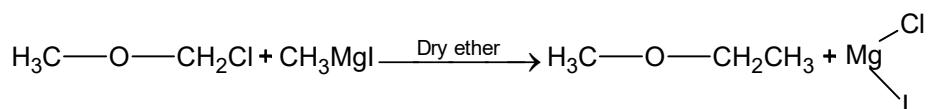


(3) **From Alkane by Alkoxymercuration demercuration (AOMDM) :**

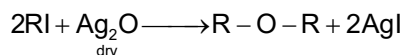


(4) From Grignard reagent :

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



(5) From Alkyl halide



Chemical Reaction :

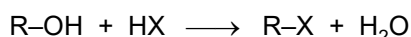
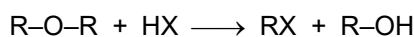
Dialkyl ethers reacts with very few reagents other than acids. The only active site for other reagents are the C — H bonds of the alkyls. Ethers has ability to solvate cations (electrophile) by donating an electron pair from their oxygen atom. These properties make ether as solvents for many reactions.

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

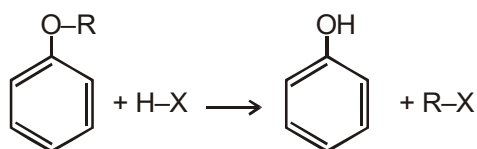
Ether gives following reactions :

Cleavage of C—O bond in ethers :

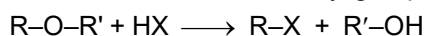
Ethers are the least reactive of the functional groups. The cleavage of C—O bond in ethers takes place under drastic conditions with excess of hydrogen halides. The reaction of dialkyl ether gives two alkyl halide molecules.



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.

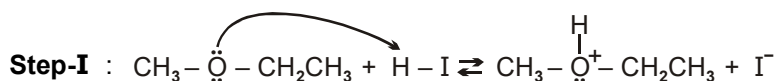


Ethers with two different alkyl groups are also cleaved in the same manner.



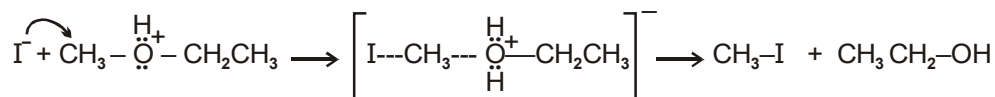
The order of reactivity of hydrogen halides is as follows : $\text{HI} > \text{HBr} > \text{HCl}$. The cleavage of ethers takes place with concentrated HI or HBr at high temperature.

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

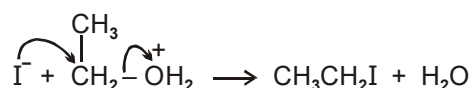
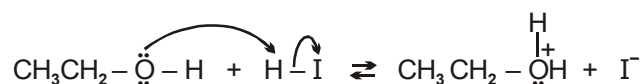


The reaction takes place with HBr or HI because these reagents are sufficiently acidic.

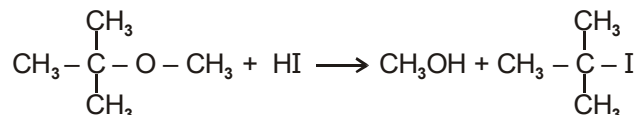
Step-II : Iodide is a good nucleophile. It attacks the least substituted carbon of the oxonium ion formed in step 1 and displaces an alcohol molecule by $\text{S}_{\text{N}}2$ mechanism. Thus, in the cleavage of mixed ethers with two different alkyl groups, the alcohol and alkyl iodide formed, depend on the nature of alkyl groups. When primary or secondary alkyl groups are present, it is the lower alkyl group that forms alkyl iodide ($\text{S}_{\text{N}}2$ reaction).



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 :

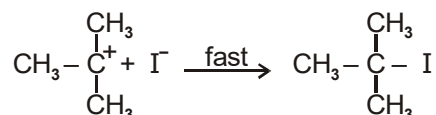
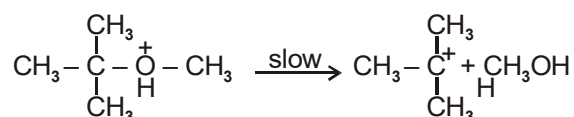
However, when one of the alkyl group is a tertiary group, the halide formed is a tertiary halide.



It is because in step 2 of the reaction, the departure of leaving group ($\text{HO}-\text{CH}_3$) creates a more stable carbocation $[(\text{CH}_3)_3\text{C}^+]$, and the reaction follows $\text{S}_{\text{N}}1$ mechanism.

In case of anisole, methylphenyl oxonium ion, $\text{C}_6\text{H}_5-\overset{+}{\underset{\text{H}}{\text{O}}}-\text{CH}_3$ is formed by protonation of ether. The bond

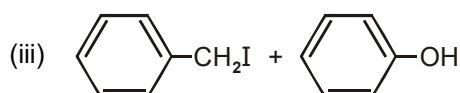
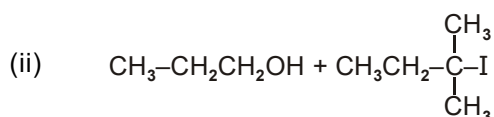
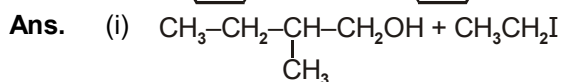
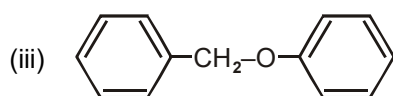
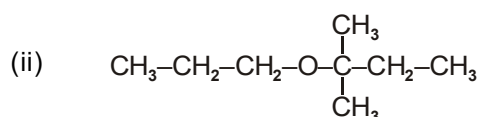
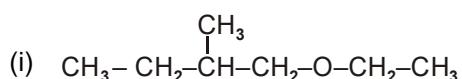
between $\text{O}-\text{CH}_3$ is weaker than the bond between $\text{O}-\text{C}_6\text{H}_5$ because the carbon of phenyl group is sp^2 hybridised and there is a partial double bond character.



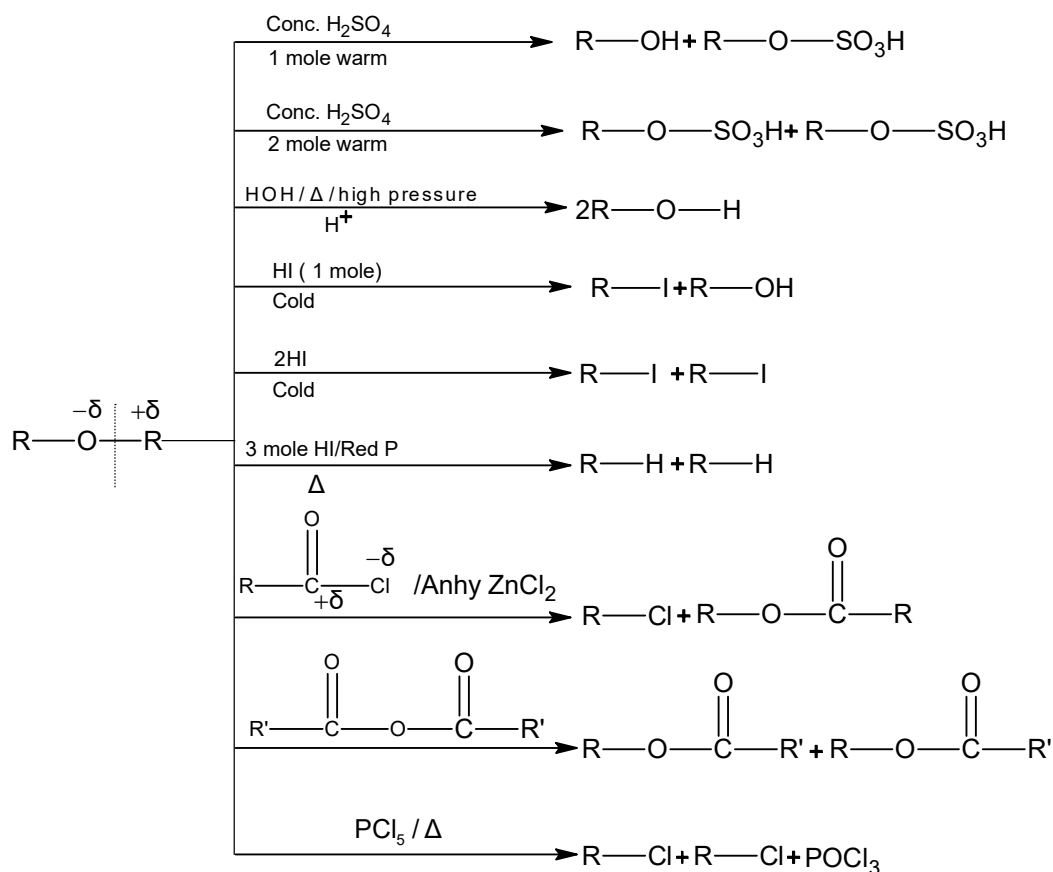
Therefore the attack by I^- ion breaks $\text{O}-\text{CH}_3$ bond to form CH_3I . Phenols do not react further to give halides because the sp^2 hybridised carbon of phenol cannot undergo nucleophilic substitution reaction needed for conversion to the halide.

Solved Example :

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

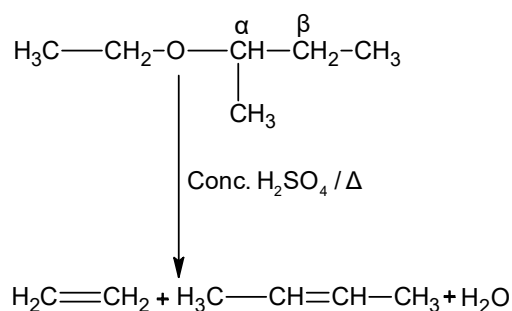


1. Nucleophilic substitution reactions

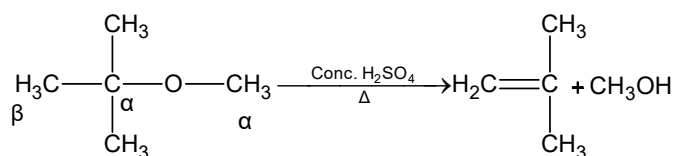


(B) Dehydration with $\text{H}_2\text{SO}_4/\Delta$ and Anhy $\text{Al}_2\text{O}_3/\Delta$

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

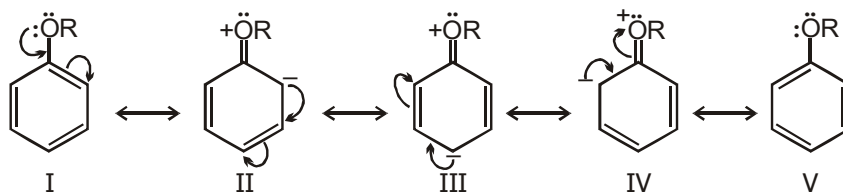


(ii) When only alkyl group has β - hydrogen.

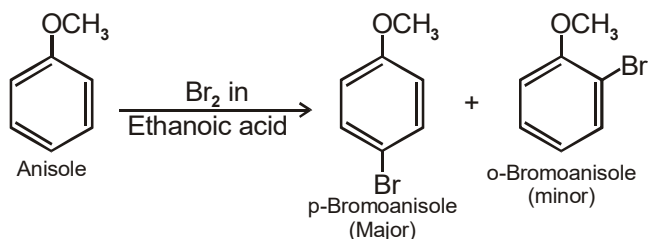


(C) Electrophilic substitution Reactions (S_E) of ether :

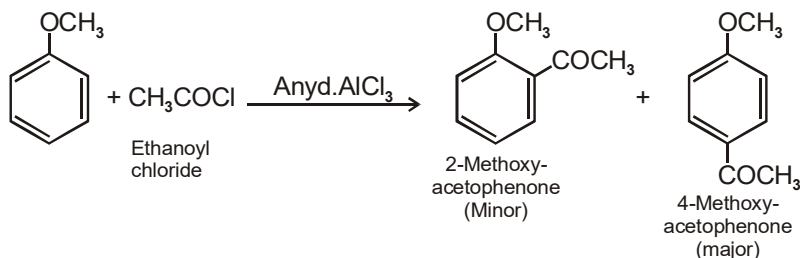
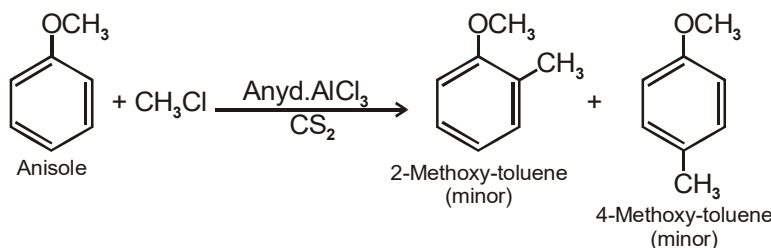
The alkoxy group ($-\text{OR}$) is ortho, para directing and activates the aromatic ring towards electrophilic substitution in the same way as in phenol.



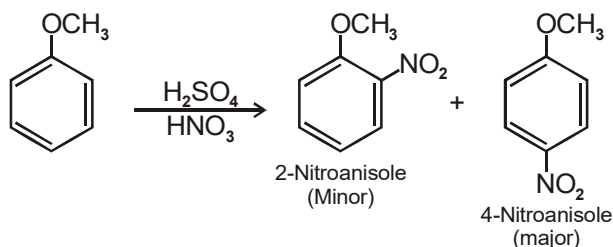
(i) **Halogenation** : Phenylalkyl ethers undergo usual halogenation in the benzene ring, e.g., anisole undergoes bromination with bromine in ethanoic acid even in the absence of iron (III) bromide catalyst. It is due to the activation of benzene ring by the methoxy group. Para isomer is obtained in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

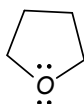


(iii) **Nitration** : Anisole reacts with a mixture of concentrated sulphuric and nitric acids to yield a mixture of ortho and para nitroanisole.



Solved Example :

Qus. 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.

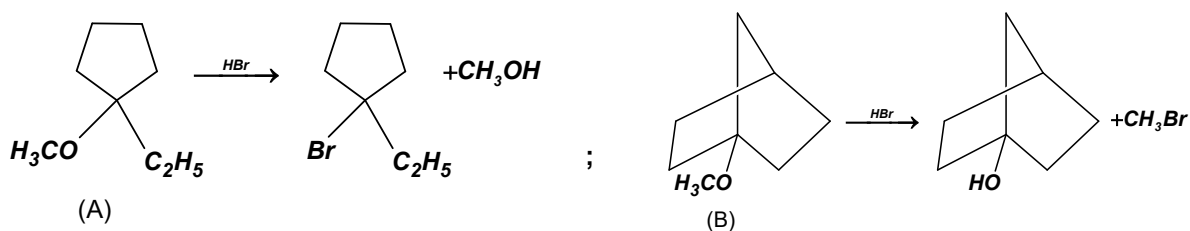
Solved Example :

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

- Ethoxy ethanol and methyl isopropyl ether.
- Butyl iodide and butyl ethyl ether.
- Ethyl propyl ether and ethyl allyl ether.

Solved Example :

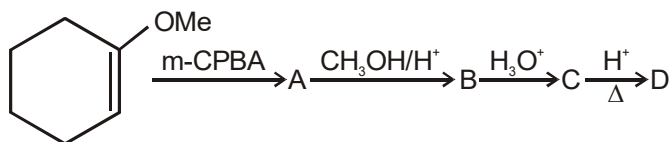
Qus. Ether A cleaves much faster than B with conc. HI. Explain.



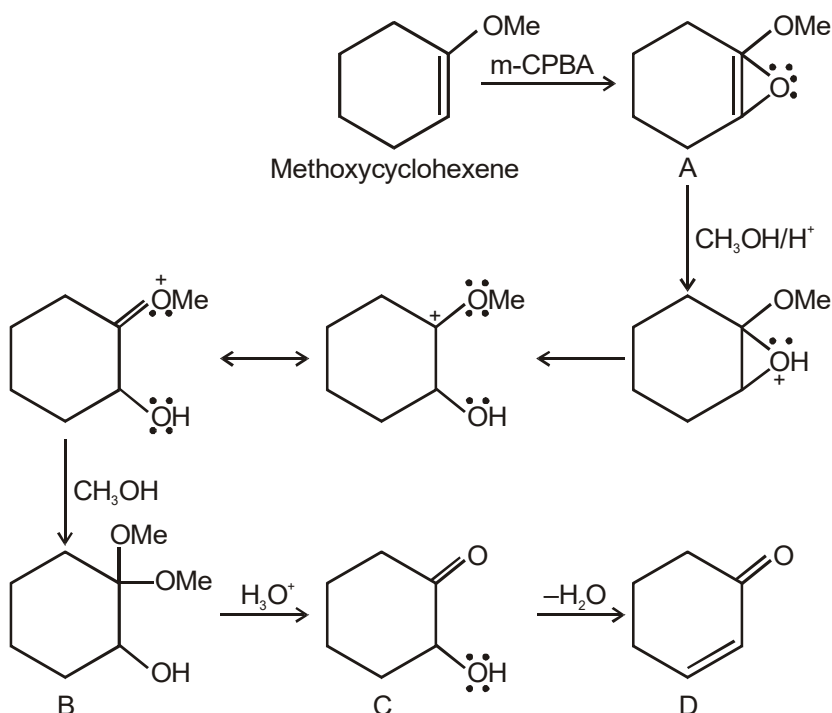
Ans. Cation is not stable on bridge head carbon on B. (Violation of Bredt's rule).

Solved Example :

Qus. Identify the products in the following sequence of reactions.

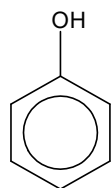


Ans. The course of the reaction and products are shown here.

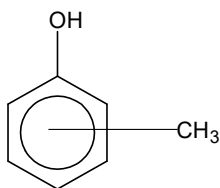


PHENOL

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



Phenol or carbolic acid



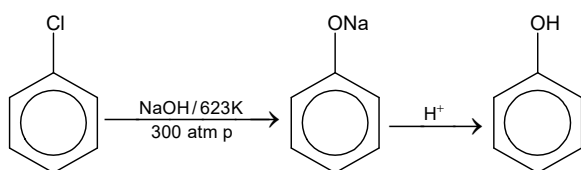
(o, p, m)
Cresol

Preparation :

Industrial Method :

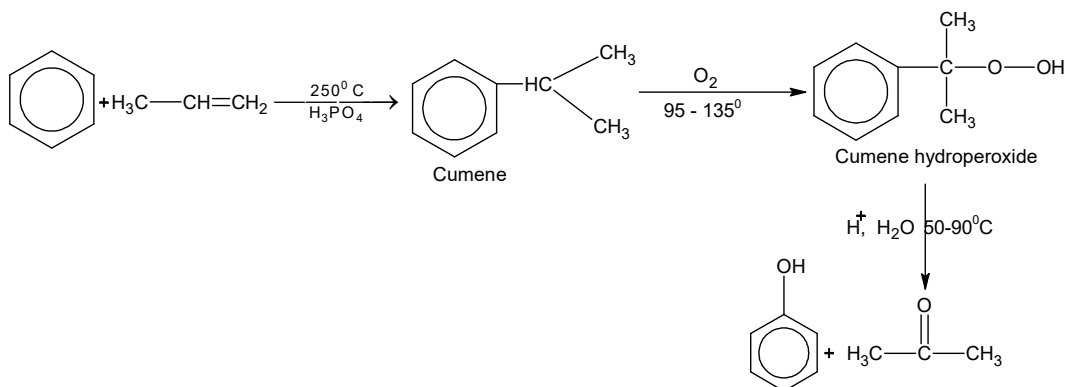
(i) From chloro benzene (Dow's process) :

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



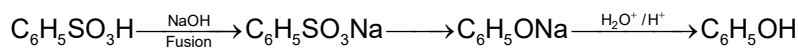
(ii) Cumene Process :

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



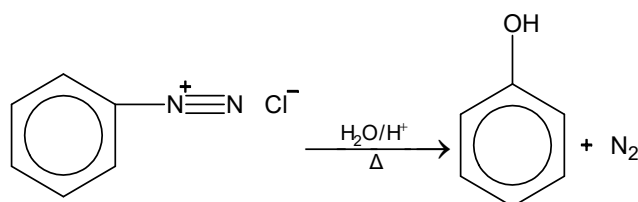
(iii) From benzene sulphonic acid

It is fused with NaOH gives sodium salt of phenol.



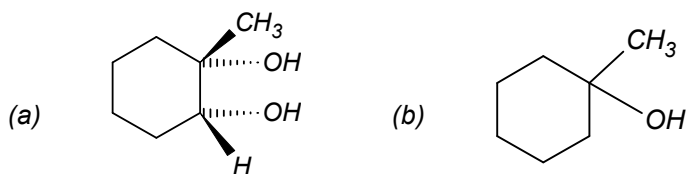
(iv) From benzene diazonium chloride :

This gives Ar SN1 reaction with H_2O to form phenol.

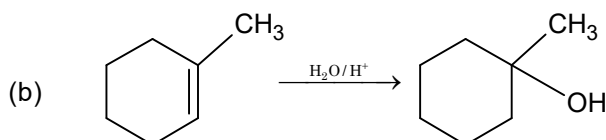
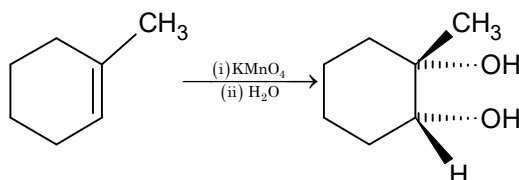


Solved Example :

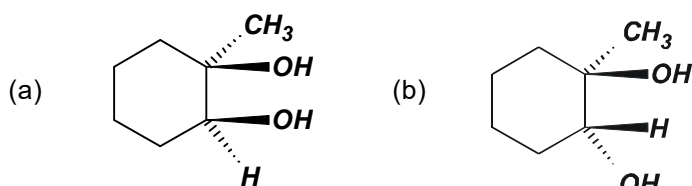
Qus. Starting from 1-methyl cyclohexene, prepare the following:



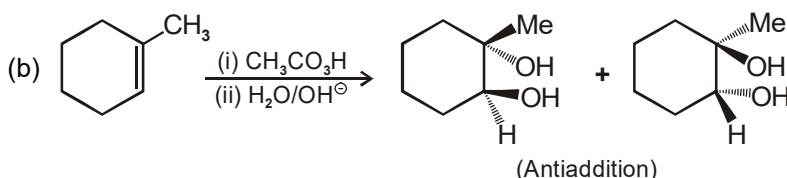
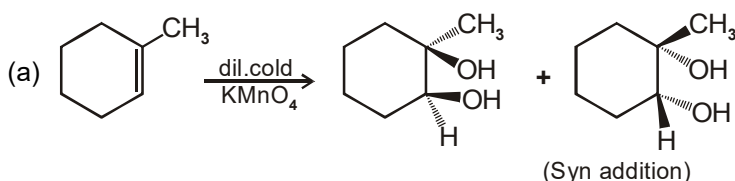
Ans. (a)

**Solved Example :**

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



Ans. (a)

**PHYSICAL PROPERTIES :**

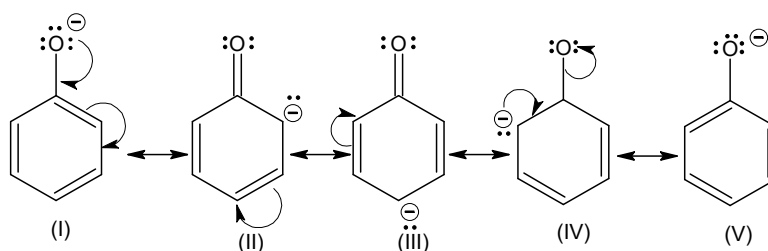
Phenol is needle shaped solid, soon liquefies due to high hygroscopic nature. It is less soluble in water, but readily soluble in organic solvents.

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 :

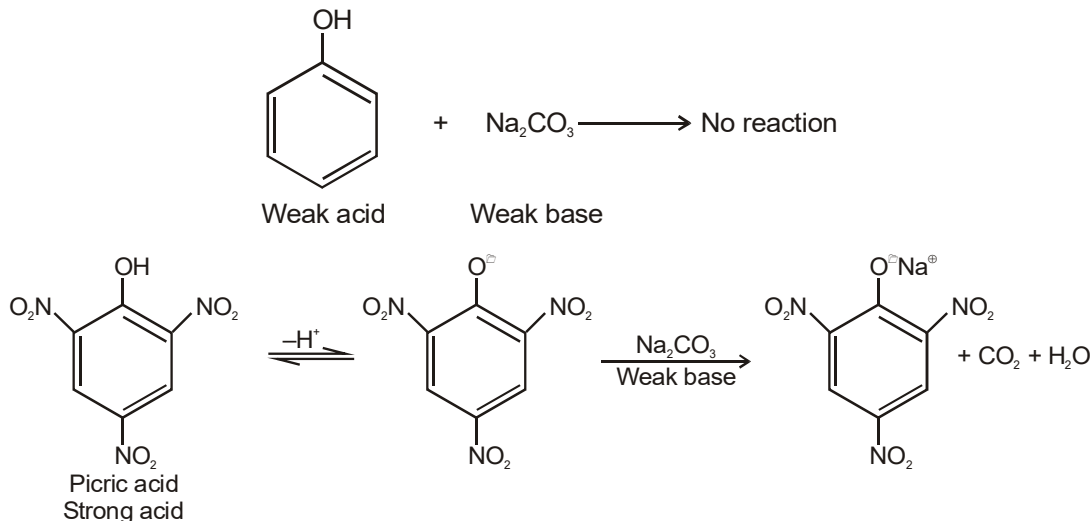


Solved Example :

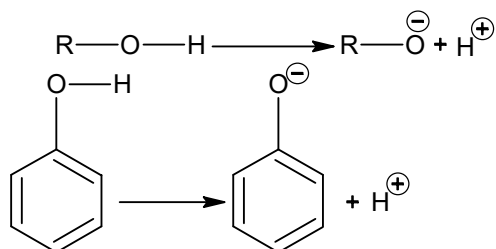
Qus. Picric acid liberates CO_2 from aqueous Na_2CO_3 but phenol does not. Explain.

Ans. Phenol itself is weakly acidic but when a strong electron withdrawing group such as $-\text{NO}_2$ and $-\text{CN}$ are present in the ortho and para positions with respect to the $-\text{OH}$ group, then acidity of phenol is very much enhanced because the resultant phenoxide ion becomes stabilized by delocalization.

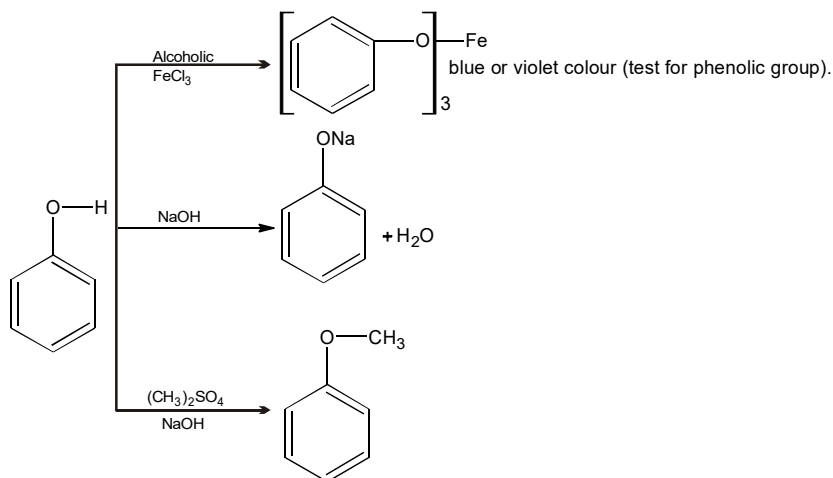
Picric acid is 2,4,6-trinitrophenol and consequently is a strong acid. For this reason picric acid can react with a weaker base to form Na-salt of picric acid and liberates CO_2 .

**CHEMICAL REACTIONS :****(A) Reaction due to breaking of O – H bond**

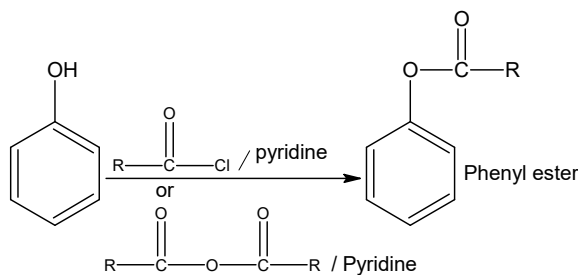
Phenol is more reactive than alcohol for this reaction because phenoxide ion is more stable than the alkoxide ion.



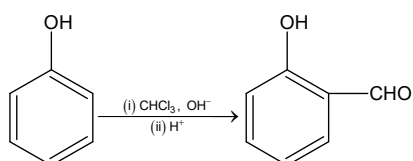
Reactions of phenol due to breaking of $-\text{O}-\text{H}$ bond are given below:



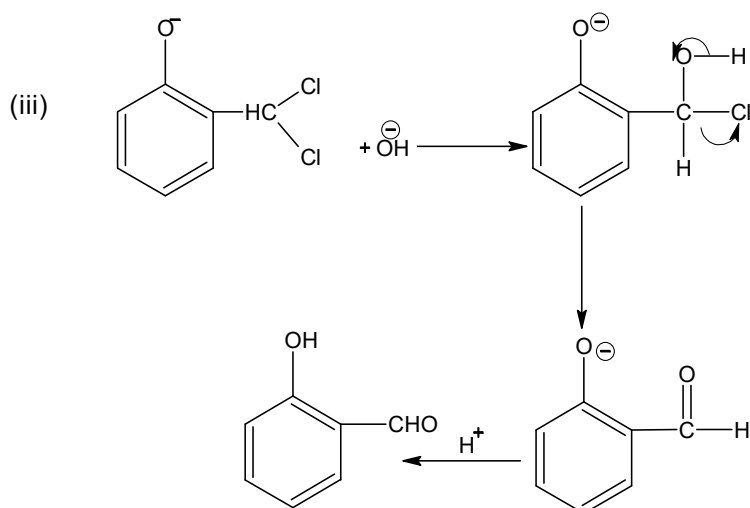
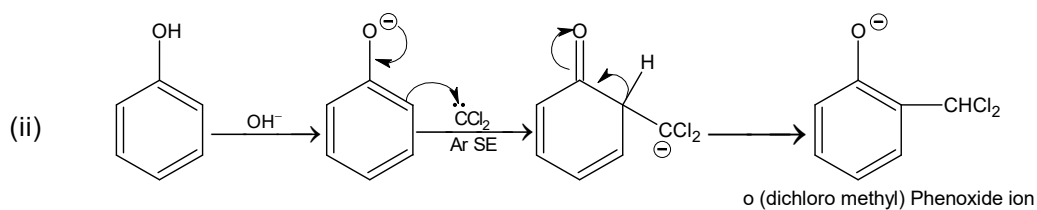
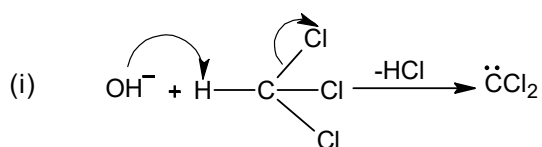
Acylation (By S_N2 mechanism) :



Reimer Tieman reaction :

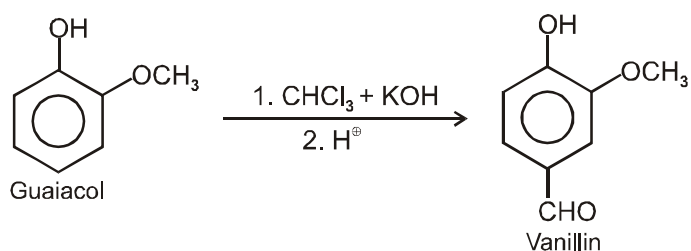


The electrophile is the dichloro carbene, $:CCl_2$, formation of carbene is an example of α - elimination.

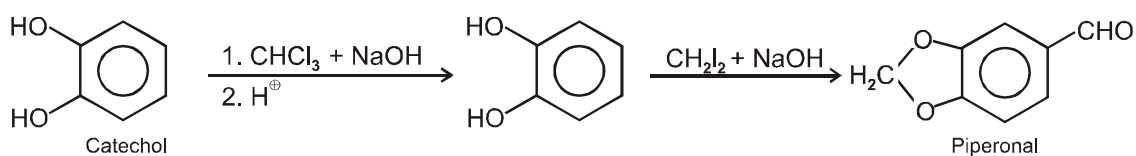


APPLICATION OF REIMER TIEMAN :

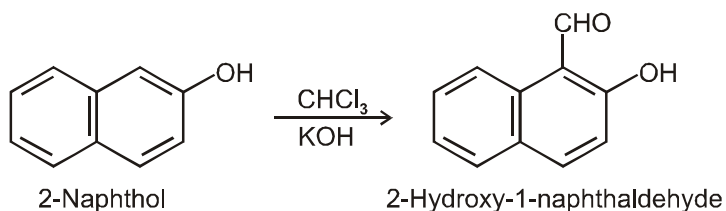
1. Preparation of vanillin



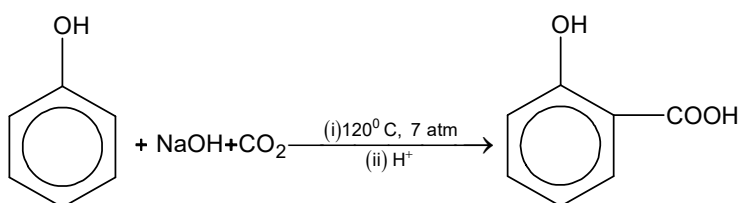
2. Preparation of piperonal



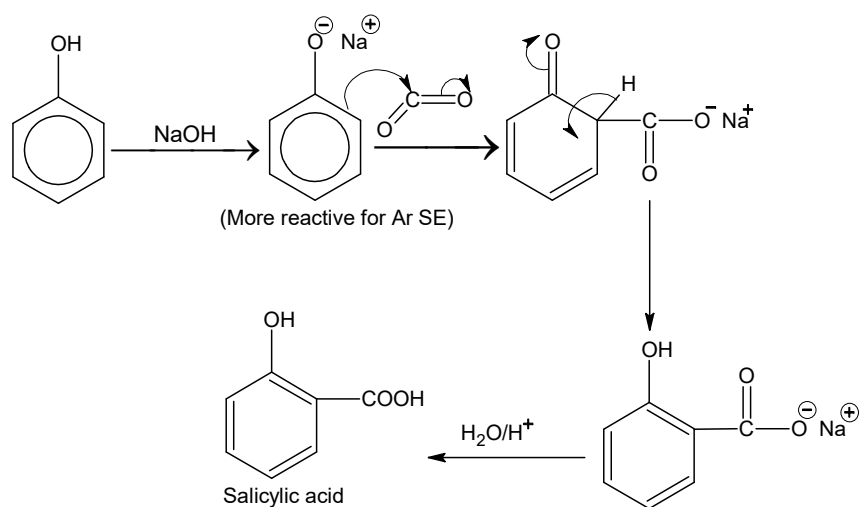
3. Formylation of naphthol



4. Kolbe's reaction



Mechanism :



Solved Example :

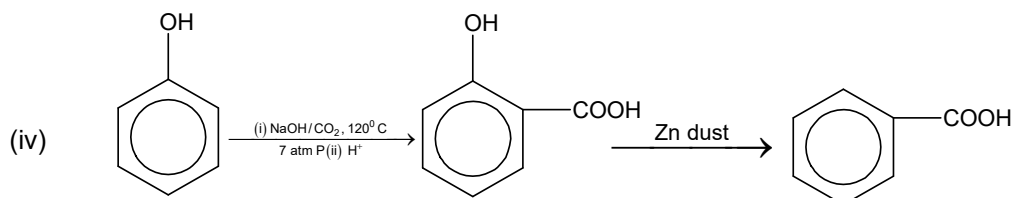
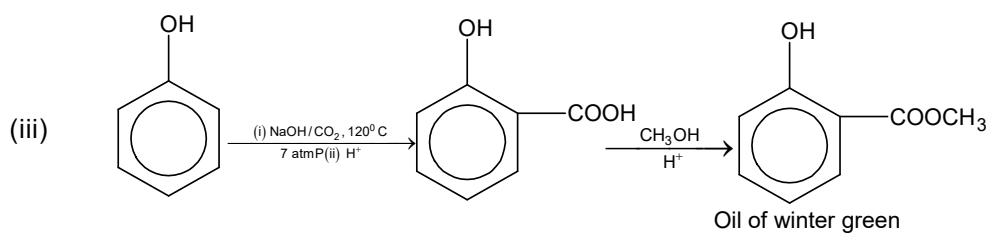
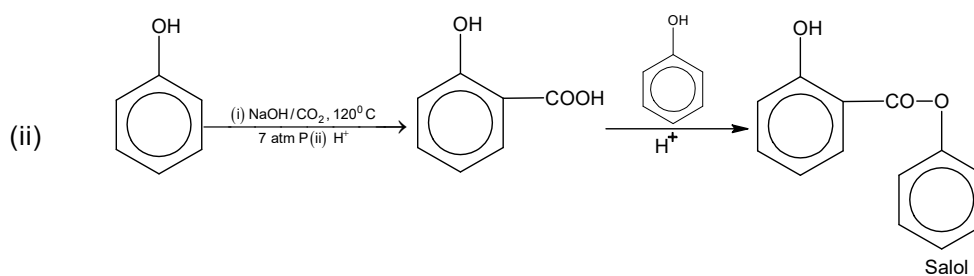
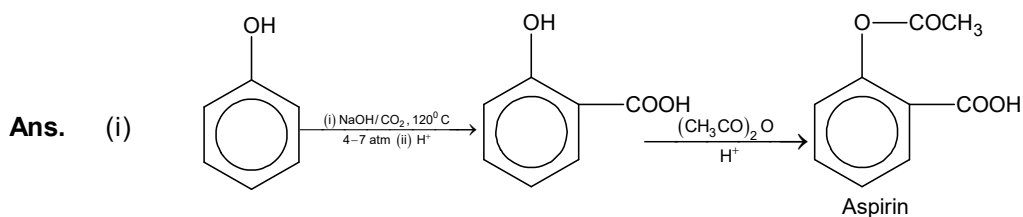
Qus. How will you convert ?

(i) phenol to aspirin

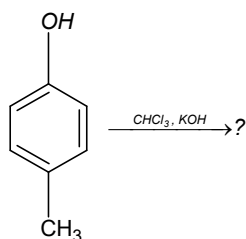
(ii) phenol to salol.

(iii) phenol to oil of winter green.

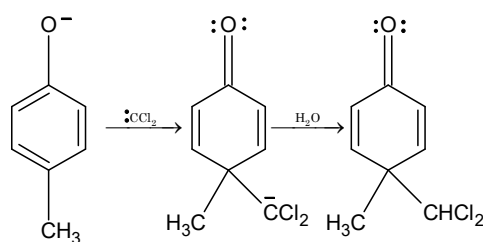
(iv) phenol to benzoic acid.

**Solved Example :**

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



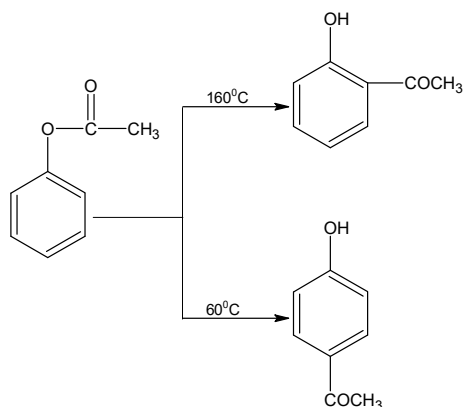
Ans. $\text{CHCl}_3 + \text{aq. KOH} \longrightarrow \text{:CCl}_2$



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 into o — and p — hydroxy ketones in the presence of anhydrous AlCl_3 . Generally low temperature favours the formation of p — isomer and higher temperature favours the o — isomer.



(B) Reactions due to breaking of carbon- Oxygen bond Nucleophilic substitution reaction

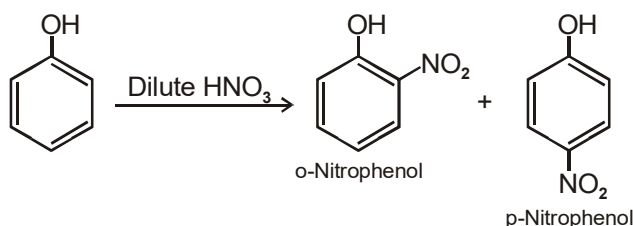
Phenols are less reactive than aliphatic compound because:

- OH group is present on sp^2 hybridised carbon. This makes C — O bond stronger.
- 'O' is more electronegative than halogens. This also makes C — O bond stronger than C — X.
- There is some double bond character between carbon and oxygen due to the resonance. This also makes C — O bond stronger.

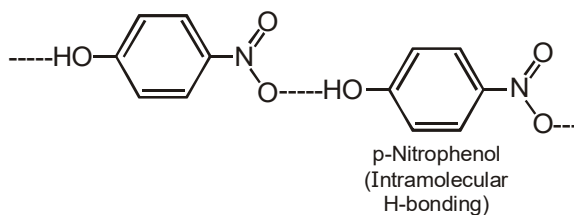
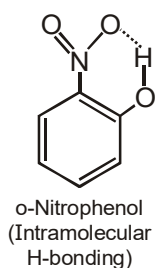
However it gives S_N under drastic condition.

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

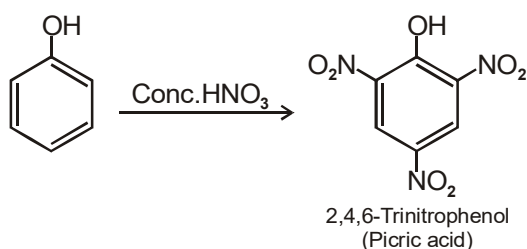
(i) **Nitration** : With dilute nitric acid at low temperature (298K), phenol yields a mixture of ortho and para nitrophenols.



The ortho and para isomers can be separated by steam distillation. 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.

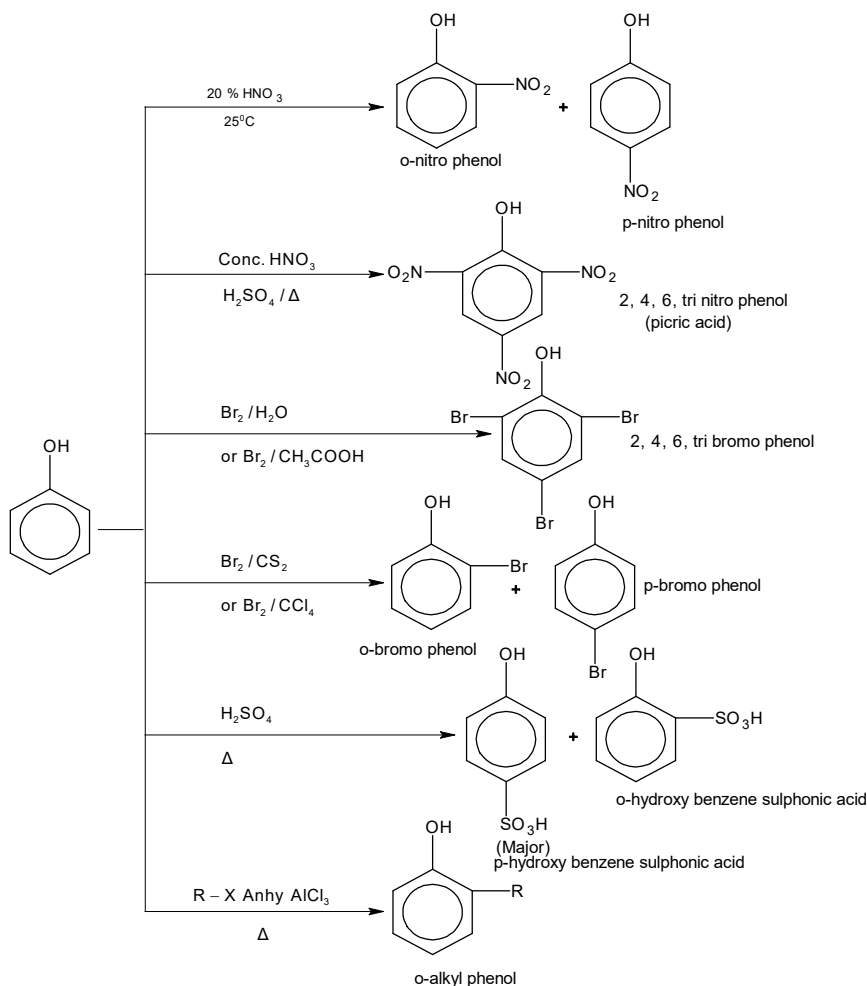


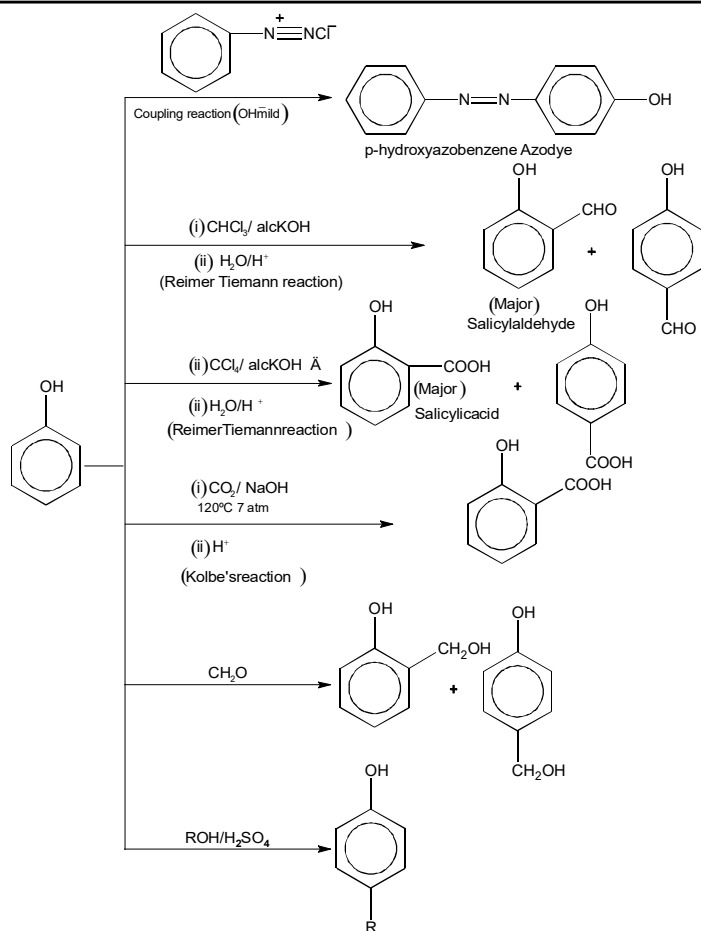
With concentrated nitric acid, phenol is converted to 2,4,6-trinitrophenol. The product is commonly known as picric acid. The yield of the reaction product is poor (due to deactivating $-\text{NO}_2$ groups toward electrophilic towards electrophilic aromatic substitution).



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

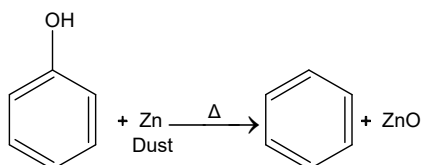
Nowadays picric acid is prepared by treating phenol first with concentrated sulphuric acid which converts it to phenol-2,4-disulphonic acid, and then with concentrated nitric acid to get 2,4,6-trinitrophenol. Can you write the equations of the reactions involved ?





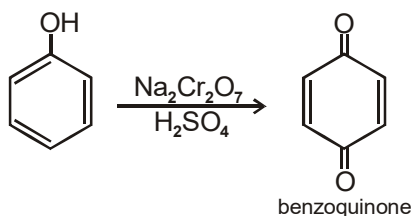
MISCELLANEOUS REACTION :

(i) Reaction with Zn dust :



(ii) Oxidation :

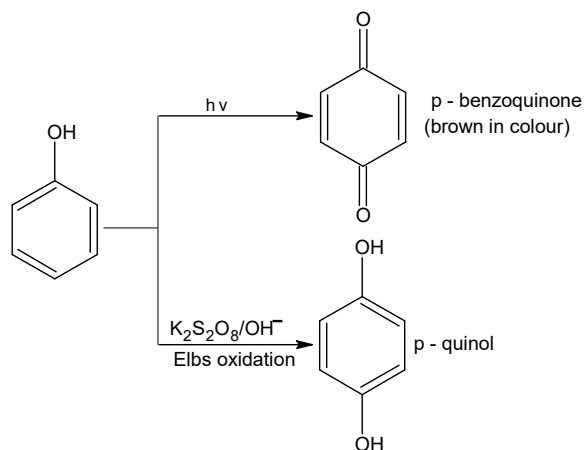
Oxidation of phenol with chromic acid produces a conjugated diketone known as benzoquinone. In the presence of air, phenols are slowly oxidised to dark coloured mixtures containing quinones.



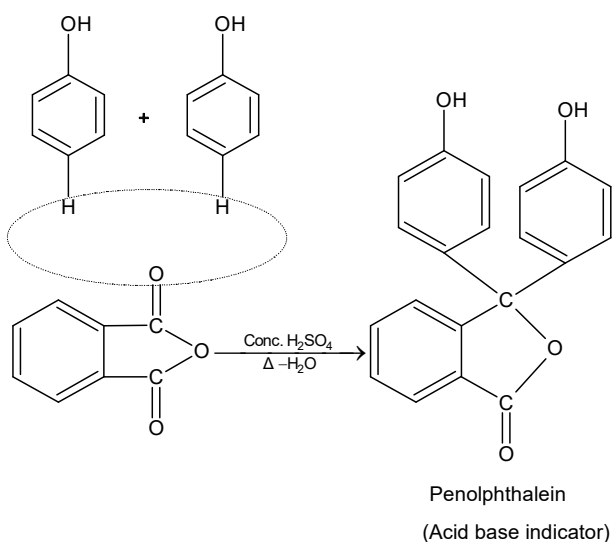
Solved Example :

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

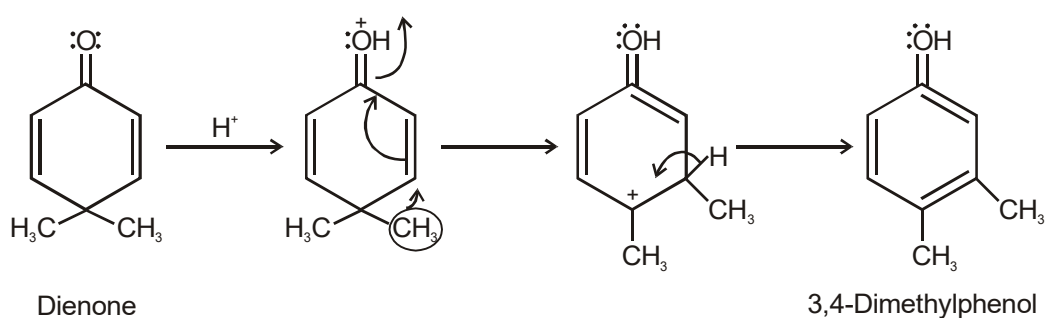


Solved Example :

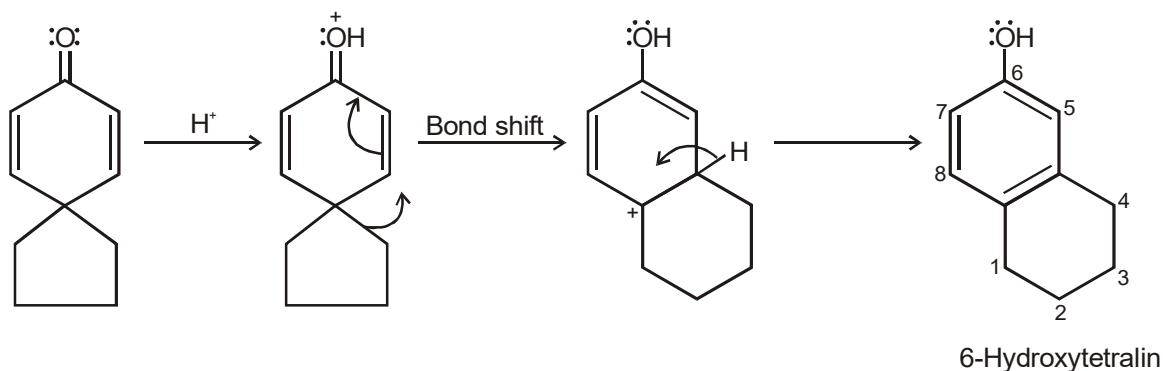
Qus. What is dienone-phenol rearrangement ? Why is it known as *retro*-pinacol rearrangement ?

Ans. Dienone-phenol rearrangement involves conversions of a cyclic dienone to phenolic compounds when treated with acid. The reaction involves 1,2-shift of an alkyl group or a bond depending on the nature of the compound. It is usually called *retro*-pinacol rearrangement because the ketonic group is transformed into hydroxy compound on treatment with acid and involves a shift. Two examples are given here.

For example :

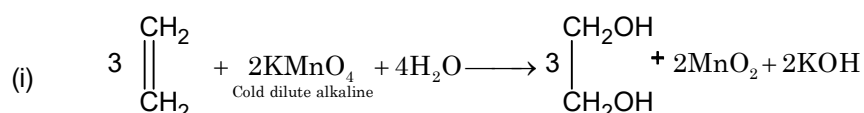


For example :

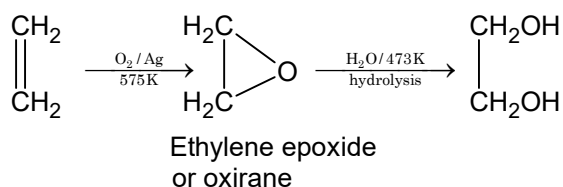


Ethylene Glycol : Ethane 1, 2 diol

Preparation : Lab preparation by hydroxylation.



Manufacture :

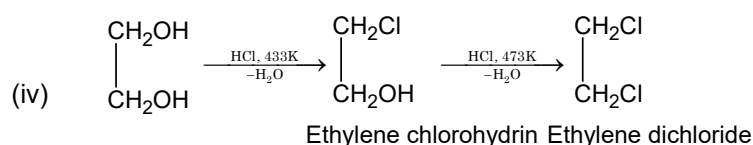
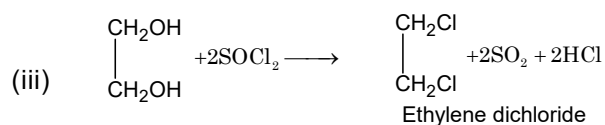
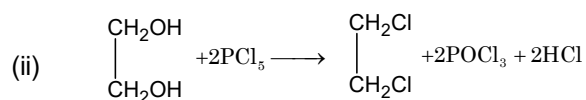
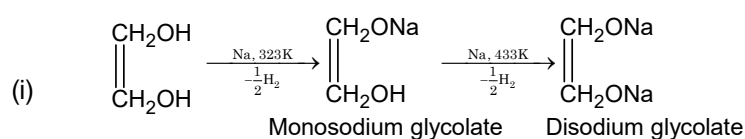


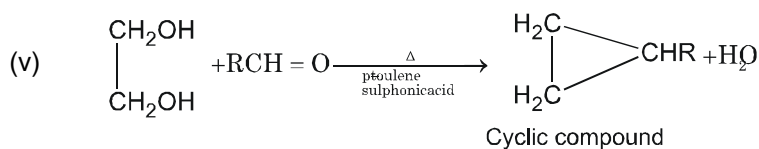
Physical properties:

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.

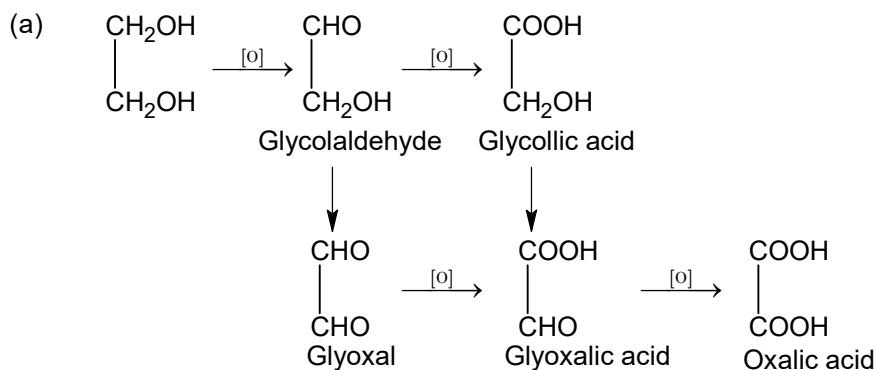
CHEMICAL PROPERTIES :

Reaction with sodium

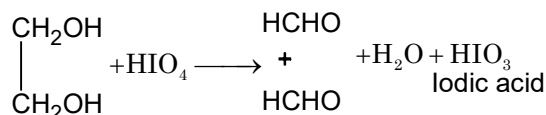




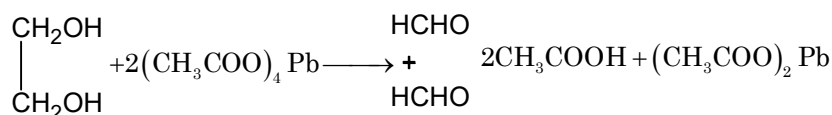
(vi) **Oxidation** : Ethylene glycol upon oxidation gives different products with different oxidising agents. For example.



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



Also called malapride reaction.



Solved Example :

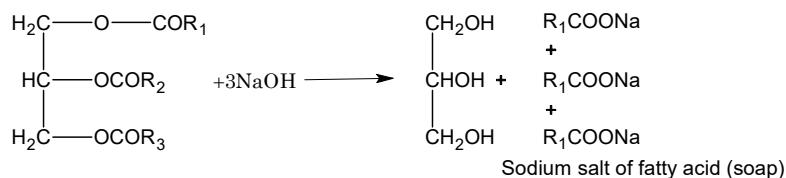
Qus. How would you convert cyclohexane to 1, 6 – hexanediol?

Glycerol (Propane 1, 2, 3 triol)

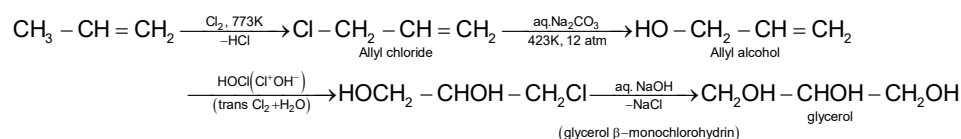
One of the most important trihydric alcohol.

Preparation:

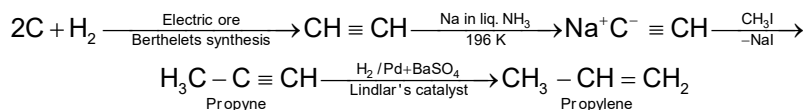
(i) **By Saponification of oils and fats.**



(ii) **From Propylene**



(iii) **Synthesis from its elements**

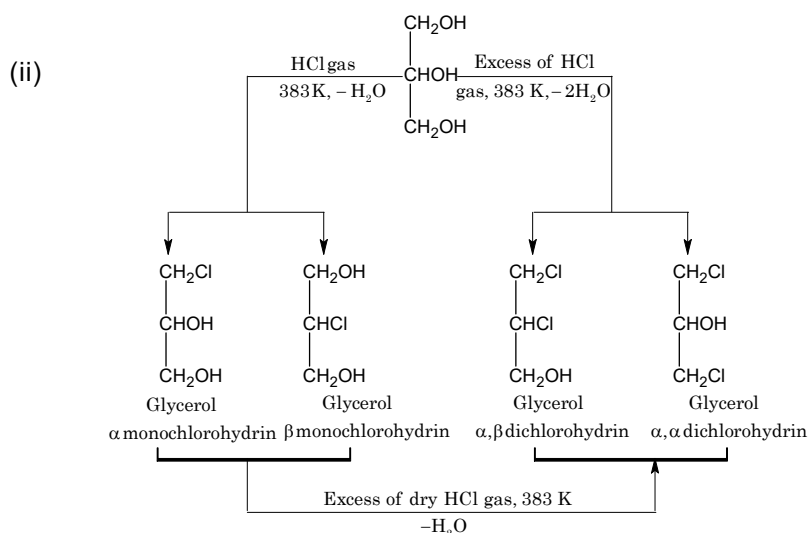
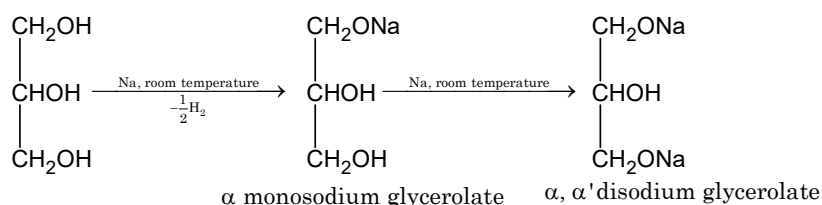


Physical Properties :

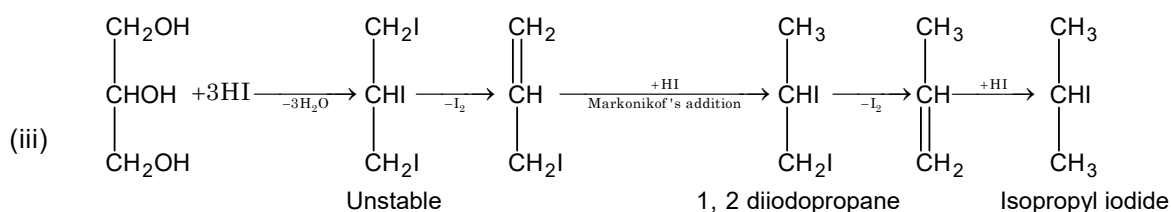
Highly viscous due to three —OH group due to which it undergoes extensive intermolecular H-bonding.

Chemical Properties :

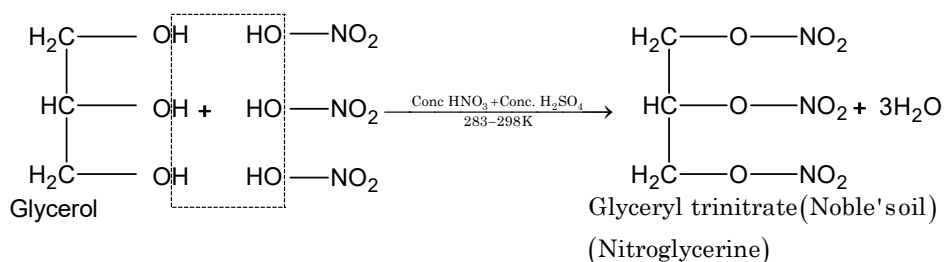
(i) It undergoes reaction of both secondary and primary alcoholic group.



To replace the third hydroxyl group in either of two dichlorohydrins, PCl₅ or PCl₃ is fused.

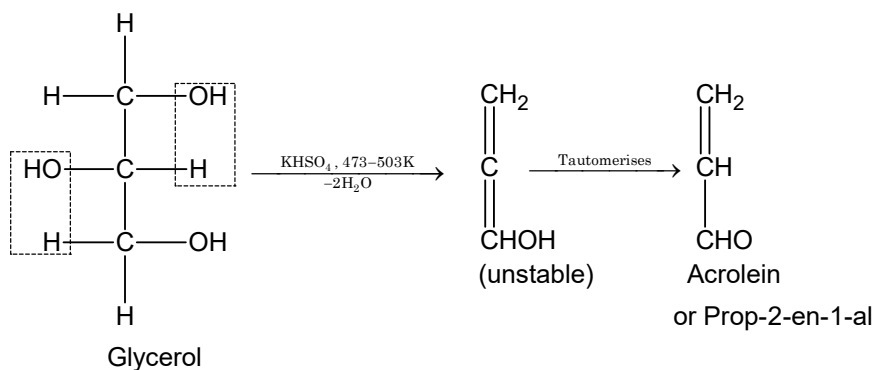


3. Reaction with concentrated nitric acid:

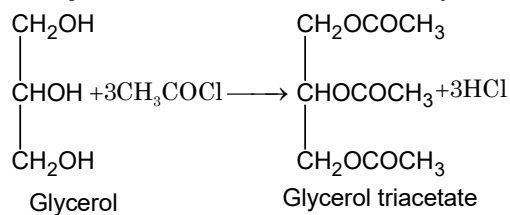


A mixture of glyceryl trinitrate and glyceryl dinitrate absorbed on Kieselguhr is called dynamite.

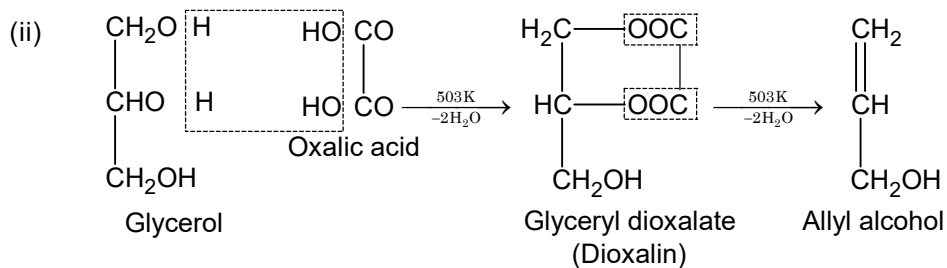
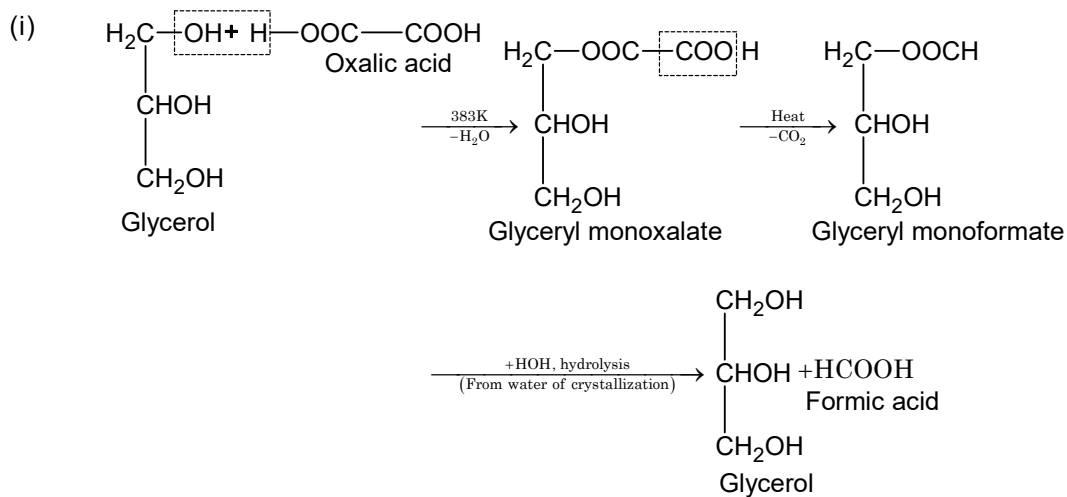
4. Reaction with KHSO_4 – Dehydration.



5. Acetylation. When treated with acetyl chloride, glycerol forms glycerol triacetate.



6. Reaction with oxalic acid



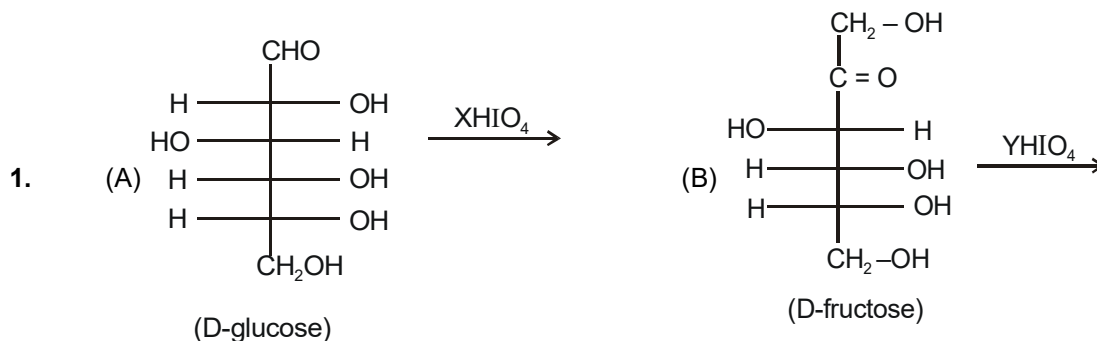
Uses: Glycerol is used :

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 hygroscopic nature.
7. As a preservative for fruits and other eatables.
8. As a sweetening agent in beverages and confectionary.

ALCOHOL ETHER & PHENOL

EXERCISE - I

Single Choice Questions :



x & y are moles of HIO_4 consumed in above reaction.

(i) Value of x in above reaction is

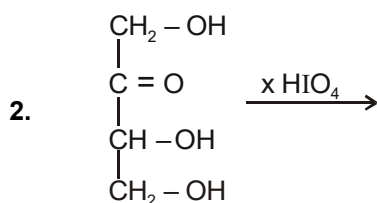
- (A) 2 (B) 3 (C) 4 (D) 5

(ii) Sum of x + y is

- (A) 8 (B) 9 (C) 10 (D) 11

(iii) Moles of HCHO formed in (A) is

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



x is moles of HIO_4 consumed.

- (A) x = 3 (B) x = 2 (C) x = 4 (D) x = 1

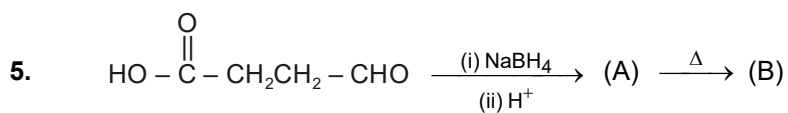


Product (B) is

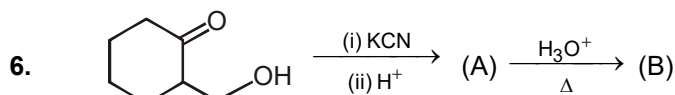
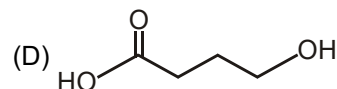
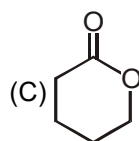
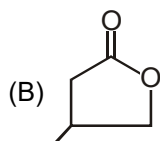
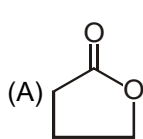


4. Which of the following compound not react with NaBH_4 ?

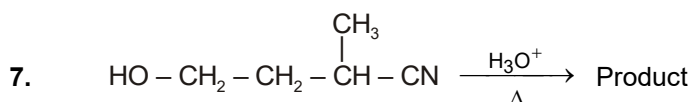
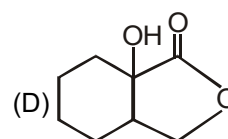
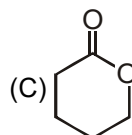
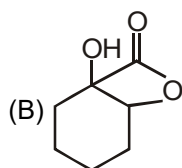
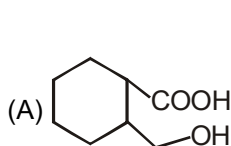




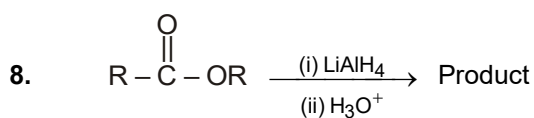
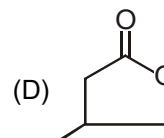
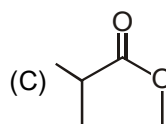
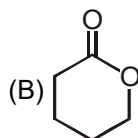
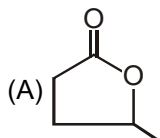
Structure of B will be :



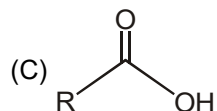
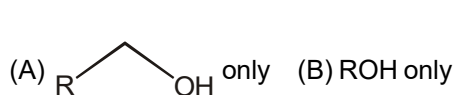
Structure of B will be :



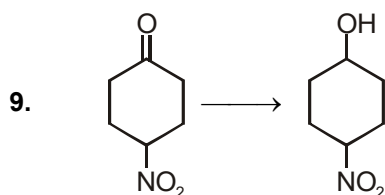
Structure of product will be :



Products will be :



(D) A and B both



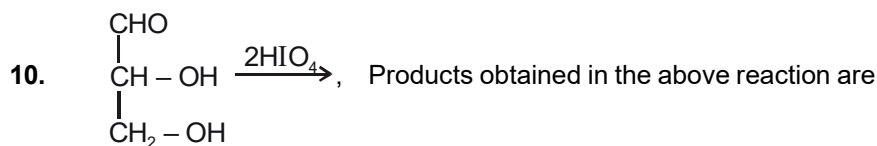
Above conversion can be achieved by :

(A) LiAlH_4

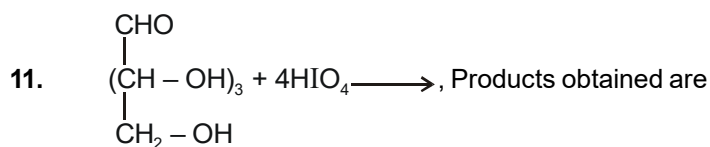
(B) H_2, Ni

(C) NaBH_4

(D) All

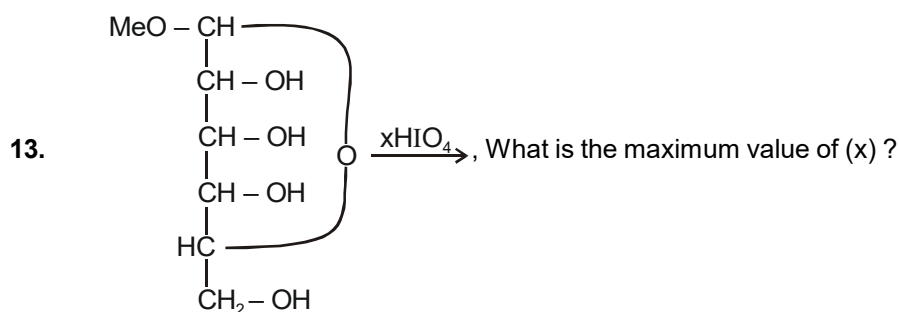
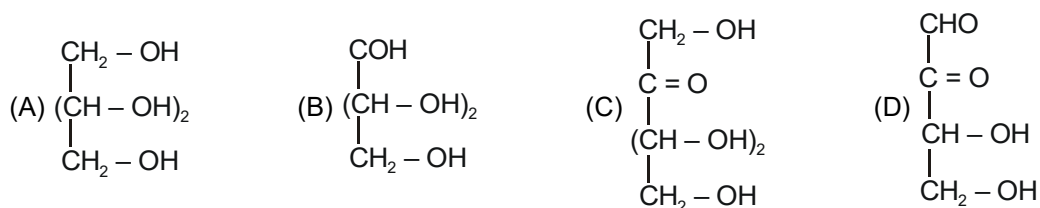


- (A) HCHO , HCO_2H (B) HCHO , $2\text{HCO}_2\text{H}$
(C) CO_2 , $2\text{HCO}_2\text{H}$ (D) CO_2 , HCHO , HCO_2H

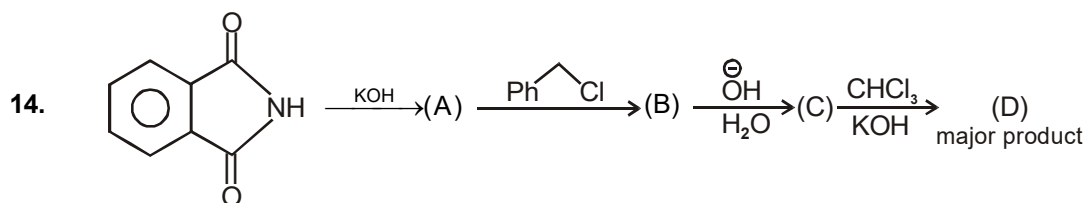


- Aldo pentose
(A) $4\text{HCO}_2\text{H}$, HCHO (B) $4\text{CH}_2\text{O}$, HCO_2H
(C) CO_2 , 4HCHO (D) CO_2 , $3\text{HCO}_2\text{H}$, HCHO

12. Which of the following compound gives 2HCHO , CO_2 , $2\text{HCO}_2\text{H}$ when oxidized by periodic acid?



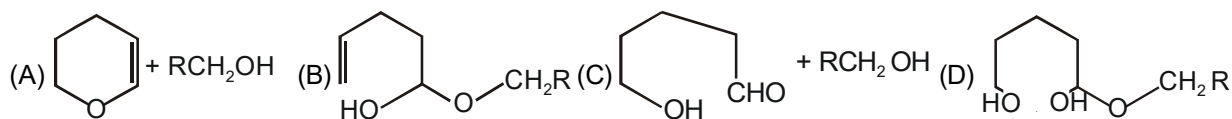
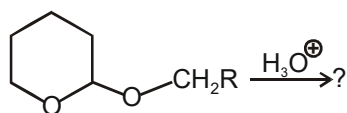
- (A) 1 (B) 2 (C) 3 (D) 4



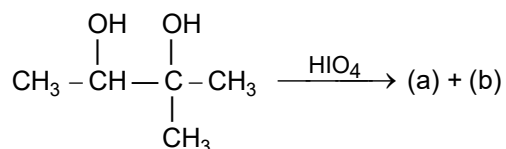
Structure of (D) is :

- (A) $\text{Ph} - \text{CH}_2\text{NH}_2$ (B) $\text{Ph} - \text{NC}$ (C) PhCH_2NC (D) PhCH_2CN

15. The major product formed in the reaction



16. In the given reaction:



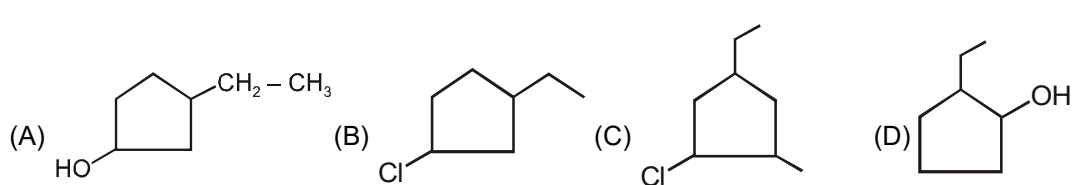
(a) and (b) respectively be:

- (A) CH₃CHO and CH₃CHO (B) CH₃COCH₃ and CH₃CHO
(C) CH₃COCH₃ and CH₃COCH₃ (D) CH₃COOH and CH₃COCH₃

17. Which of the following compound undergoes acid catalysed hydrolysis :

- (A) RCN (B) RCOOR (C) $\text{R} - \overset{\text{O}}{\parallel} \text{C} - \text{O} - \overset{\text{O}}{\parallel} \text{C} - \text{R}$ (D) All

18. $\xrightarrow[\Delta]{\text{NH}_2\text{-NH}_2/\text{HO}^\ominus}$ (A) ; Identify the A.



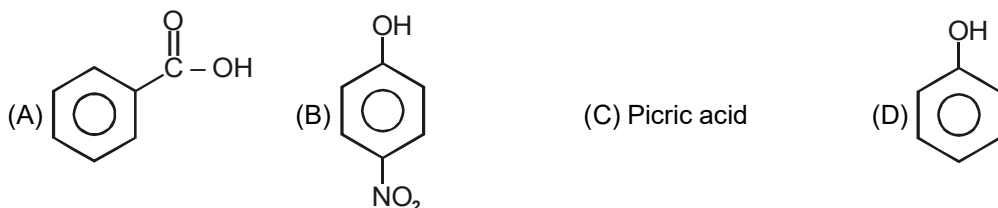
19. Which of the following compound react with DIBAL – H

- (A) (B) RCN (C) RCOOR (D) All

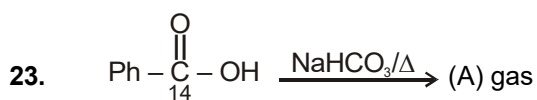
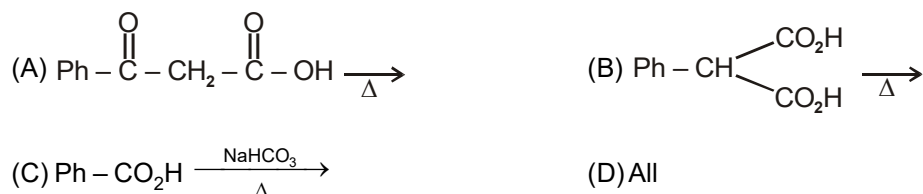
20. $\text{Ph} - \overset{\text{O}}{\parallel} \text{C} - \text{O} - \text{H} \xrightarrow{+ \text{Na}^{14}\text{HCO}_3^-}$ gas evolved is

- (A) CO₂ (B) ¹⁴CO₂ (C) H₂ (D) NH₃

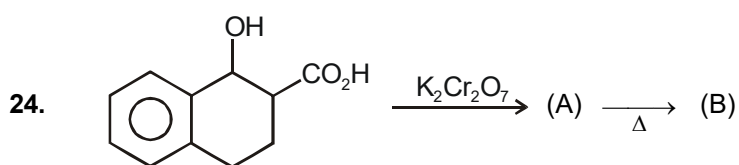
21. Which of the following not react with NaHCO_3 ?



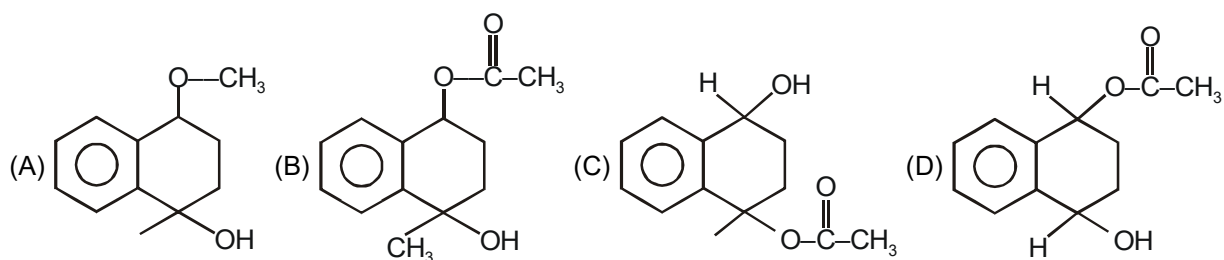
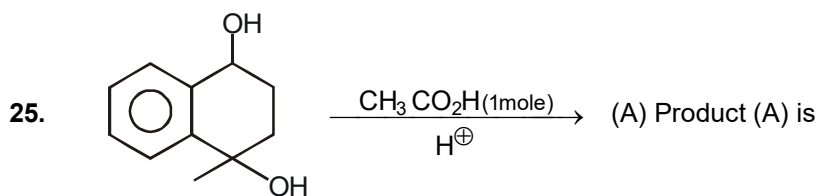
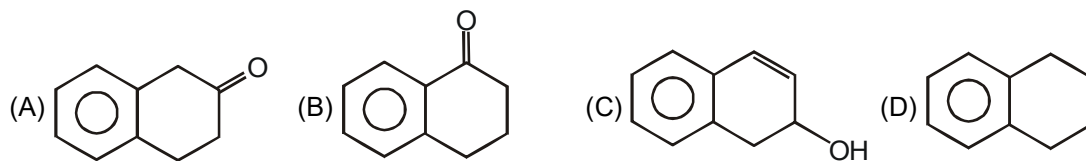
22. In which of the reaction CO_2 gas will evolve.

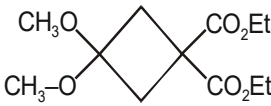
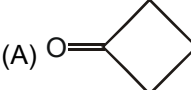
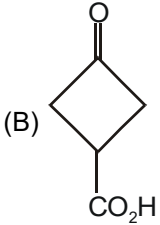
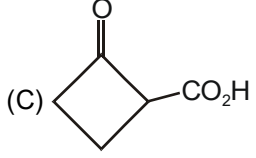
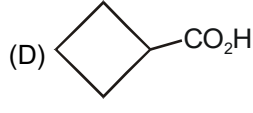


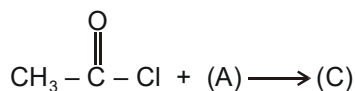
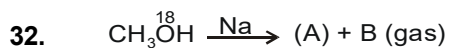
Gas (A) is



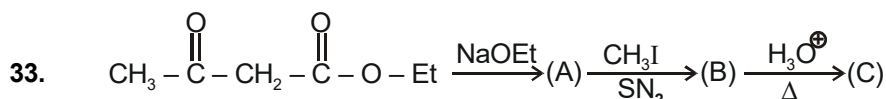
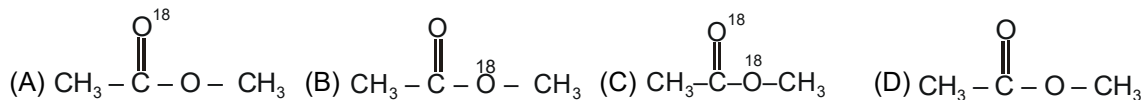
Product (B) is



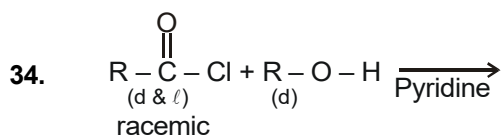
26.  ; Product (A) is
 $\xrightarrow[\text{(A)}]{\text{H}_3\text{O}^+ / \text{strongly heated}}$
- (A)  (B)  (C)  (D) 
27. $\text{Ph}-\text{C}(=\text{O})-\text{CH}_2-\text{C}(=\text{O})-\text{OEt} \xrightarrow{\text{H}_3\text{O}^+} \text{(A)} \xrightarrow{\Delta} \text{(B)}$
 Product (B) is
- (A) $\text{Ph}-\text{C}(=\text{O})-\text{H}$ (B) $\text{Ph}-\text{C}(=\text{O})-\text{CH}_3$ (C) $\text{Ph}-\text{CH}_2-\text{C}(=\text{O})-\text{OH}$ (D) $\text{Ph}-\text{CO}_2\text{H}$
28. $\text{R}-\text{C}(=\text{O})-\text{OH} + \text{R}'-\text{OH} \xrightleftharpoons{\text{H}^+} \text{R}-\text{C}(=\text{O})-\text{OR}'$
 In above esterification reaction rate of reaction is maximum. when $\text{R}'-\text{OH}$ is
 (A) 1° alcohol (B) 3° alcohol (C) 2° alcohol (D) CH_3OH
29. $\text{R}_1-\text{C}(=\text{O})-\text{OH} + \text{R}-\text{OH} \xrightleftharpoons{\text{H}_3\text{O}^+} \text{R}_1-\text{C}(=\text{O})-\text{OR} + \text{H}_2\text{O}$
 In above esterification reaction rate of reaction maximum when.
- (A) $\text{R}_1 = -\text{CH}_3$ (B) $\text{R}_1 = -\text{CH}_2-\text{CH}_3$ (C) $\text{R}_1 = -\text{CH}(\text{CH}_3)_2$ (D) $\text{R}_1 = -\text{C}(\text{CH}_3)_3$
30. $\text{CH}_3-\text{C}(=\text{O})-\text{CH}_2-\text{CH}_3 \xrightarrow{\text{Br}_2 / \text{H}^+} \text{A (major)}$
- (A) CHBr_3 (B) $\text{CH}_3-\text{C}(=\text{O})-\text{CH}(\text{Br})-\text{CH}_3$
 (C) $\text{CH}_2(\text{Br})-\text{C}(=\text{O})-\text{CH}_2-\text{CH}_3$ (D) $\text{CH}_3-\text{C}(=\text{O})-\text{CH}_2-\text{CH}_2-\text{Br}$
31. Which of the following compound not reacts with NaOH
 (A) $\text{Ph}-\text{CH}_2-\text{OH}$ (B) $\text{Ph}-\text{OH}$ (C) $\text{Ph}-\text{CO}_2\text{H}$ (D) $\text{Ph}-\text{SO}_3\text{H}$



Product (C) of above reaction is

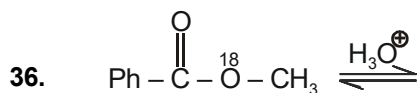
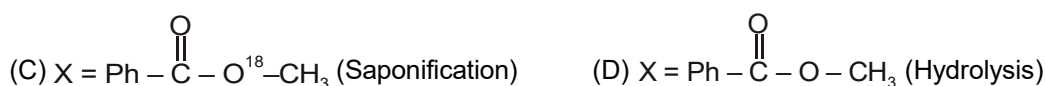
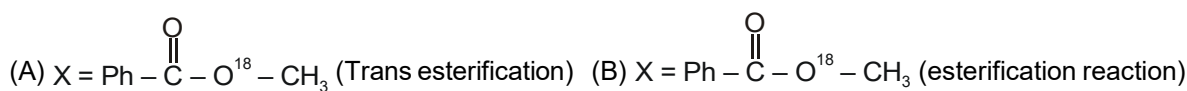
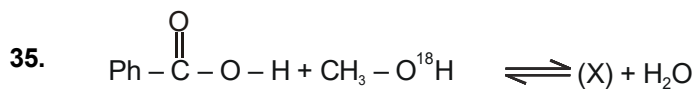


Product (C) is



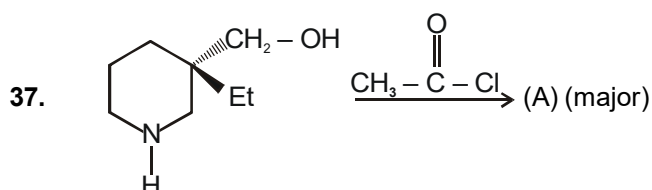
Products of above reaction is

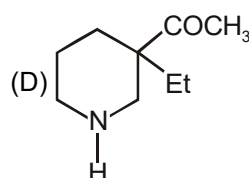
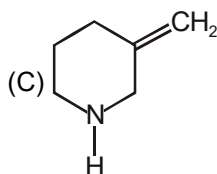
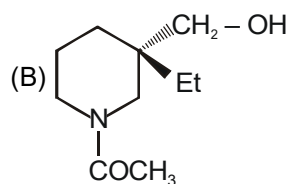
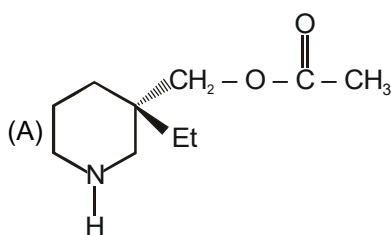
- (A) Enantiomer (B) Racemic (C) Diastereomers (D) Meso.



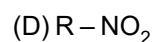
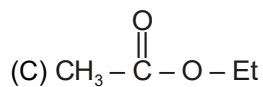
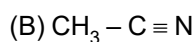
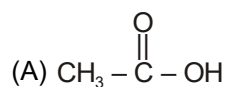
O^{18} is present in

- (A) Carboxylic acid (B) Alcohol (C) Water (D) Cannot predict

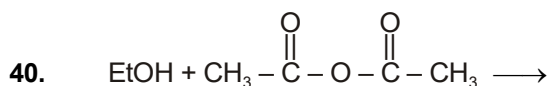
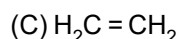
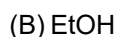
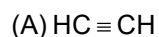




38. Which of following compound not reduced by DIBAL-H ?



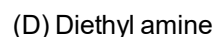
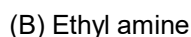
39. Which of the following compound not reacts with NaOH ?



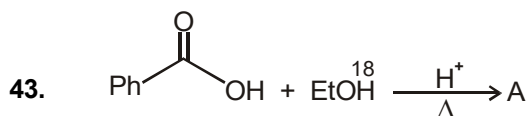
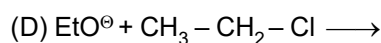
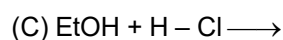
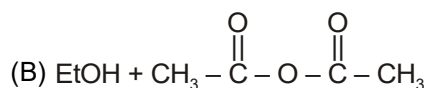
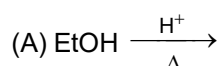
In above reaction molecular weight of alcohol increases by.



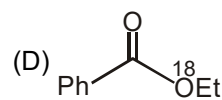
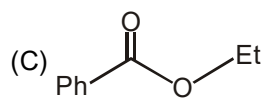
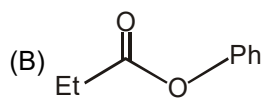
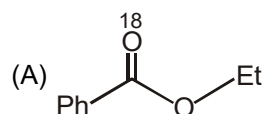
41. N-Ethyl phthalamide on hydrolysis gives:

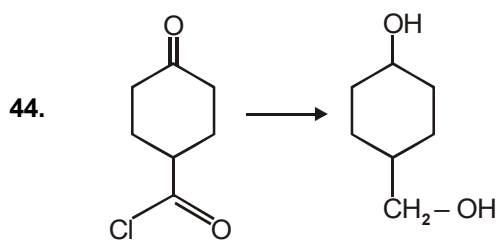


42. Which of the following is acetylation reaction :



Major product A is

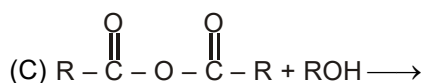
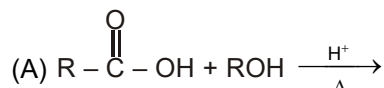




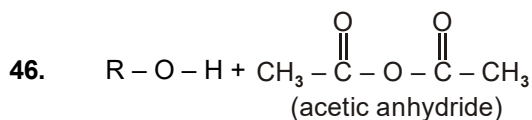
Reagent used is

- (A) LiAlH_4 (B) NaBH_4 (C) DIBAL - H (D) Both (A) and (B)

45. Which of following is esterification reaction ?



(D) All

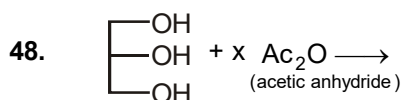


Above reaction is

- (A) Acetylation reaction (B) Nitration (C) Sulphonation (D) Alkylation reaction

47. In above reaction molecular weight of alcohol increases by

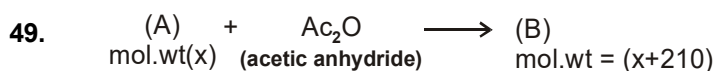
- (A) 40 (B) 41 (C) 42 (D) 43



Glycerol

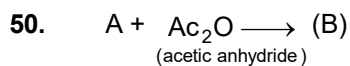
How many moles of acetic anhydride consumed in this reaction ?

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



Number of (OH) group present in (A) is

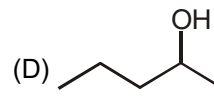
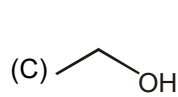
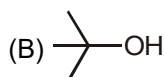
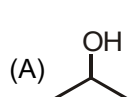
- (A) 3 (B) 4 (C) 5 (D) 6



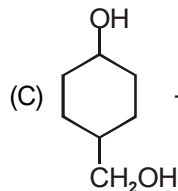
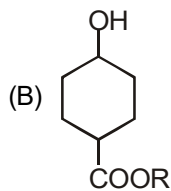
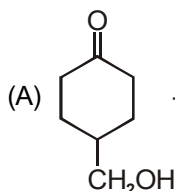
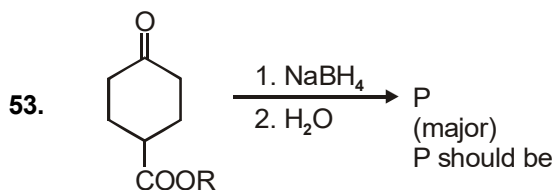
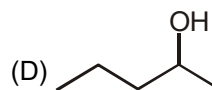
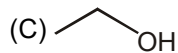
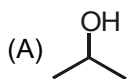
Molecular formula of A increases by $\text{C}_8\text{H}_8\text{O}_4$. Number of OH group present in A are

- (A) 3 (B) 4 (C) 5 (D) 6

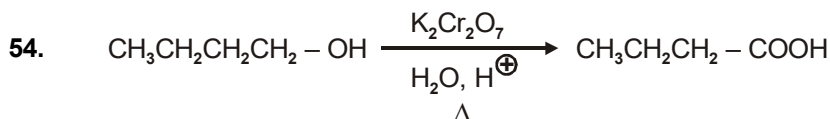
51. Which of following alcohol will not undergo oxidation ?



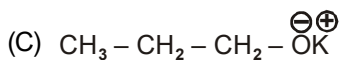
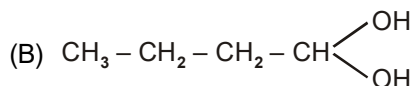
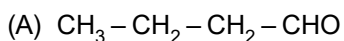
52. Which of following alcohol will not undergo iodoform test -



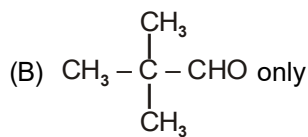
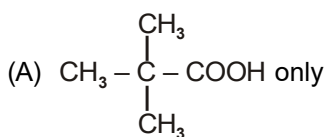
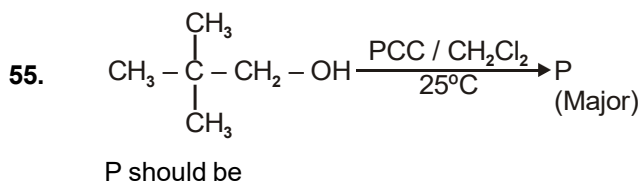
(D) None of these



This oxidation occurs through the generation of

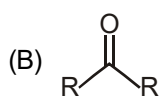
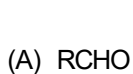
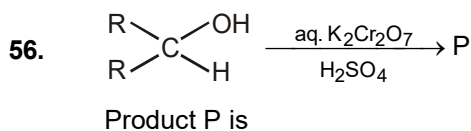


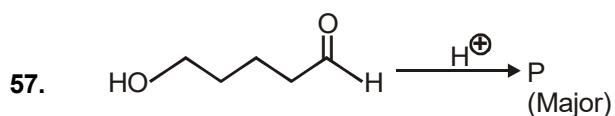
(D) Both (A) and (B)



(C) A mixture of both (A) and (B)

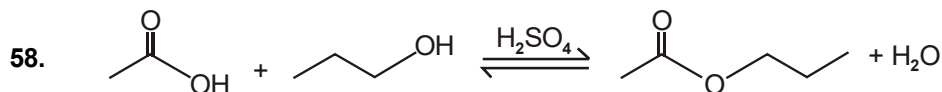
(D) None of these





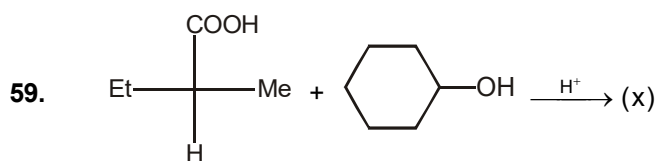
P should be

- (A) OCC1OCCCC1 (B) OCC1OCCCC1 (C) OC1OCCCC1 (D) None of these
- (Acetal) (Hemiacetal)



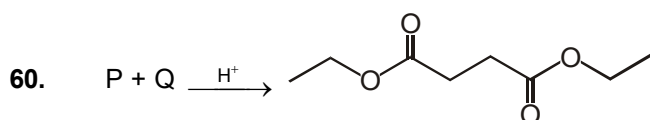
In given reaction yield of product can be increased by

- (A) Adding excess of alcohol (B) Remove water
(C) Removing of alcohol (D) A and B both



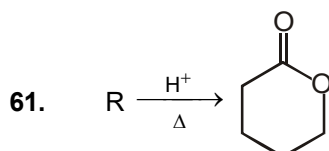
(x) may be

- (A) CC(C)(C)C(=O)OC1CCCCC1 (B) CC(C)(C)C(=O)OC1CCCCC1
(C) CC(C)(C)C(=O)OC1CCCCC1 (D) B and C both



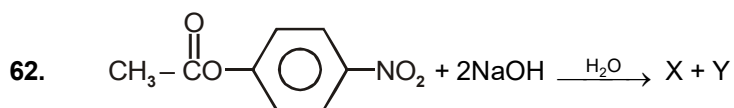
P and Q may be

- (A) Adipic acid + EtOH (B) Malonic acid + EtOH
(C) Succinic acid + EtOH (D) Gluteric acid + EtOH



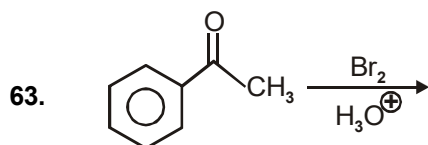
Structure of R is

- (A) OHCH2CH2CH2CH2CH2COOH (B) HOCH2CH2CH2CH2COOH
(C) HOCH2CH2CH2CH2COOH (D) None



X + Y will be

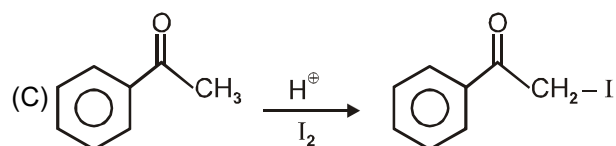
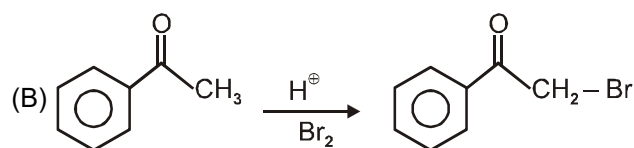
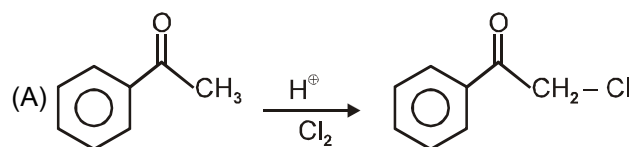
- (A) CH_3COONa (B) $\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{OH}$ (C) $\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{ONa}$ (D) A and C both



This reaction is known as

- (A) Acid-catalysed α -bromination of ketone (B) Acid-promoted α -bromination of ketone
(C) Acid-catalysed bromination of benzene ring (D) Acid-promoted bromination of benzene ring

64. Ease of reaction is maximum in which of the following cases?



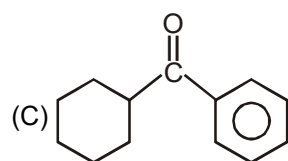
(D) Rate is independent of halogens

65. Which of the following ketone / aldehyde can undergoes haloform reaction?

- (A) $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$ (B) CH_3-CHO (C) (D) All of these

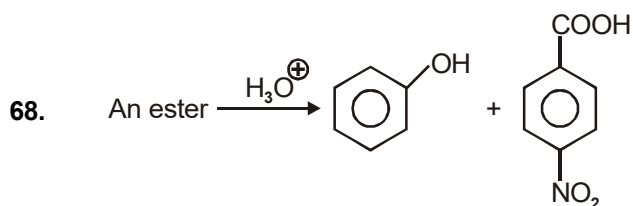
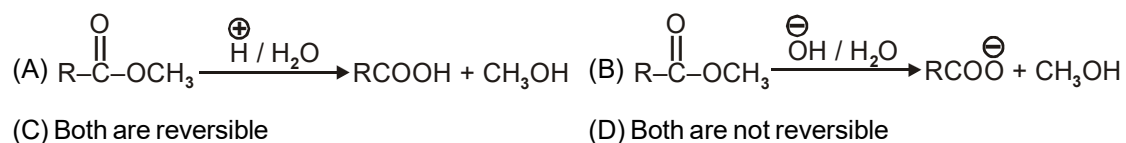
66. Which of the following compounds can undergoes haloform reaction?

- (A) $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{CH}_2-\text{CH}_3$ (B)

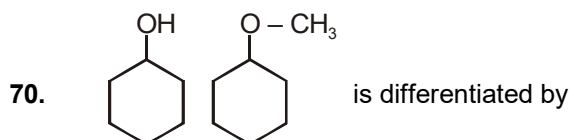
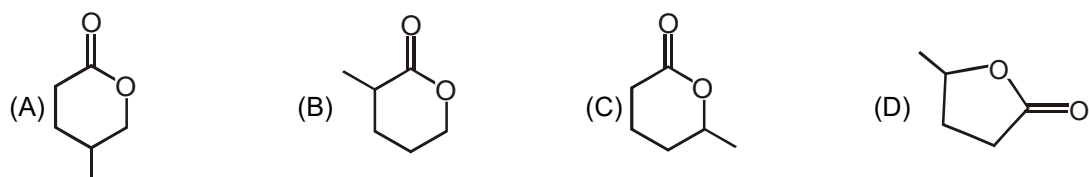
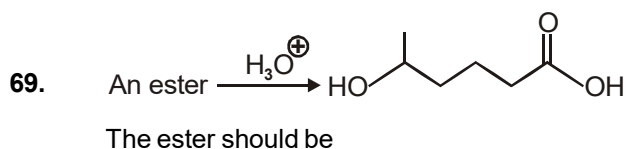
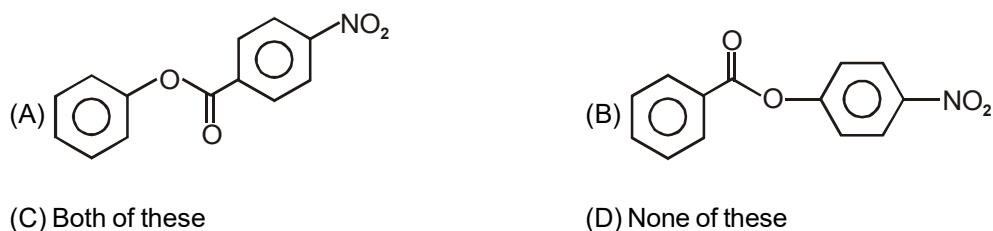


- (D) $\text{CH}_3-\text{CH}_2-\text{CHO}$

67. Which of the following reactions is reversible?




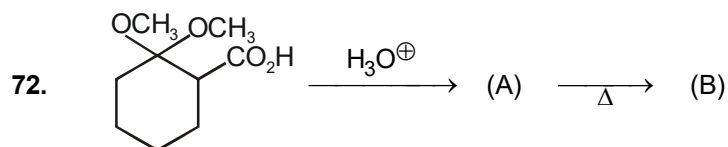
The ester should be



- (A) Iodoform test (B) Na-metal (C) 2, 4-DNP (D) All of these

71. Which of the following properties is correctly written

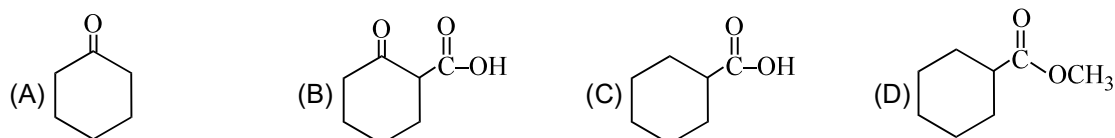
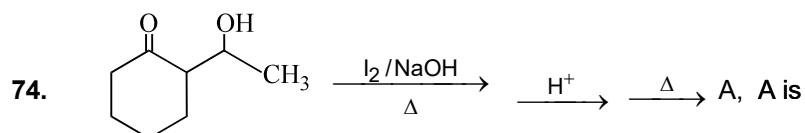
- (A) Ph – OH (Transparent crystalline solid) (B)  (Colourless liquid)
 (C) Ph – CO₂H (White crystalline solid) (D) All



Product (B) is



73. Which of following ether on hydrolysis give two alcohol, both of them give (+)ve Iodoform test ?



75. Glycol on treatment with PI_3 mainly gives—

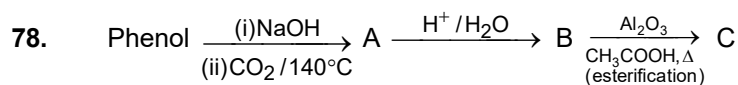
- (A) Ethylene (B) Ethylene iodide (C) Ethyl iodide (D) Ethane

76. A compound 'X' with molecular formula $\text{C}_3\text{H}_8\text{O}$ can be oxidised to a compound 'Y' with the molecular formula $\text{C}_3\text{H}_6\text{O}_2$, 'X' is most likely to be

- (A) Primary alcohol (B) Secondary alcohol
(C) Aldehyde (D) Ketone

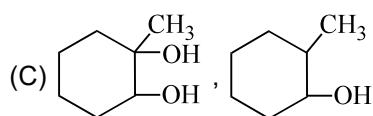
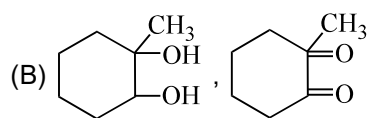
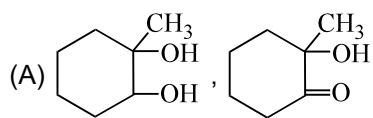
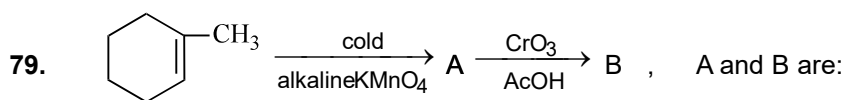
77. Phenol react with Hinsberg's reagent gives

- (A) Sulphone (B) Sulphanilic acid
(C) Sulphonic ester (D) Sulphonal

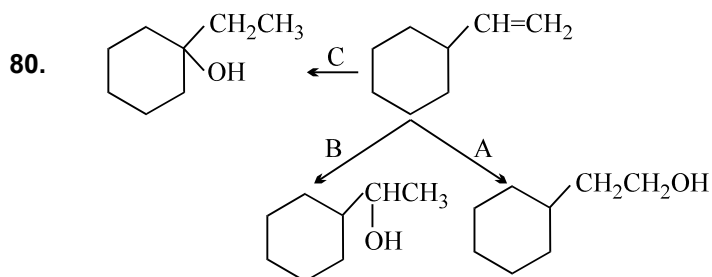


In this reaction, the end product C is:

- (A) salicylaldehyde (B) salicylic acid
(C) phenyl acetate (D) aspirin



(D) no formation of A and B



Select schemes A, B, C out of

I. acid catalysed hydration

II. HBO

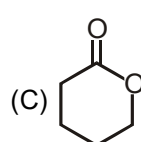
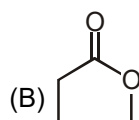
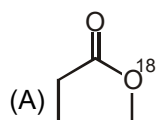
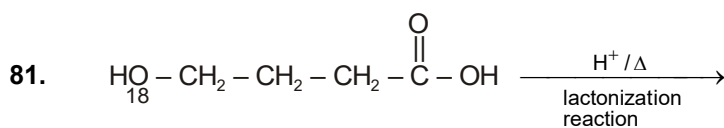
III. oxymercuration-demercuration

(A) I in all cases

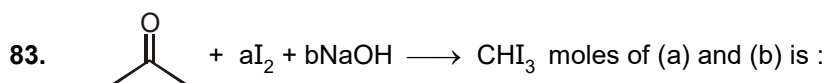
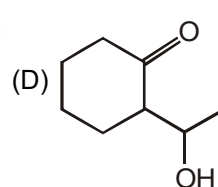
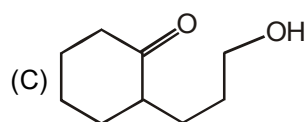
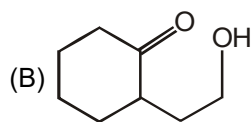
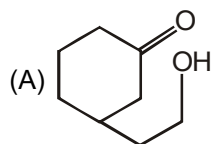
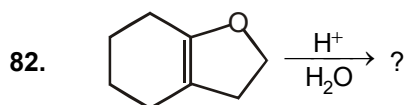
(B) I, II, III

(C) II, III, I

(D) III, I, II



(D) None

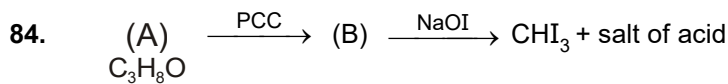


(A) 3, 3

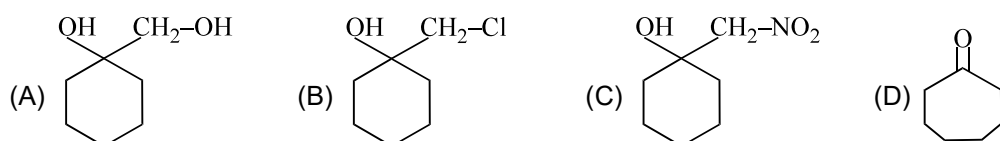
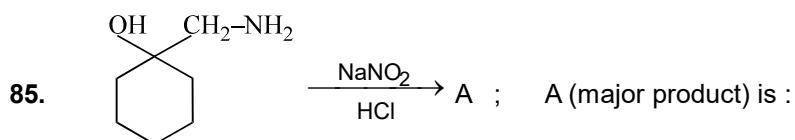
(B) 3, 4

(C) 4, 4

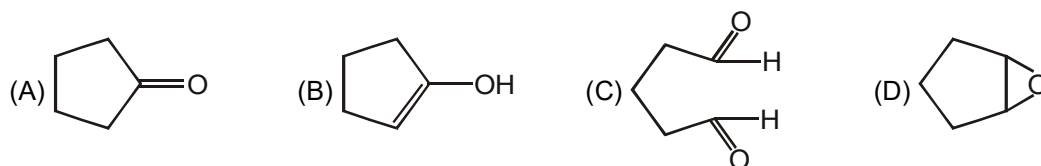
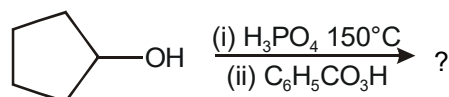
(D) 5, 4



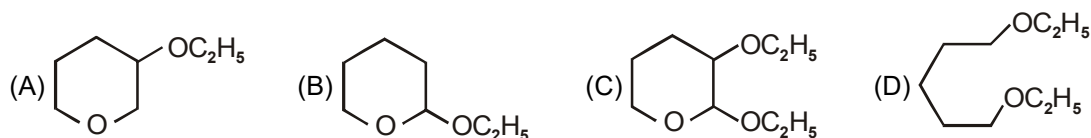
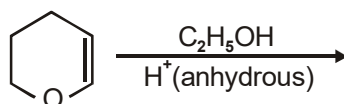
reactant (A) is :



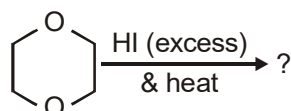
86. What will be the chief product from the following reaction sequence?



87. Which of the following is the product from ethanol addition to dihydropyran (shown on the left below)?



88. What product(s) are expected from the following reaction?



EXERCISE-II

1. $\text{CH}_3\text{CH}_2\text{COOH} \xrightarrow[\text{red P}]{\text{Cl}_2} \text{A} \xrightarrow{\text{alc. KOH}} \text{B}$. What is B ? [AIEEE-2002 & IIT 1995]

- (A) $\text{CH}_3\text{CH}_2\text{COCl}$ (B) $\text{CH}_3\text{CH}_2\text{CHO}$
 (C) $\text{CH}_2=\text{CHCOOH}$ (D) $\text{ClCH}_2\text{CH}_2\text{COOH}$

2. On vigorous oxidation by permanganate solution [AIEEE-2002]
 $(\text{CH}_3)_2\text{C}=\text{CH}-\text{CH}_2-\text{CHO}$ gives

- (A) $\text{CH}_3-\overset{\text{CH}_3\text{OH}}{\underset{\text{CH}_3}{\text{C}}}-\overset{\text{OH}}{\text{CH}}-\text{CH}_2\text{CH}_3$ (B) $\text{CH}_3\text{COCH}_3 + \text{CH}_2 \begin{matrix} \nearrow \text{CO}_2\text{H} \\ \searrow \text{CO}_2\text{H} \end{matrix}$
 (C) $\text{CH}_3 \begin{matrix} \nearrow \\ \searrow \end{matrix} \text{CH}-\text{OH} + \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (D) $\text{CH}_3 \begin{matrix} \nearrow \\ \searrow \end{matrix} \text{C}=\text{O} + \text{CH}_3\text{CH}_2\text{CHO}$

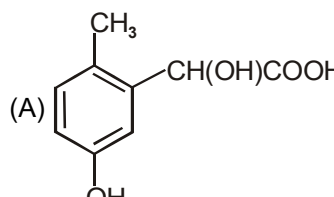
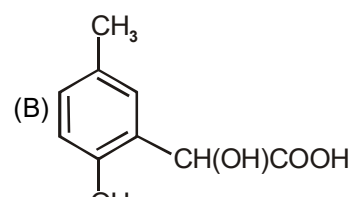
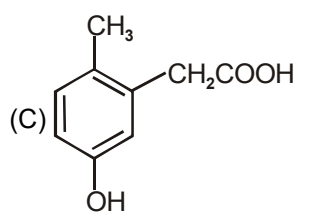
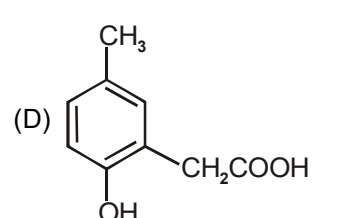
3. An ether is more volatile than an alcohol having the same molecular formula. This is due to [AIEEE-2003]

- (A) dipolar character of ethers
 (B) alcohols having resonance structures
 (C) inter-molecular hydrogen bonding in ethers
 (D) inter-molecular hydrogen bonding in alcohols

4. Acid catalyzed hydration of alkenes except ethene leads to the formation of [AIEEE-2005]

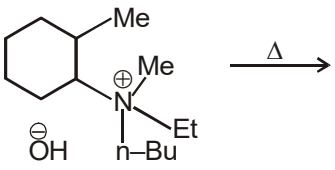
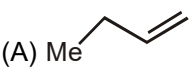
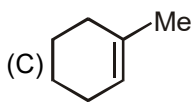
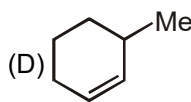
- (A) primary alcohol (B) secondary or tertiary alcohol
 (C) mixture of primary and secondary alcohols (D) mixture of secondary and tertiary alcohols

5. p-cresol reacts with chloroform in alkaline medium to give the compound A which adds hydrogen cyanide to form, the compound B. The latter on acidic hydrolysis gives chiral carboxylic acid. The structure of the carboxylic acid is [AIEEE-2005]

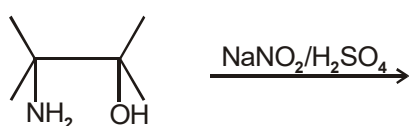
- (A)  (B) 
 (C)  (D) 

6. Reaction of one molecule of HBr with one molecule of 1, 3-butadiene at 40°C gives predominantly

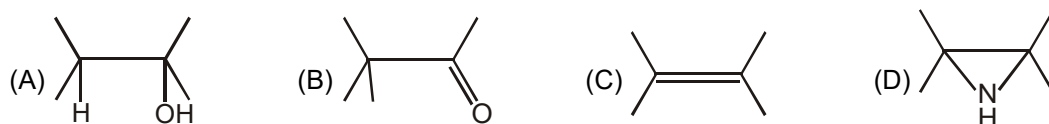
- (A) 3-bromobutene under kinetically controlled conditions [AIEEE-2005]
 (B) 1-bromo-2-butene under thermodynamically controlled conditions
 (C) 3-bromobutene under thermodynamically controlled conditions
 (D) 1-bromo-2-butene under kinetically controlled conditions

7. Which one of the following methods is neither meant for the synthesis nor for separation of amines? [AIEEE-2005]
- (A) Hinsberg method (B) Hofmann method
(C) Wurtz reaction (D) Curtius reaction
8. Among the following the one that gives positive iodoform test upon reaction with I_2 and NaOH is [AIEEE-2006]
- (A) $CH_3CH_2CH(OH)CH_2CH_3$ (B) $C_6H_5CH_2CH_2OH$
(C) $H_3C-CH(CH_3)-CH_2OH$ (D) $PhCHOHCH_3$
9.  The alkene formed as a major product in the above elimination reaction is [AIEEE-2006]
- (A)  (B) $CH_2 = CH_2$ (C)  (D) 
10. HBr reacts with $CH_2 = CH - OCH_3$ under anhydrous conditions at room temperature to give [AIEEE-2006]
- (A) CH_3CHO and CH_3Br (B) $BrCH_2CHO$ and CH_3OH
(C) $BrCH_2 - CH_2 - OCH_3$ (D) $H_3C - CHBr - OCH_3$
11. The compound formed as a result of oxidation of ethyl benzene by $KMnO_4$ is : [AIEEE-2007]
- (A) benzophenone (B) acetophenone (C) benzoic acid (D) benzyl alcohol
12. In the following sequence of reactions, the alkene affords the compound 'B' [AIEEE-2008]
- $$CH_3CH = CHCH_3 \xrightarrow{O_3} A \xrightarrow[Zn]{H_2O} B.$$
- The compound B is
- (A) CH_3CH_2CHO (B) CH_3COCH_3 (C) $CH_3CH_2COCH_3$ (D) CH_3CHO
13. A liquid was mixed with ethanol and a drop of concentrated H_2SO_4 was added. A compound with a fruity smell was formed. The liquid was : [AIEEE-2009]
- (A) CH_3COCH_3 (B) CH_3COOH (C) CH_3OH (D) $HCHO$
14. Iodoform can be prepared from all except : [AIEEE-2012]
- (A) Ethyl methyl ketone (B) Isopropyl alcohol
(C) 3-Methyl-2-butanone (D) Isobutyl alcohol
15. Rate of dehydration of alcohols follows the order : [JEE MAINS ONLINE-2013]
- (A) $3^\circ > 2^\circ > 1^\circ > CH_3OH$ (B) $2^\circ > 3^\circ > 1^\circ > CH_3OH$
(C) $CH_3OH > 1^\circ > 2^\circ > 3^\circ$ (D) $2^\circ > 1^\circ > CH_3OH > 3^\circ$
16. An ether (A), $C_5H_{12}O$, when heated with excess of hot concentrated HI produced two alkyl halides which when treated with NaOH yielded compounds (B) and (C). Oxidation of (B) and (C) gave a propanone and an ethanoic acid respectively. The IUPAC name of the ether (A) is : [JEE MAINS ONLINE-2013]
- (A) 2-methoxybutane (B) Methoxybutane (C) 2-ethoxypropane (D) Ethoxypropane

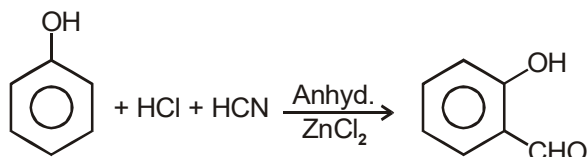
17. The major product formed when 1,1,1-trichloro-propane is treated with aqueous potassium hydroxide is : **[JEE MAINS Online-2014]**
 (A) Propyne (B) 1-Propanol (C) 2-Propanol (D) Propionic acid
18. The final product formed when Methyl amine is treated with NaNO_2 and HCl is : **[JEE MAINS Online-2014]**
 (A) Diazomethane (B) Methylalcohol (C) Methylcyanide (D) Nitromethane
19. Williamson synthesis of ether is an example of : **[JEE MAINS Online-2014]**
 (A) Nucleophilic addition (B) Electrophilic addition
 (C) Electrophilic substitution (D) Nucleophilic substitution
20. In the hydroboration-oxidation reaction of propene with diborane, H_2O_2 and NaOH , the organic compound formed is : **[JEE MAINS Online-2014]**
 (A) $\text{CH}_3\text{CH}_2\text{OH}$ (B) $\text{CH}_3\text{CHOHCH}_3$ (C) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (D) $(\text{CH}_3)_3\text{COH}$
21. The major product of the reaction **[JEE MAINS Online-2014]**



is :

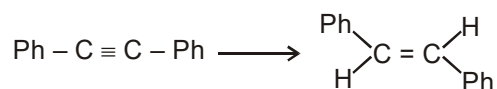


22. The following reaction **[JEE MAINS Online-2014]**



is known as :

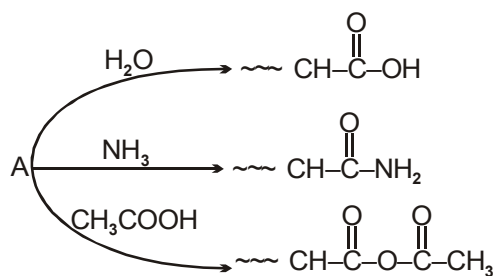
- (A) Perkin reaction (B) Gattermann-Koch Formylation (C) Kolbe's reaction (D) Gattermann reaction
23. The reagent needed for converting **[JEE MAINS Online-2014]**



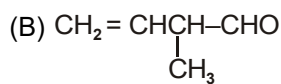
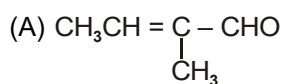
is :

- (A) Cat. Hydrogenation (B) $\text{H}_2/\text{Lindlar Cat.}$ (C) Li/NH_3 (D) LiAlH_4
24. Complete reduction of benzene-diazonium chloride with Zn/HCl gives : **[JEE MAINS Online-2014]**
 (A) Aniline (B) Phenylhydrazine (C) Azobenzene (D) Hydrazobenzene

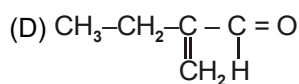
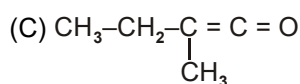
25. An organic compound A, C_5H_8O ; reacts with H_2O , NH_3 and CH_3COOH as described below :



A is :

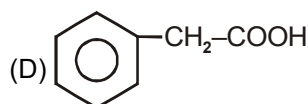
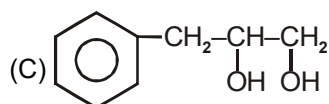
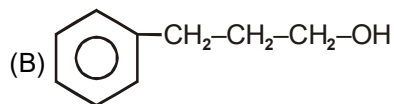
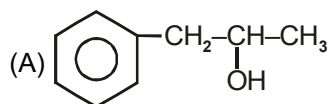


[JEE MAINS Online-2014]



26. on mercuric-ion-catalyzed hydration produces the major product :

[JEE MAINS Online-2014]



27. In the Victor-Meyer's test, the colour given by 1°, 2° and 3° alcohols are respectively :

[JEE MAINS Online-2014]

- (A) Red, colourless, blue
(C) Colourless, red, blue

- (B) Red, blue, colourless
(D) Red, blue, violet

28. In the reaction, $CH_3COOH \xrightarrow{LiAlH_4} A \xrightarrow{PCl_5} B \xrightarrow{\text{Alc. KOH}} C$, the product C is [JEE MAINS-2014]

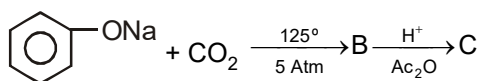
- (A) Acetylene (B) Ethylene (C) Acetyl chloride (D) Acetaldehyde

29. The most suitable reagent for the conversion of $R - CH_2 - OH \rightarrow R - CHO$ is

[JEE MAINS-2014]

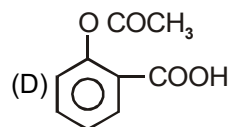
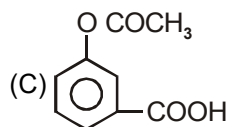
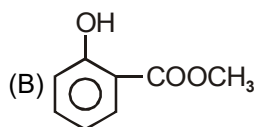
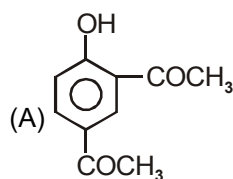
- (A) $K_2Cr_2O_7$ (B) CrO_3
(C) PCC (Pyridinium Chlorochromate) (D) $KMnO_4$

30. Sodium phenoxide when heated with CO_2 under pressure at $125^\circ C$ yields a product which on acetylation produces C.



The major product C would be

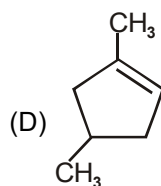
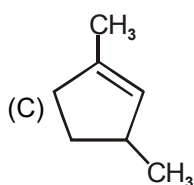
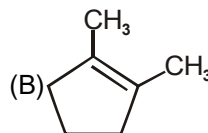
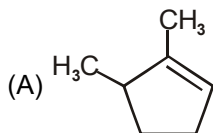
[JEE MAINS-2014]



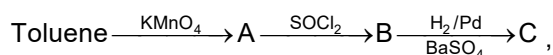
31. The synthesis of alkyl fluorides is best accomplished by [JEE Main-2015]
 (A) Swarts reaction (B) Free radical fluorination
 (C) Sandmeyer's reaction (D) Finkelstein reaction

32. Which of the following compounds will exhibit geometrical isomerism? [JEE Main-2015]
 (A) 1, 1-Diphenyl-1-propane (B) 1-Phenyl-2-butene
 (C) 3-Phenyl-1-butene (D) 2-Phenyl-1-butene

33. Which compound would give 5-keto-2-methyl hexanal upon ozonolysis? [JEE Main-2015]

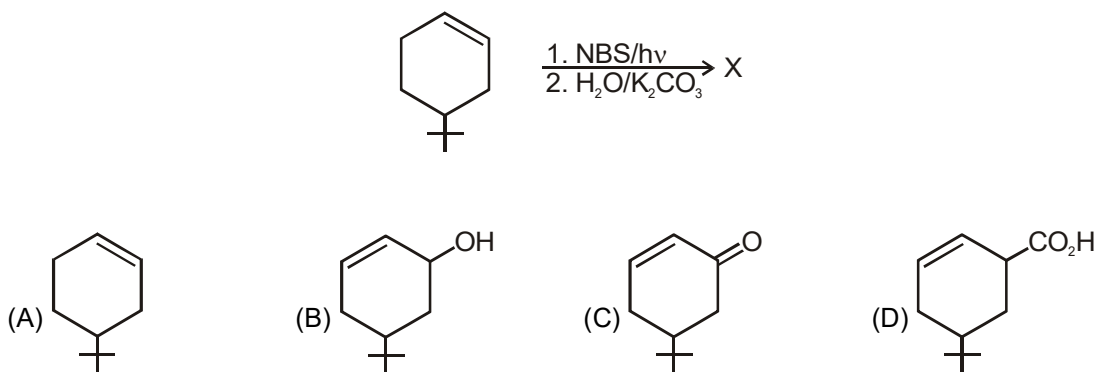


34. In the following sequence of reaction

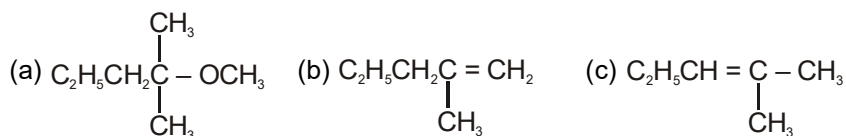


the product C is

- (A) $\text{C}_6\text{H}_5\text{CHO}$ (B) $\text{C}_6\text{H}_5\text{COOH}$ (C) $\text{C}_6\text{H}_5\text{CH}_3$ (D) $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ [JEE Main-2015]
35. The product of the reaction given below is : [JEE-Main-2016]



36. 2-chloro-2methylpentane on reaction with sodium methoxide in methanol yields : [JEE-Main-2016]



- (A) All of these (B) (a) and (c) (C) (c) only (D) (a) and (b)

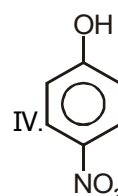
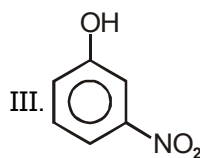
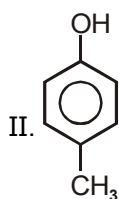
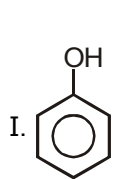
37. The reaction of propene with HOCl ($\text{Cl}_2 + \text{H}_2\text{O}$) proceeds through the intermediate : [JEE-Main-2016]

- (A) $\text{CH}_3-\text{CH}^+-\text{CH}_2-\text{OH}$ (B) $\text{CH}_3-\text{CH}^+-\text{CH}_2-\text{Cl}$
 (C) $\text{CH}_3-\text{CH}(\text{OH})-\text{CH}_2^+$ (D) $\text{CH}_3-\text{CHCl}-\text{CH}_2^+$

EXERCISE - III

Single Choice Question :

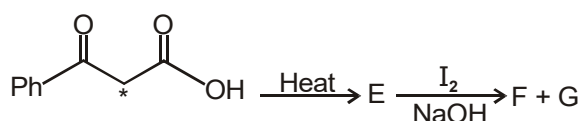
1. Which of the following is soluble in water ? [IIT 1980]
 (A) CS_2 (B) $\text{C}_2\text{H}_5\text{OH}$ (C) CCl_4 (D) CHCl_3
2. Ethyl alcohol is heated with conc. H_2SO_4 . The product formed is : [IIT 1980]
 (A) $\text{CH}_3\text{COOC}_2\text{H}_5$ (B) C_2H_2 (C) C_2H_4 (D) C_2H_6
3. A compound that gives a positive iodoform test is [IIT 1982]
 (A) 1-pentanol (B) 3-pentanone (C) 2-pentanone (D) pentanal
4. Acetamide is treated separately with the following reagents. Which of these would give methyl amine ? [IIT 1983]
 (A) PCl_5 (B) $\text{NaOH} + \text{Br}_2$ (C) soda lime (D) hot conc. H_2SO_4
5. An industrial method of preparation of methanol is : [IIT 1984]
 (A) catalytic reduction of carbon monoxide in presence of $\text{ZnO}-\text{Cr}_2\text{O}_3$
 (B) by reacting methane with steam at 900°C with nickel catalyst
 (C) by reducing formaldehyde with LiAlH_4
 (D) by reacting formaldehyde with aqueous sodium hydroxide solution
6. The compound that will not give iodoform on treatment with alkali and iodine is [IIT 1985]
 (A) acetone (B) ethanol (C) diethyl ketone (D) isopropyl alcohol
7. Hydrogen bonding is maximum in [IIT 1987]
 (A) ethanol (B) diethyl ether (C) ethyl chloride (D) triethyl amine
8. Which of the following compounds is oxidised to prepare methyl ethyl ketone ? [IIT 1987]
 (A) 2-propanol (B) 1-butanol (C) 2-butanol (D) t-butyl alcohol
9. In $\text{CH}_3\text{CH}_2\text{OH}$, the bond that undergoes heterolytic cleavage most readily is : [IIT 1988]
 (A) $\text{C}-\text{C}$ (B) $\text{C}-\text{O}$ (C) $\text{C}-\text{H}$ (D) $\text{O}-\text{H}$
10. Hydrogenation of benzoyl chloride in the presence of Pd and BaSO_4 gives: [IIT 1992]
 (A) Benzyl alcohol (B) Benzaldehyde (C) Benzoic acid (D) Phenol
11. In the following compounds [IIT 1996]



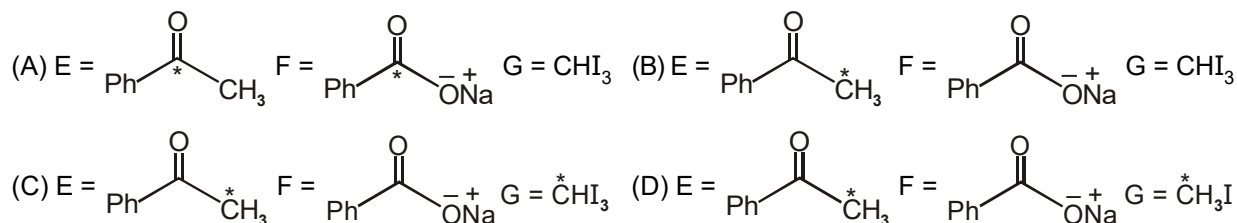
the order of acidity is

- (A) $\text{III} > \text{IV} > \text{I} > \text{II}$ (B) $\text{I} > \text{IV} > \text{III} > \text{II}$ (C) $\text{II} > \text{I} > \text{III} > \text{IV}$ (D) $\text{IV} > \text{III} > \text{I} > \text{II}$
12. Among the following compounds, the strongest acid is: [IIT 1998]
 (A) $\text{HC}\equiv\text{CH}$ (B) C_6H_6 (C) C_2H_6 (D) CH_3OH
 13. When propionic acid is treated with aqueous NaHCO_3 , CO_2 is liberated. The 'C' of CO_2 comes from [IIT 1999]
 (A) Methyl group (B) Carboxylic acid group
 (C) methylene group (D) bicarbonate

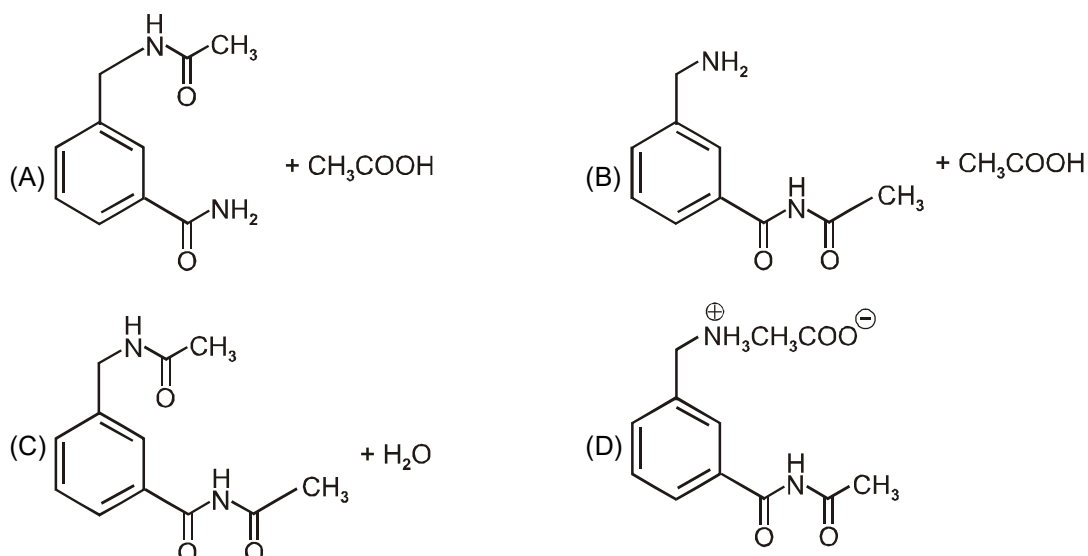
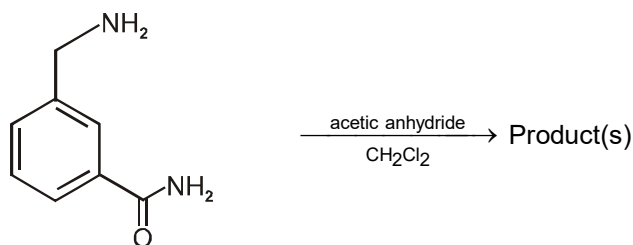
14. Reaction of enantiomerically pure acid with 1 chiral carbon and racemic alcohol with 1 chiral carbon gives an ester which is: [IIT 2003]
 (A) Meso (B) Optically active mixture
 (C) Racemic mixture (D) Enantiomerically pure
15. When benzene sulphonic acid and p-nitrophenol are treated with NaHCO_3 , the gases released, respectively, are
 (A) SO_2 , NO_2 (B) SO_2 , NO (C) SO_2 , CO_2 (D) CO_2 , CO_2 [IIT 2006]
16. (I) 1, 2-dihydroxy benzene (II) 1, 3-dihydroxy benzene
 (III) 1, 4-dihydroxy benzene (IV) Hydroxy benzene
 The increasing order of boiling points of above mentioned alcohols is [IIT 2006]
 (A) $\text{I} < \text{II} < \text{III} < \text{IV}$ (B) $\text{I} < \text{II} < \text{IV} < \text{III}$ (C) $\text{IV} < \text{I} < \text{II} < \text{III}$ (D) $\text{IV} < \text{II} < \text{I} < \text{III}$
17. In the following reaction sequence, the correct structures of E, F, and G are [IIT 2008]



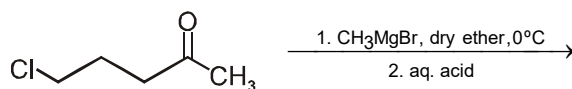
(implies ^{13}C labeled carbon)

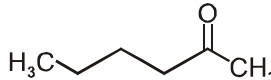
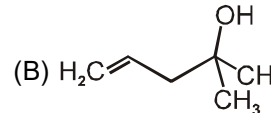
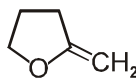
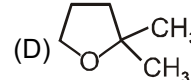


18. In the reaction shown below, the major product(s) formed is/are [JEE ADV. -2014]

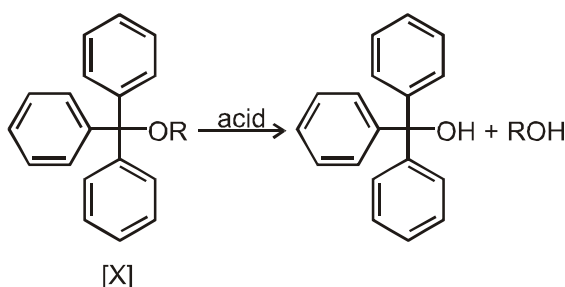


19. The major product in the following reaction is



- (A)  (B) 
- (C)  (D) 

20. The acidic hydrolysis of ether (X) shown below is fastest when



- (A) one phenyl group is replaced by a methyl group.
 (B) one phenyl group is replaced by a para-methoxyphenyl group.
 (C) two phenyl groups are replaced by two para-methoxyphenyl groups.
 (D) No structural change is made to X.

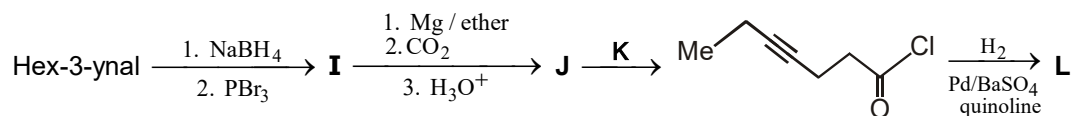
Assertion & Reason :

21. **Statement-1** : Solubility of n-alcohol in water decreases with increase in molecular weight. [IIT 1988]
Statement-2 : The relative proportion of the hydrocarbon part in alcohols increases with increasing molecular weight which permit enhanced hydrogen bonding with water.
 (A) Statement-1 is true, Statement-2 is true and Statement-2 is correct explanation for Statement-1
 (B) Statement-1 is true, Statement-2 is true and Statement-2 is **NOT** the correct explanation for Statement-1
 (C) Statement-1 is true, Statement-2 is false
 (D) Statement-1 is false, Statement-2 is true
22. **Statement-1** : p-Nitrophenol is a stronger acid than o-nitrophenol. [IIT 1989]
Statement-2 : Intramolecular hydrogen bonding makes the o-somer weaker than the p-isomer.
 (A) Statement-1 is true, Statement-2 is true and Statement-2 is correct explanation for Statement-1
 (B) Statement-1 is true, Statement-2 is true and Statement-2 is **NOT** the correct explanation for Statement-1
 (C) Statement-1 is true, Statement-2 is false
 (D) Statement-1 is false, Statement-2 is true

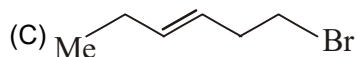
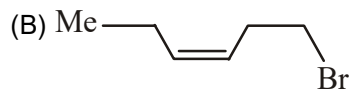
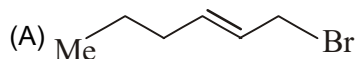
Comprehension :

Paragraph for Question No. 23 to 25

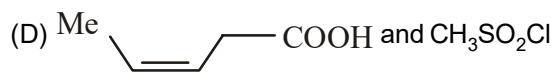
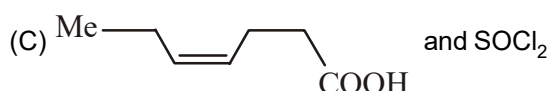
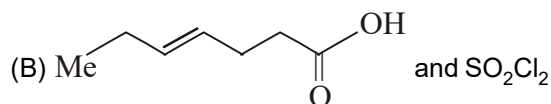
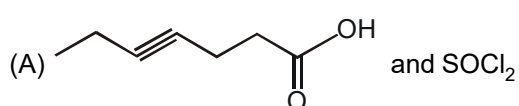
In the following reaction sequence, products **I**, **J** and **L** are formed. **K** represents a reagent. [IIT 2008]



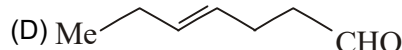
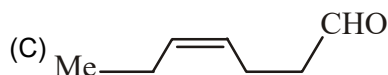
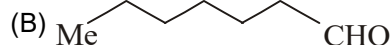
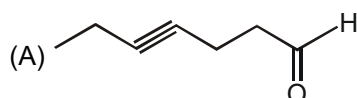
23. The structure of the product **I** is



24. The structures of compounds **J** and **K**, respectively, are

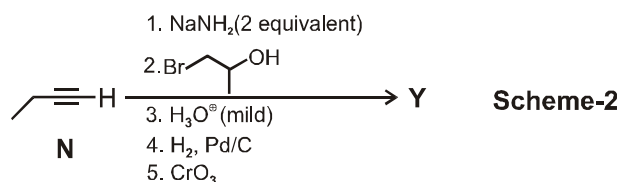
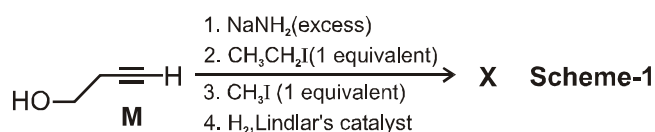


25. The structure of product **L** is



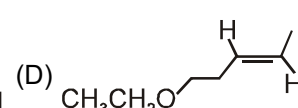
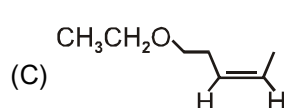
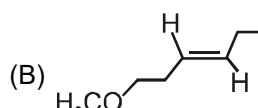
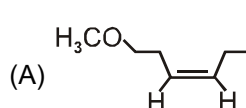
Paragraph for question no. 26 to 27

Schemes 1 and 2 describe sequential transformation of alkynes **M** and **N**. Consider only the **major products** formed in each step for both the schemes.

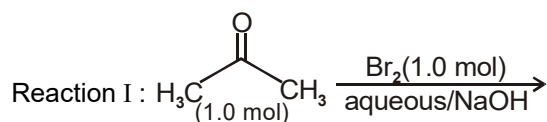


26. The product **X** is

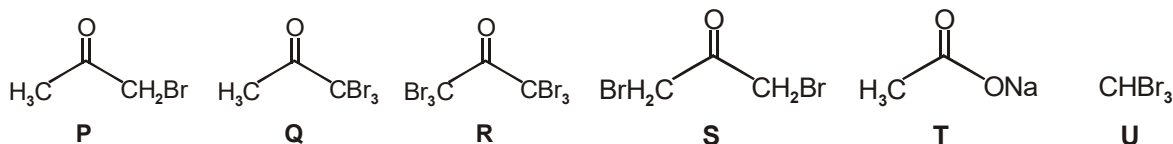
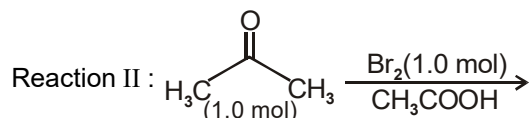
[JEE ADV. -2014]



27. The correct statement with respect to product Y is [JEE ADV. -2014]
- (A) It gives a positive Tollens test and is a functional isomer of **X**.
 (B) It gives a positive Tollens test and is a geometrical isomer of **X**.
 (C) It gives a positive iodoform test and is a functional isomer of **X**.
 (D) It gives a positive iodoform test and is a geometrical isomer of **X**.
28. After completion of the reactions (I and II), the organic compound(s) in the reaction mixtures is(are)

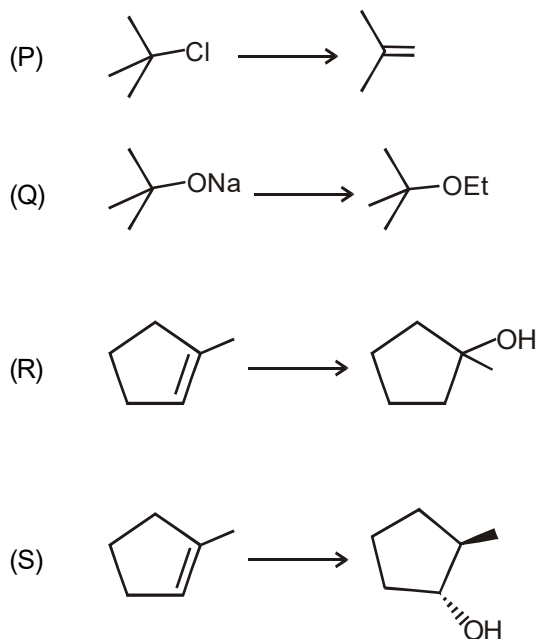


[JEE ADVANCE : 2013]



- (A) Reaction I : **P** and Reaction II : **P**
 (B) Reaction I : **U**, acetone and Reaction II : **Q**, acetone
 (C) Reaction I : **T**, **U**, acetone and Reaction II : **P**
 (D) Reaction I : **R**, acetone and Reaction II : **S**, acetone
29. Match the chemical conversions in List I with the appropriate reagents in List II and select the correct answer using the code given below the lists : [JEE ADVANCE : 2013]

List I



List II

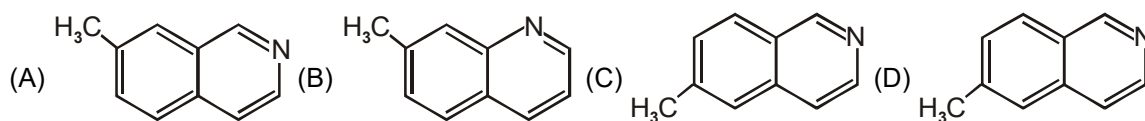
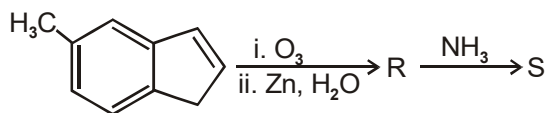
- (i) $\text{Hg}(\text{OAc})_2$; (ii) NaBH_4
- NaOEt
- Et-Br
- (i) BH_3 ; (ii) $\text{H}_2\text{O}_2/\text{NaOH}$

Codes :

	P	Q	R	S
(A)	2	3	1	4
(B)	3	2	1	4
(C)	2	3	4	1
(D)	3	2	4	1

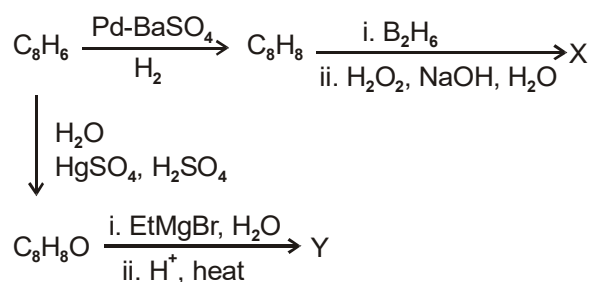
30. In the following reactions, the product S is

[JEE-Advance-2015]



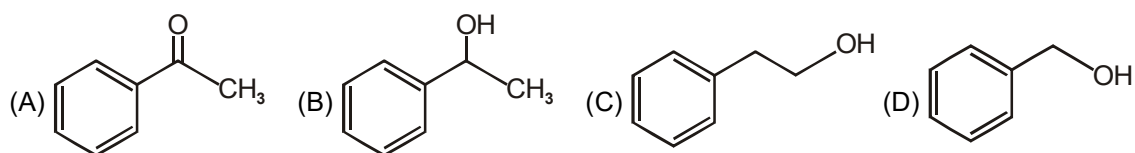
Paragraph for question no. 31 to 32

In the following reactions

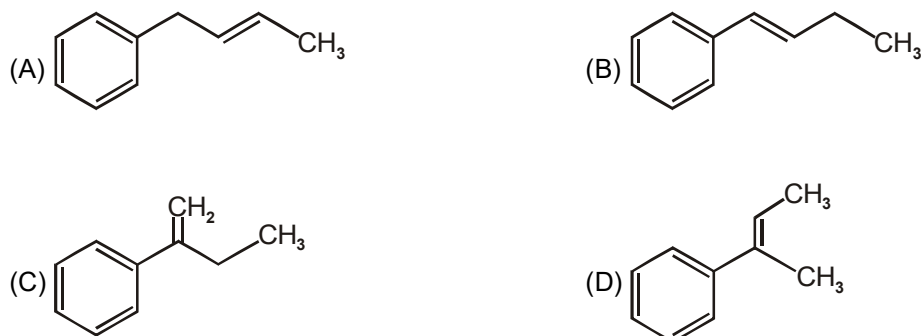


31. Compound X is

[JEE-Advance-2015]



32. The major compound Y is



ANSWER KEY

EXERCISE - I

1.	(i) D	(ii) C	(iii) A	2.	A	3.	B	4.	C	5.	A	6.	D
7.	C	8.	D	9.	C	10.	B	11.	A	12.	C	13.	B
14.	C	15.	C	16.	B	17.	D	18.	A	19.	D	20.	B
21.	D	22.	D	23.	A	24.	B	25.	B	26.	B	27.	B
28.	D	29.	A	30.	B	31.	A	32.	B	33.	C	34.	C
35.	B	36.	B	37.	B	38.	D	39.	D	40.	C	41.	B
42.	B	43.	D	44.	D	45.	D	46.	A	47.	C	48.	C
49.	C	50.	B	51.	B	52.	B	53.	B	54.	D	55.	B
56.	B	57.	C	58.	D	59.	D	60.	C	61.	B	62.	D
63.	A	64.	D	65.	D	66.	A	67.	A	68.	A	69.	C
70.	B	71.	D	72.	B	73.	C	74.	A	75.	A	76.	A
77.	C	78.	D	79.	A	80.	C	81.	A	82.	B	83.	B
84.	B	85.	D	86.	D	87.	B	88.	A				

EXERCISE-II

1.	C	2.	B	3.	D	4.	B	5.	B	6.	B	7.	C
8.	D	9.	B	10.	D	11.	C	12.	D	13.	B	14.	D
15.	A	16.	C	17.	D	18.	B	19.	D	20.	C	21.	B
22.	D	23.	C	24.	A	25.	C	26.	A	27.	B	28.	B
29.	C	30.	D	31.	A	32.	B	33.	C	34.	A	35.	B
36.	C	37.	B										

EXERCISE - III

1.	B	2.	C	3.	C	4.	B	5.	A	6.	C	7.	A
8.	C	9.	D	10.	B	11.	D	12.	D	13.	D	14.	B
15.	D	16.	C	17.	C	18.	A	19.	D	20.	C	21.	C
22.	A	23.	D	24.	A	25.	A	26.	A	27.	C	28.	C
29.	A	30.	A	31.	C	32.	D						

