CHAPTER 2

Alcohols, Ethers and Phenol

INTRODUCTION

ALCOHOLS

- Alcohols are organic compounds in which –OH group is directly attached with carbon.
- Alcohols are hydroxy derivatives of alkanes and mono alkyl derivatives of water.
- General formula of alcohols is $C_nH_{2n+1}OH$ or $C_nH_{2n+2}O$.
- The hybridisation state of carbon, with which – OH group is directly attached, is sp^3. Therefore geometry around this carbon atom is tetrahedral.
- In these compounds C–O bond length is 1.42 Å.
- Depending on the number of –OH groups alcohols are classified into the following:
  - (i) Monohydric alcohol: Contains only one –OH group; example- Ethanol
  - (ii) Dihydric alcohol: Contains two –OH groups; example- Ethylene glycol
  - (iii) Trihydric alcohol: Contains three –OH groups; example- Glycerol
- Alcohols shows chain, position and functional group isomerism. If chiral carbon atom is present, they show optical isomerism.

PHYSICAL PROPERTIES

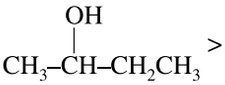
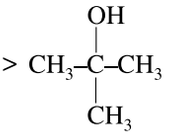
(I) Nature of alcohol:

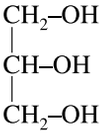
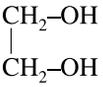
- Alcohols are poisonous in nature. Poisonous character increases with increment in molecular mass or branching. Ethanol is exception, which is non-poisonous in nature. Methanol causes blindness.
- Isopropyl alcohol is called as rubbing alcohol.
- Cholesterol is also alcohol, it causes heart attack. Hence it is also called as notorious alcohol.
- Ethanol is liquid while glucose is solid because of more intermolecular H–bonding in glucose.
- Alcohols are neutral substances towards litmus paper.
- Lower members containing upto 12 carbon atoms are liquids.
- The higher members are solids and are almost odourless.
- They have a distinctive smell and a burning taste.

(II) Boiling point:

- $\boxed{\text{Boiling point} \propto \text{Molecular mass} \propto \frac{1}{\text{Number of branches}}}$
- Boiling point of alcohols in water increases as the extent of hydrogen bonding increases.
- Boiling point of alcohols are higher than ethers of comparable molecular masses because intermolecular hydrogen bonding is present in alcohols.

- Order of Boiling point:
  (i) $CH_3OH < CH_3CH_2OH < CH_3CH_2CH_2OH$

  (ii) $CH_3CH_2CH_2OH >$  $>$ 

  (iii)  $>$  $>$ CH_3CH_2OH

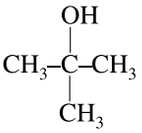
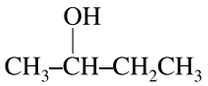
  (Max. H-bond)

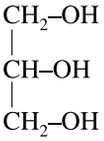
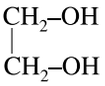
(III) Solubility in water:

- Lower alcohols are soluble in water and the solubility diminishes as the molecular mass increases.

$$\text{Solubility} \propto \frac{1}{\text{Molecular mass}} \propto \text{number of branches}$$

- Their solubility in water is to be expected, since the oxygen atom of hydroxyl group in alcohols can form hydrogen bonds with water molecules.
- Solubility of alcohols in water increases as extent of hydrogen bonding increases.
  (i) $CH_3OH > CH_3CH_2OH > CH_3CH_2CH_2OH$
- Order of solubility in water:

  (ii)  $>$  $> CH_3CH_2CH_2CH_2OH$

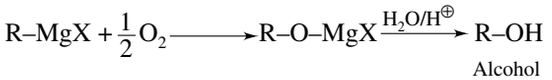
  (iii)  $>$  $> CH_3CH_2OH$

  (Max. H-bond)

METHODS OF PREPARTION OF ALCOHOL

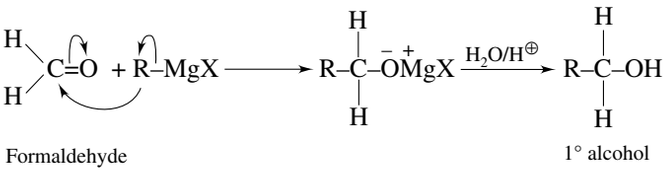
Grignard Synthesis of Alcohols

(I) Reaction of oxygen with RMgX



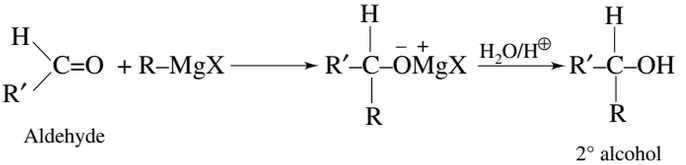
Alcohol

(II) Reaction of carbonyl compounds with RMgX



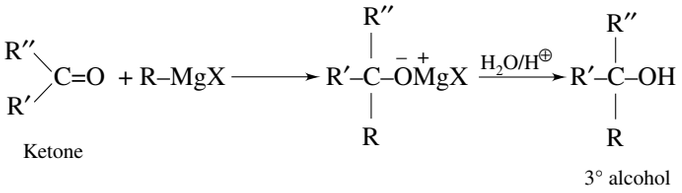
Formaldehyde

1° alcohol

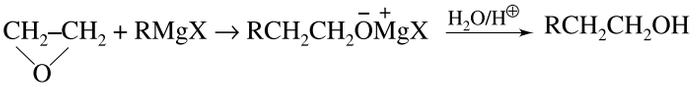


Aldehyde

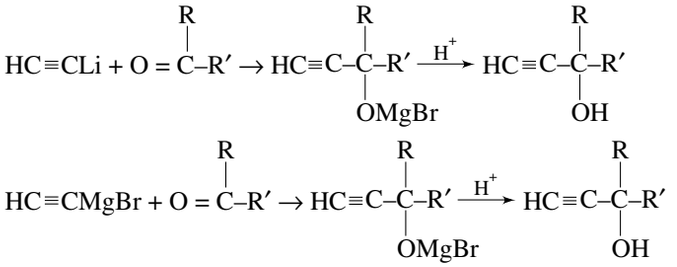
2° alcohol



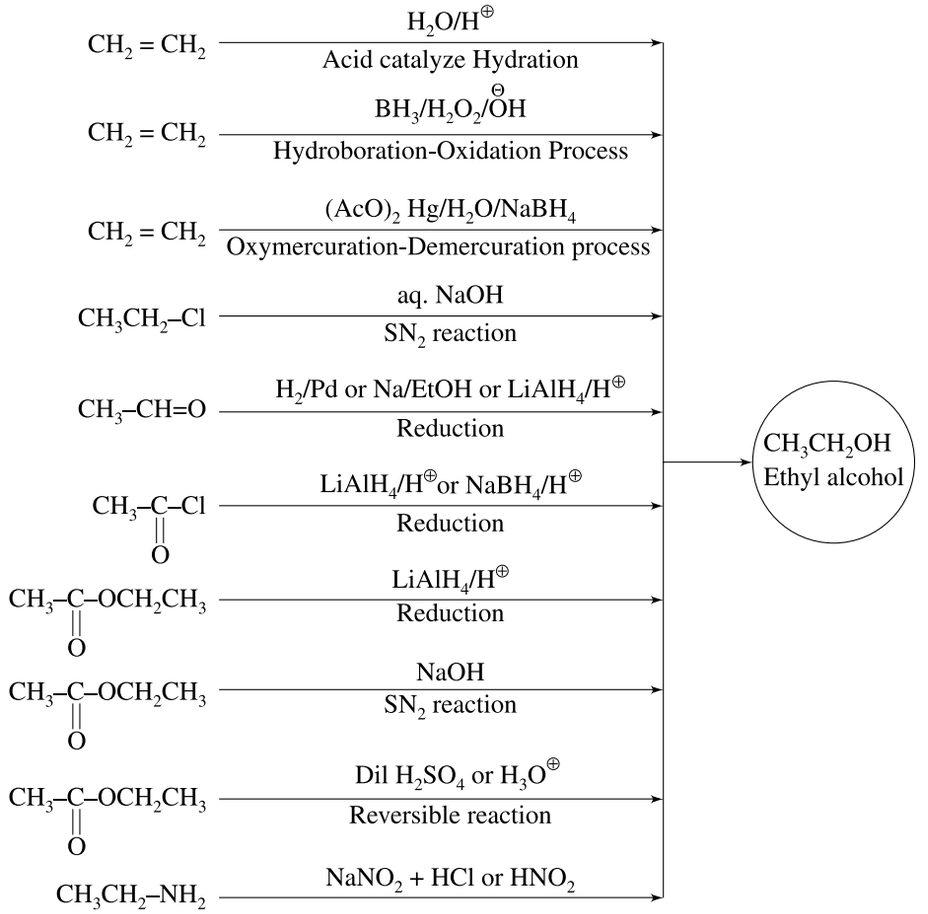
(III) Reaction of ethylene oxide with RMgX



(IV) Reaction of lithium acetylides or alkynyl Grignard Reagents with aldehyde or ketone



Other methods of preparation of alcohols



CHEMICAL PROPERTIES OF ALCOHOL

The general formula of simple alcohol is ROH. Reactions shown by alcohols may be classified into two categories, namely, cleavage of R….OH bond and cleavage of RO….H bond.

(I) Reactions exhibiting cleavage of RO….H bond

Reaction with active metals

$$RO{-}H + M \rightarrow R{-}\overset{-}{O}\overset{+}{M} + \frac{1}{2}H_2$$

(M = Na, K, Mg, Al, etc.)

Reactivity of alcohol $CH_3OH > 1° > 2° > 3°$

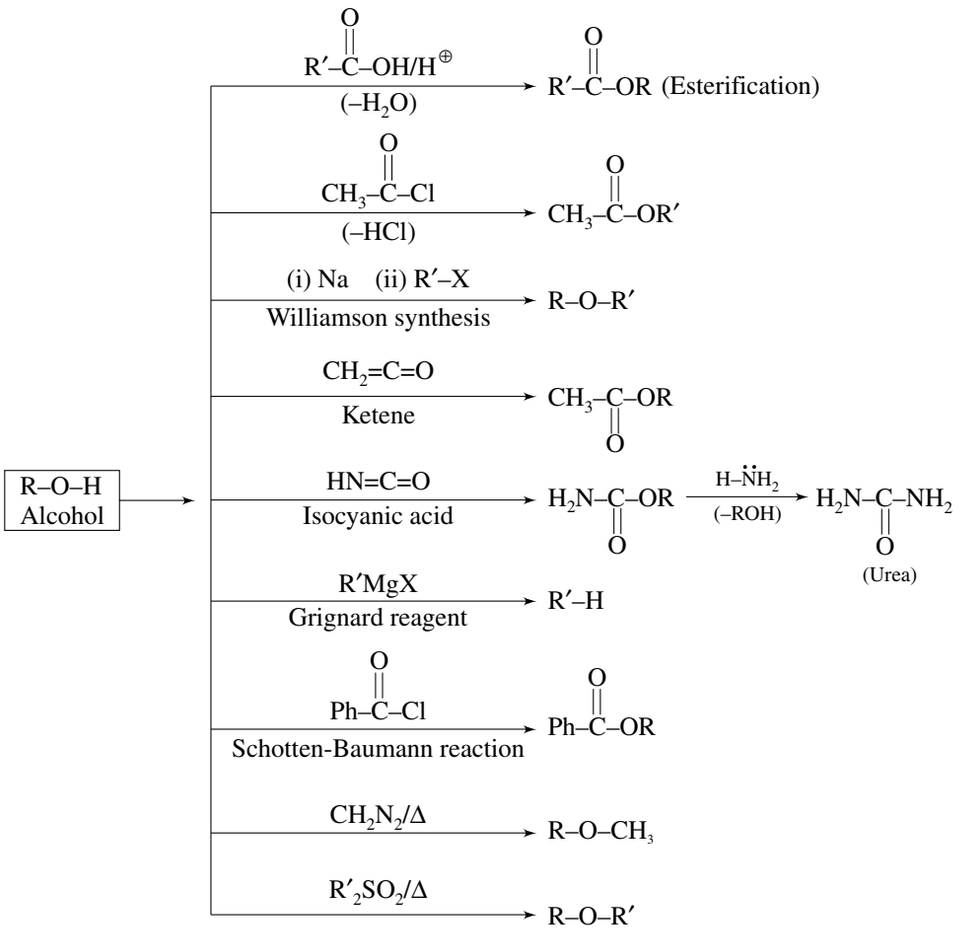
The above reaction shows alcohol as an acid. It is worth comparing the acid strength of alcohol with other species.

$H_2O > ROH > HC \equiv CH > NH_3 > RH$

The relative order of basicity follows the reverse order, i.e.,

$OH^- < OR^- < HC \equiv C^- < NH_2^- < R^-$

Other Reaction



(II) Reactions exhibiting cleavage of R….OH Bond

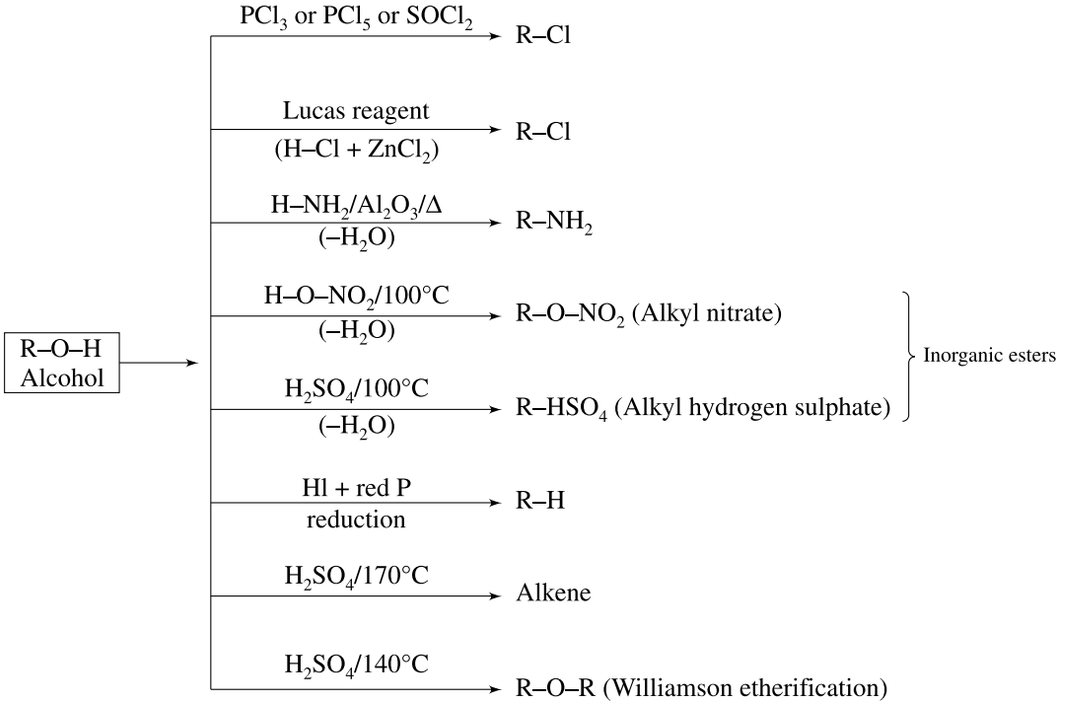
Reaction with hydrogen halides

$R{-}OH + HX \rightarrow RX + H_2O$

As such $-OH$ is a poor leaving group. But its protonation converts into a good leaving group. There is formation of carbocation as the intermediate and thus the reaction may show rearrangement. The following is the reactivity of HX and ROH.

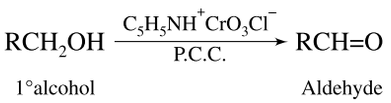
HI > HBr > HCl; allyl, benzyl > 3° > 2° > 1°

The reagents used are concentrated HBr or NaBr + concentrated H_2SO_4, HCl + $ZnCl_2$, and concentrated HCl.

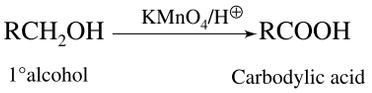


Oxidation Reaction:

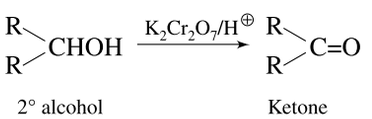
- Primary alcohol gives aldehyde on oxidation, secondary alcohol gives ketone and tertiary alcohol is resistant to oxidation.
- The oxidation of an alcohol involves the loss of one or more α-hydrogens.
- 1° alcohol is changed to an aldehyde by using the reagent pyridinium chlorochromate ($C_5H_5NH^+CrO_3Cl^-$)



- 1° alcohol is directly converted into a carboxylic acid by the use of potassium permanganate.



- 2° alcohol is changed into a ketone by the use of potassium dichromate or CrO_3 in glacial acetic acid or CrO_3 in pyridine.



- 3° alcohol is not oxidisable as it does not contain α-hydrogen.

Summery of Oxidation:

	Reagent/Alcohol	CH_3CH_2OH	>CH–OH	>C(R)–OH
(1)	PCC or PDC	CH_3CHO	>C=O	×
(2)	CrO_3 in CH_2Cl_2 Solvent	CH_3CHO	>C=O	×
(3)	CuO/Δ	CH_3CHO	>C=O	>C=CH_2
(4)	$KMnO_4/H^+$	CH_3COOH	>C=O	×
(5)	$K_2Cr_2O_7/H_2CrO_4$	CH_3COOH	>C=O	×
(6)	CrO_3 in water	CH_3COOH	>C=O	×

Note: MnO_2 is regioselective reagent for oxidation of only allylic and benzylic –OH into carbonyl group.

DIFFERENCE BETWEEN PRIMARY, SECONDARY AND TERITARY ALCOHOLS

(1) Oxidation method:

(A) Dichromate test:

(i) 1°-alcohol $\xrightarrow[\text{orange } [Cr^{+6}]]{H^{\oplus}/K_2Cr_2O_7}$ aldehyde + Cr^{+3} [green colour]

(ii) 2°-alcohol $\xrightarrow[\text{orange } [Cr^{+6}]]{H^{\oplus}/K_2Cr_2O_7}$ ketone + Cr^{+3} [green colour]

(iii) 3°-alcohol $\xrightarrow[\text{orange } [Cr^{+6}]]{H^{\oplus}/K_2Cr_2O_7}$ No oxidation [No green colour]

(B) By catalytical oxidation/dehydrogenation:

When vapours of alcohols are passed over hot metallic Cu at 300°C, limited oxidation takes place.

(i) Primary alcohol gives aldehyde on oxidation

(ii) Secondary alcohol gives ketone, and

(iii) Tertiary alcohol gives alkene (dehydration takes place in tertiary alcohols.)

(2) Lucas Test:

A mixture of (anhydrous $ZnCl_2$ + Conc. H_2SO_4) is called as **Lucas Reagent**

(i) Tertiary alcohol gives white ppt. with Lucas reagent in 2–3 seconds only.

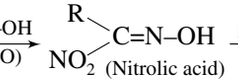
(ii) Secondary alcohol takes 5–10 minutes.

(iii) Primary alcohol does not give white ppt. at room temperature.

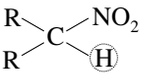
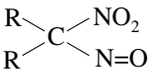
(iv) Allyl alcohol reacts as rapidly as tertiary alcohol but remains in the solution.

(3) Victor Meyer Test:

This test is also known as RBC (Red, Blue, Colourless) test.

(i) $R–CH_2–OH \xrightarrow{\text{red P/ } I_2} R–CH_2–I \xrightarrow[-AgI]{AgNO_2} R–\boxed{CH_2}–NO_2 \xrightarrow[(-H_2O)]{O=N–OH}$  $\xrightarrow{NaOH}$ Red solution (salt)

(Nitrolic acid)

(ii) $R_2CH–OH \xrightarrow{\text{red P/ } I_2} R_2CH–I \xrightarrow{AgNO_2}$  $\xrightarrow{HO–N=O}$  $\xrightarrow{NaOH}$ No reaction

(Pseudo nitrole)
Blue-colour

(iii) $R_2C–OH \xrightarrow{\text{red P/ } I_2} R_3C–I \xrightarrow{AgNO_2} R_3C–NO_2 \xrightarrow{HNO_2}$ No reaction

(white)

(4) Characteristic test of CH_3CO- group

An alcohol of the type $R-\underset{\underset{CH_3}{|}}{CH}-OH$ is oxidised to $R-\underset{\underset{O}{||}}{C}-CH_3$ which gives iodoform test.

The reagent used is iodine and sodium hydroxide (sodium hypoiodite, NaOI)

The reactions involved are

$$R-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-CH_3 + NaOI \rightarrow R-\underset{\underset{O}{||}}{C}-CH_3 + Na + H_2O$$

$$R-\underset{\underset{O}{||}}{C}-CH_3 + 3NaOI \rightarrow R-\underset{\underset{O}{||}}{C}-CCl_3 + 3NaOH$$

$$R-\underset{\underset{O}{||}}{C}-CCl_3 + NaOI \rightarrow \underset{\text{Iodoform (yellow Ppt.)}}{RCOO^-Na^+CHI_3}$$

(5) Analysis of molecules containing –OH or =O group attached to adjacent carbon atoms

Molecules containing –OH or =O groups attached to adjacent carbon atoms undergo oxidation with cleavage of carbon–carbon bonds when treated with periodic acid. Example:

$$R-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-R' \longrightarrow \left[R-\underset{\underset{OH}{|}}{CH}-OH\right] + \left[R'-\underset{\underset{OH}{|}}{CH}-OH\right] \longrightarrow RCHO + R'COH$$

$$R-\underset{\underset{OH}{|}}{CH}-\underset{\underset{O}{||}}{C}-R' \xrightarrow{HIO_4} \left[R-\underset{\underset{OH}{|}}{CH}-OH\right] + HO-\underset{\underset{O}{||}}{C}R' \longrightarrow RCHO + R'COOH$$

$$R-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-R' \xrightarrow{2HIO_4} RCHO + HCOOH + R'CHO$$

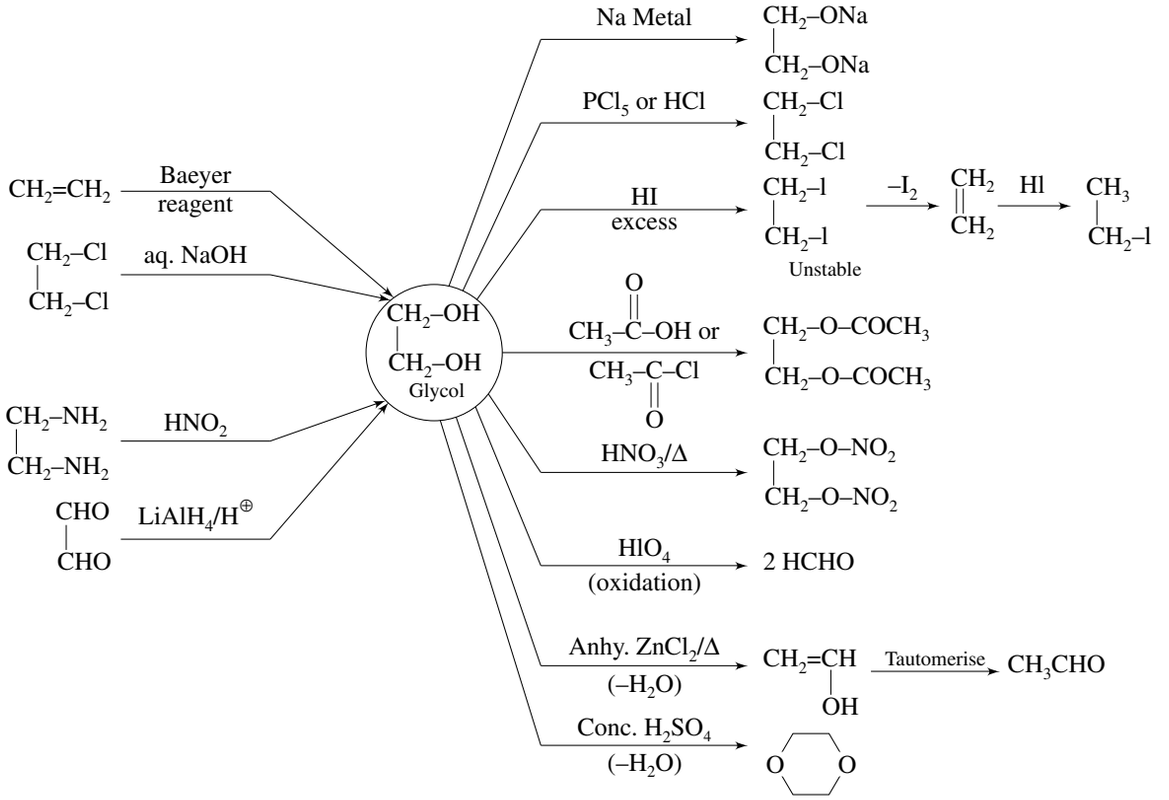
$$R-\underset{\underset{O}{||}}{C}-\underset{\underset{O}{||}}{C}-R' \xrightarrow{HIO_4} RCOOH + R'COOH$$

The amount of HIO_4 consumed is equal to the amount of carbon–carbon bond broken in the molecule.

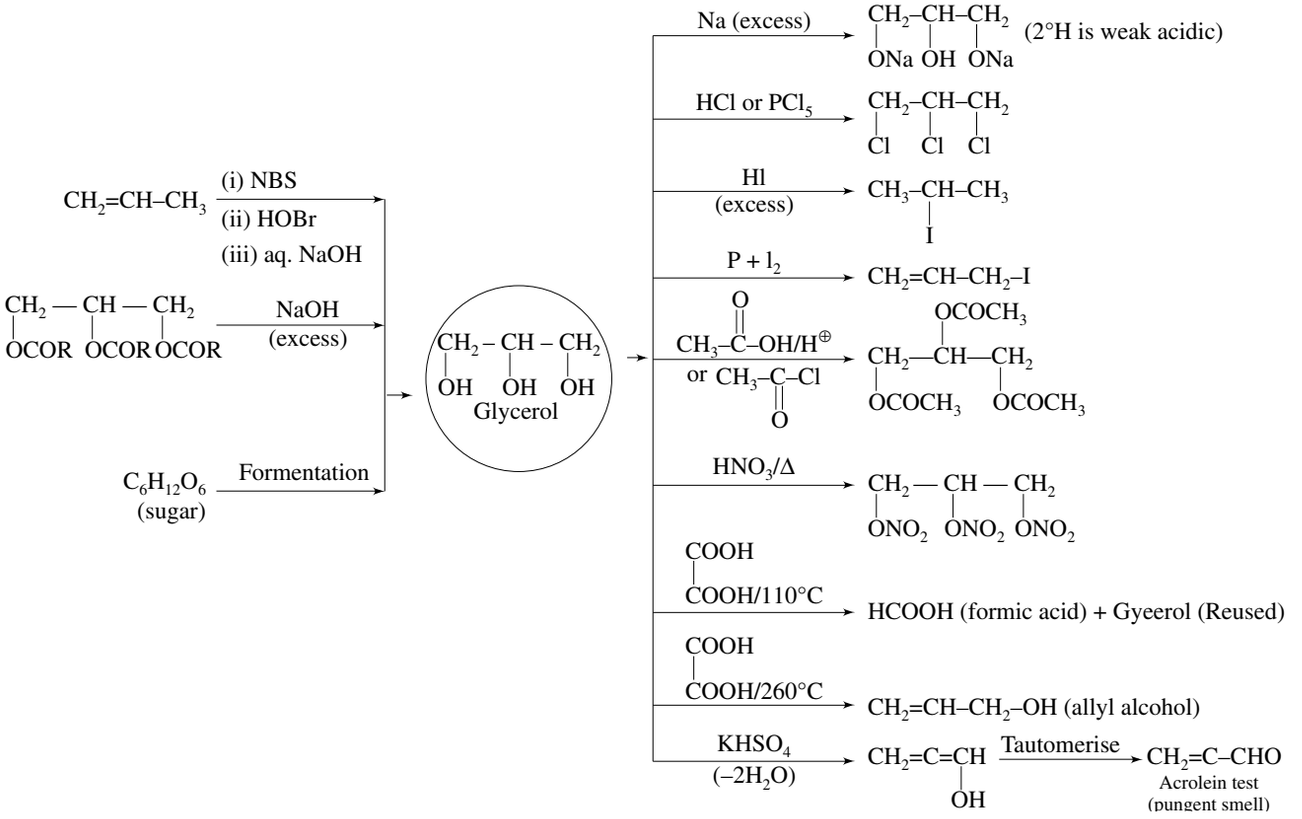
(4) Difference between methanol and ethanol:

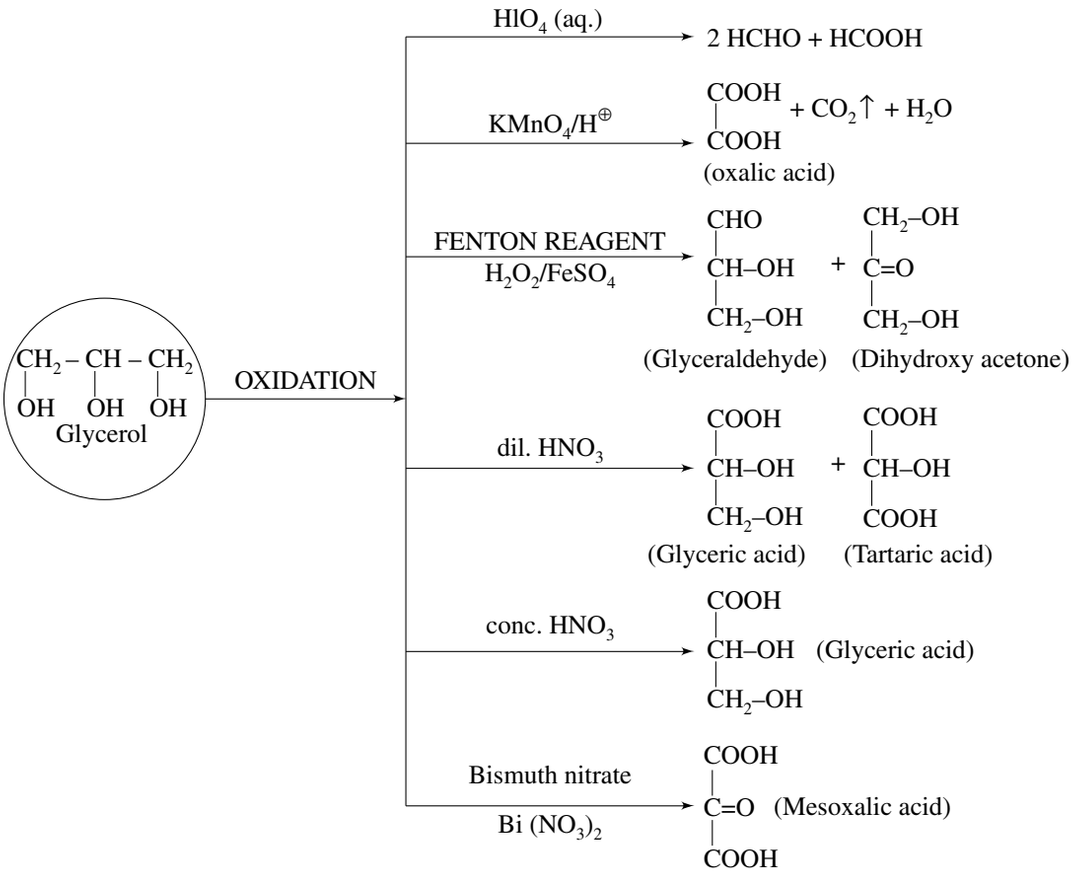
S. N.	Methanol	Ethanol
1.	When CH_3OH is heated on Cu coil it gives formalin like smell.	It does not give formalin like smell.
2.	When CH_3OH is heated with salicylic acid in H_2SO_4 (conc.) then methyl salicylate is formed which has odour like winter green oil	No such odour is given.
3.	It does not give Iodoform test	It gives Iodoform test
4.	Boiling point = 65°C	Boiling point = 78°C

Chemical Properties and Methods of Preparation of Glycol:



Chemical Properties and Methods of Preparation of Glycerol:





Special Points

- Glycol is used as antifreeze for automobile radiators and as a coolant for aeroplane aviation petrol under the name **prestone**.
- Glyceryl trinitrate is an inorganic ester.
- Glyceryl trinitrate is colourless, oily liquid insoluble in water and is called **Nobel's oil**.
- On detonating it explodes violently giving CO_2, N_2, O_2 as gaseous products.

$$4\ \begin{matrix}CH_2\text{–}ONO_2\\ |\\ CH\text{–}ONO_2\\ |\\ CH_2\text{–}ONO_2\end{matrix} \longrightarrow 12CO_2 + 10\ H_2O + 6N_2 + O_2$$

- It is a safer explosive when adsorbed on keiselguhr and is known as **DYNAMITE.**
- Its mixture with cellulose nitrate is known as **blasting gelatine** or **gelignite**.
- Its mixture with cellulose nitrate (gun cotton) and vaseline is called cordite. It is a smokeless powder.
- Nobel's oil is also used in the treatment of angina pectoris and asthma.
- Dunstan's test for glycerol: A drop of phenolphthalein is added to approx. 5 mL of borax solution. The pink colour appears. On adding 2–3 drops of glycerol, the pink colour disappears. The pink colour reappears on heating and disappears on cooling again.

ETHERS

- Compounds that contain an oxygen atom bonded to two alkyl groups. R–O–R', are called ether.

  When R and R' are same, they are called as symmetrical ethers and when both are different, they are called mixed or unsymmetrical ether.
- Ether have general formula $C_nH_{2n+2}O$. where n = 2, 3...
- These may be considered as dialkyl derivatives of water.
- The oxygen atom in ethers is sp^3 hybridised.
- In IUPAC system ethers are named as alkoxyalkanes.
- Ether shows chain, positional, functional isomerism and metamerism.
- Ether are functional isomers of alcohols.

Physical Properties

(i) Dimethyl ether and ethyl methyl ether are gases. All others are colourless liquids with pleasant smell.

(ii) Ethers are sparingly soluble in water, but readily soluble in organic solvents.

(iii) Ethers are lighter than water. Lower ethers are highly volatile and inflammable.

(iv) Boiling points of ethers show a gradual increase with increase in molecular mass.

(v) Ethers have low boiling points than isomeric alcohols, as there is association between the alcohol molecules due to hydrogen bonding. The boiling points of ethers are close to the boiling points of alkanes.

(vi) Due to bond angle of 110°, ethers are partial polar.

(vii) Lower ethers act as **anaesthetics**.

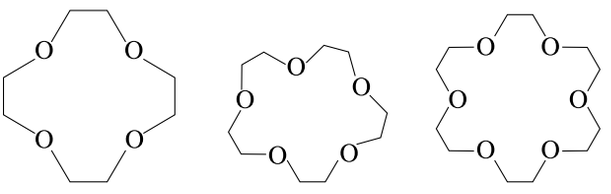
- **Test of ether** before anaesthetic use:

(i) ether (peroxide) + $Fe^{+2} \longrightarrow Fe^{+3} \xrightarrow{KCNS}$ Red colour $[Fe(CNS)_3]$
(ii) ether (peroxide) KI $\xrightarrow{Starch}$ Blue colour $[I_2]$

Use of ether

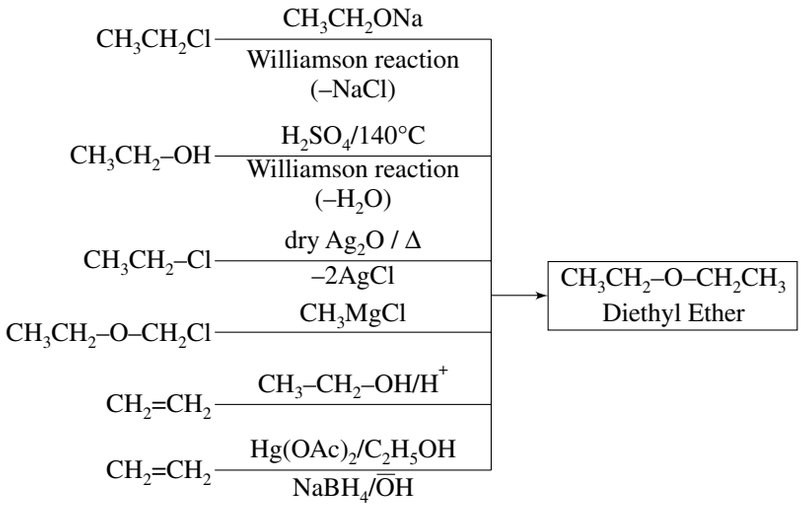
- Reaction of HI with ether is used to estimate alkoxy group (mainly CH_3O-) in organic compound. This method is called **Zeisel method.**
- Mixture of diethyl ether and ethyl alcohol is known as **NATALITE** used in place of petrol.
- **CROWN** ether is the cyclic polyether which has at least four oxygen atoms.
- Crown ethers are mainly used as an antibiotic.

  Examples:

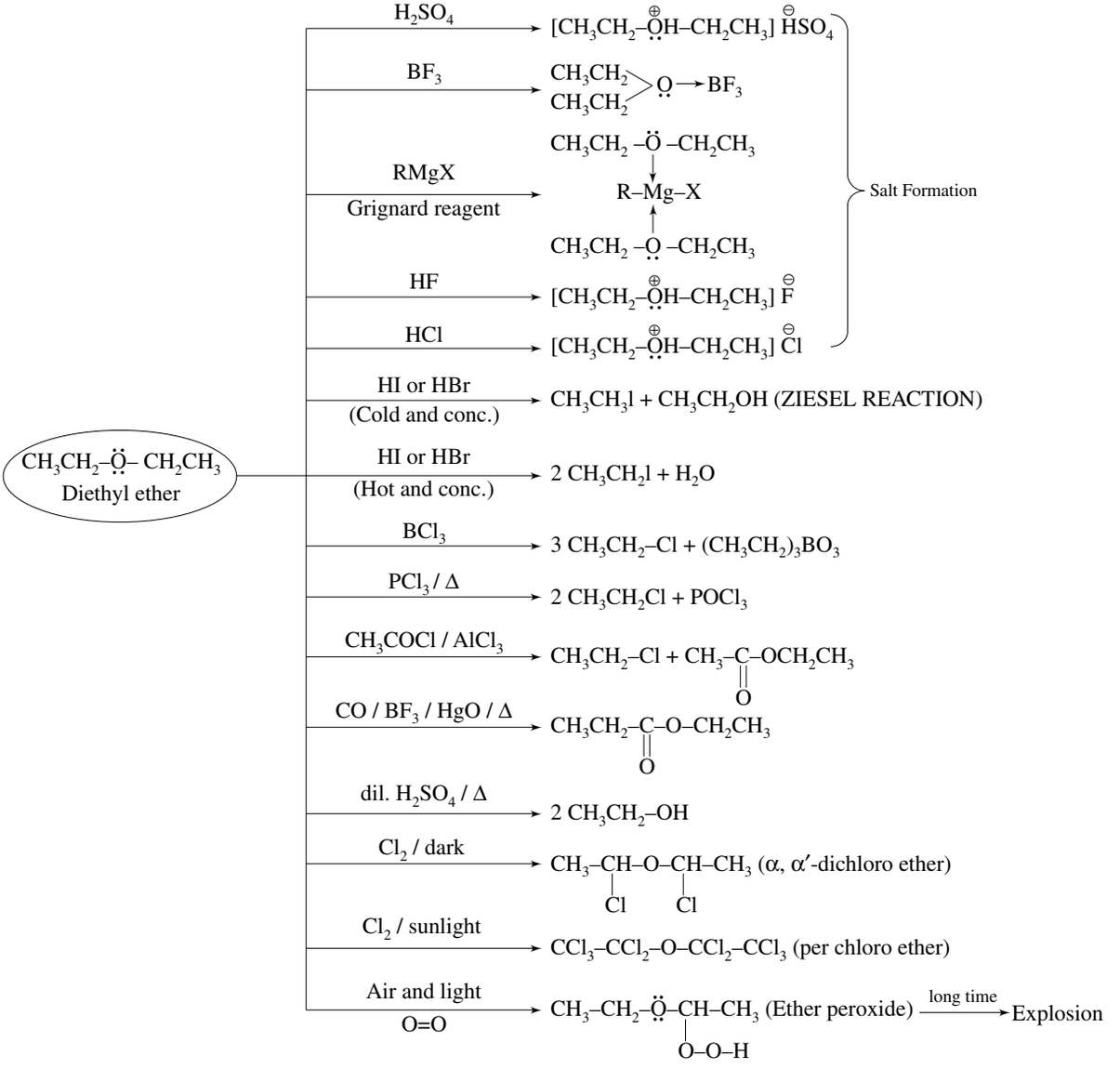


12-Crown-4 15-Crown-5 18-Crown-6

Methods of Preparation of Ether:



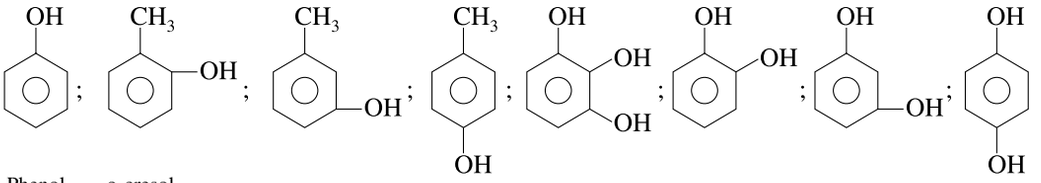
Chemical Properties of Ether:



PHENOL

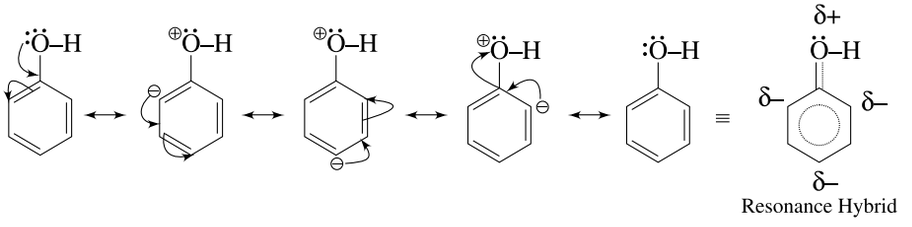
- Phenol is also called as **carbolic acid.**
- Compounds in which —OH group is directly attached with benzene ring are called as Phenols.
- Phenol is discovered by **Runge**
- **Hofmann,** another scientist, prepared it first from 'coal tar'.
- Aromatic hydroxy compounds in which a single –OH group is attached with benzene ring are called phenols.

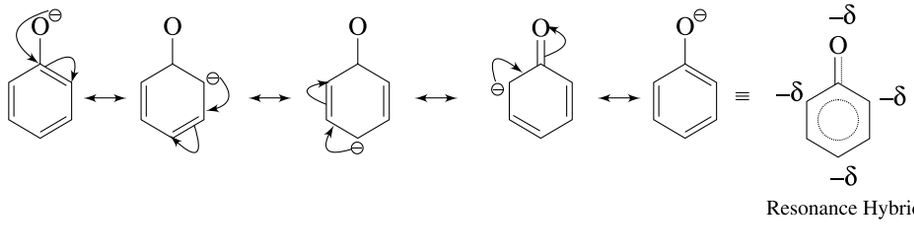
  Examples are:



- Physical properties of phenol are strongly influenced by the hydroxyl group which permits phenols to form hydrogen bond with other phenol molecules as well with water
- Thus, phenols have higher melting points (40°C) and boiling points (132°C).
- Phenols are more soluble in water than arenes and aryl halides of comparable molecular weight.
- Some *ortho*-substituted phenols, such as *ortho*-nitro phenol, have boiling point that are significantly lower than those of the *meta* and *para* isomers.

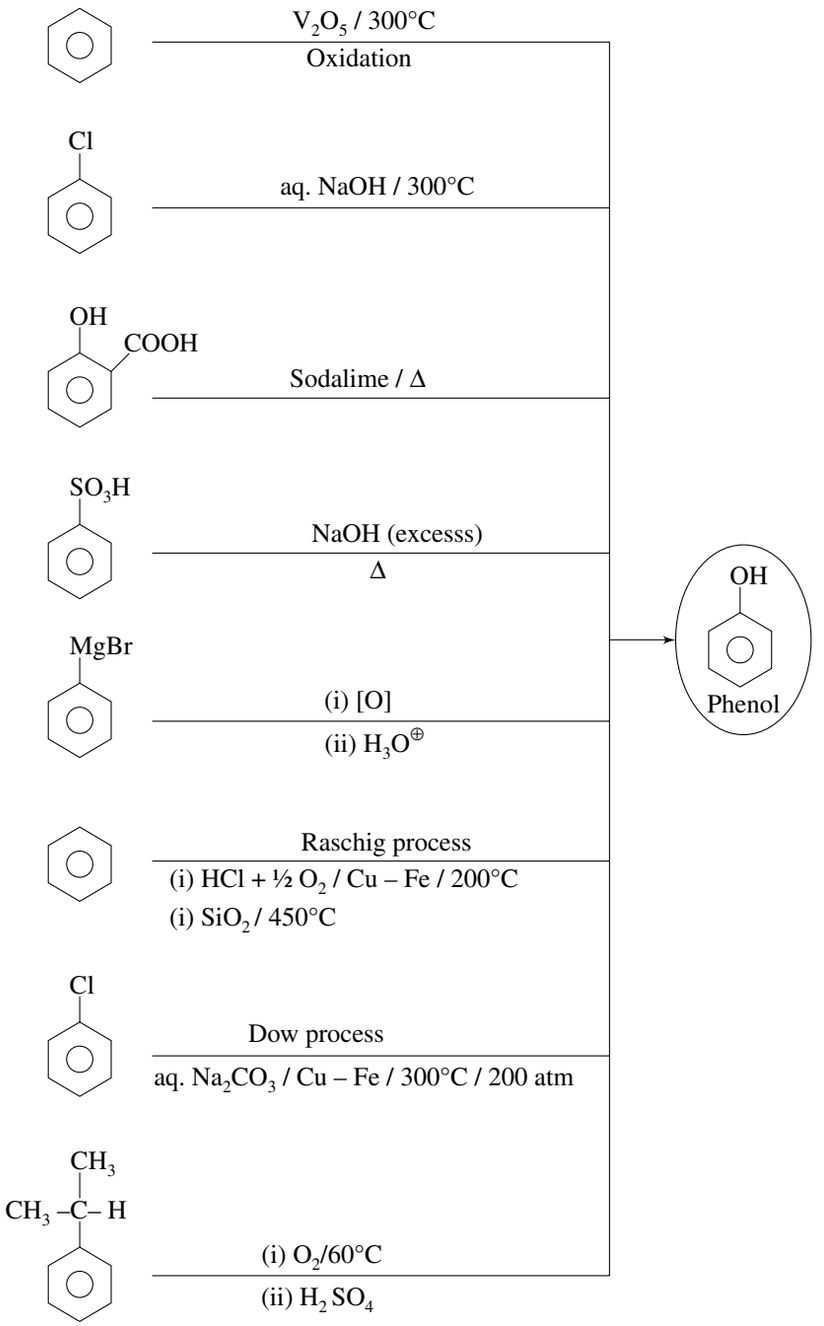
  Reason: Intermolecular hydrogen bonds that are formed between the hydroxyl group and substituent, partially compensates states for the energy required to go from the liquid state to the vapour.
- **Resonance in phenol and phenoxide ion:**



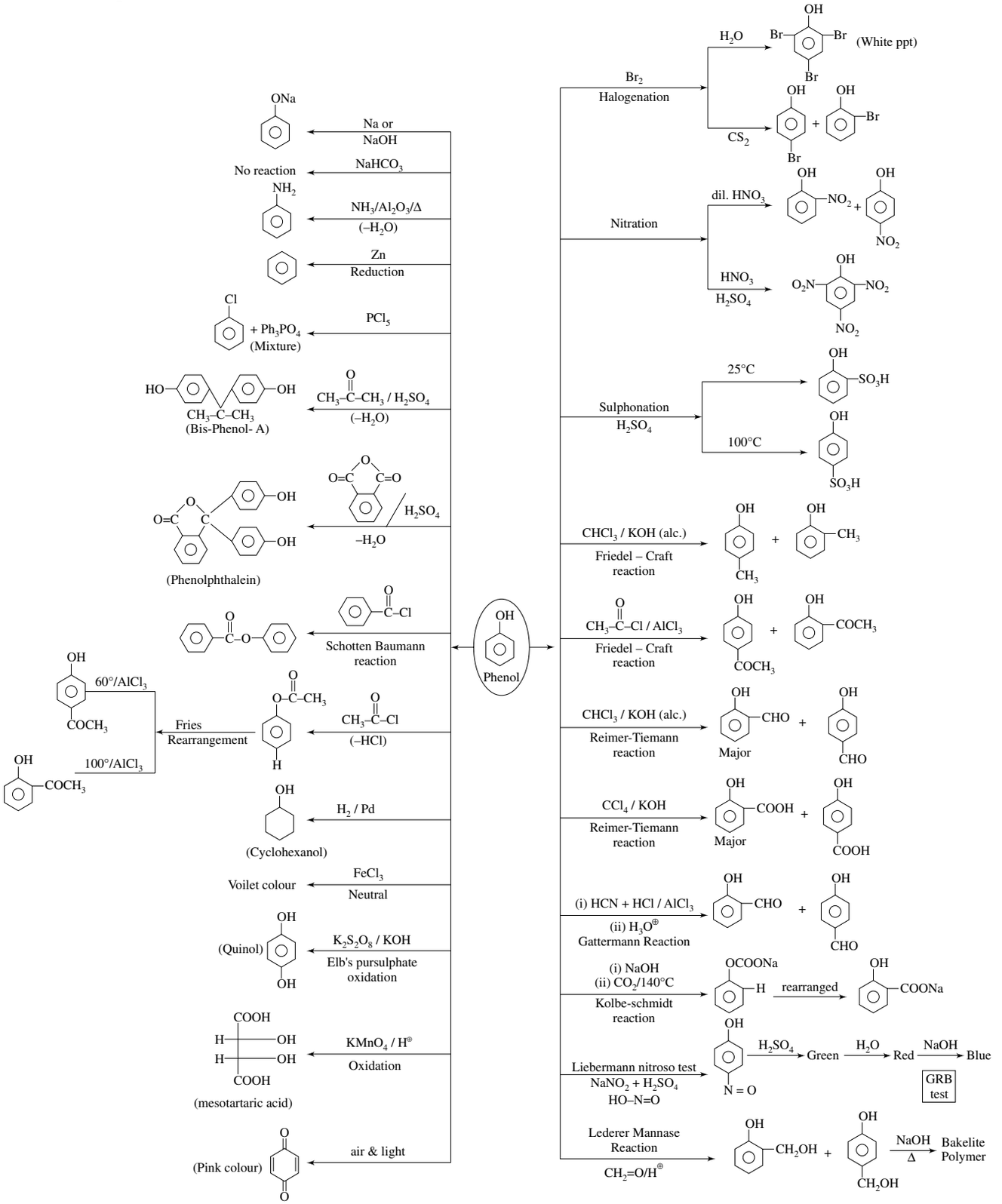


  It is evident from the above structures that — OH group of phenol is o- and p-directing, as these are electron richer places; so electrophiles attack at these positions.
- Phenoxide ion is resonance stabilised. That is why phenol shows acidic character.
- The hydroxyl oxygen is less basic, and the hydroxyl proton is more acidic in phenol than in alcohol.

Methods of Preparation of Phenol:

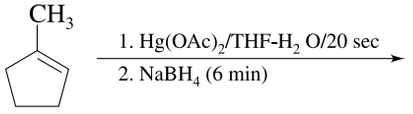


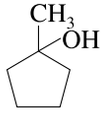
Chemical Properties of Phenol:

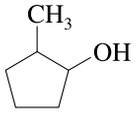


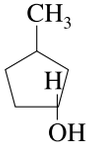
SOLVED EXAMPLE

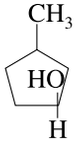
1. The final product obtained in the reaction



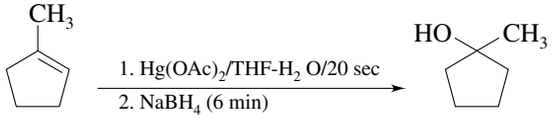
(1) 

(2) 

(3) 

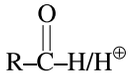
(4) 

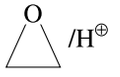
Sol. **[1]**



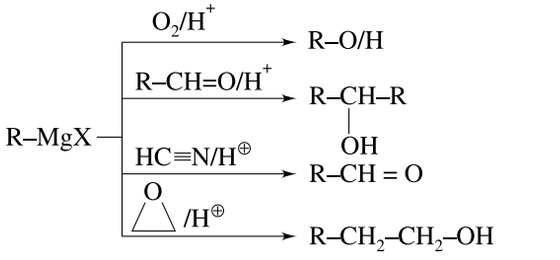
Hydration (addition of H^+/OH^-) takes place according to Markownikoff rule.

2. Which of the following compounds does not give alcohol on reaction with RMgX?

(1) $O_2/H^{\oplus}$ (2) 

(3) $HC{\equiv}N/H^{\oplus}$ (4) 

Sol. **[3]**



3. Which one/ones of the following reactions will yield 2-propanol? Choose the right answer from (I), (II), (III) and (IV)

(I) $CH_2 = CH - CH_3 + H_2O \xrightarrow{H^+}$

(II) $CH_3 - CHO \xrightarrow[(ii)\ H_2O]{(i)\ CH_3MgI}$

(III) $CH_2O \xrightarrow[(ii)\ H_2O]{(i)\ C_2H_5MgI}$

(IV) $CH_2{=}CH{-}CH_3 \xrightarrow{\text{Neutral } KMnO_4}$

(1) I and II (2) II and III

(3) III and I (4) II and IV

Sol. **[1]**

(I) $CH_2{=}CH{-}CH_3 + H_2O \xrightarrow[EAR]{H^+} CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3$

2-propanol

(II) $CH_2{-}CHO \xrightarrow[(ii)\ H_2O]{(i)\ CH_3MgI} CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3$

NAR

2-propanol

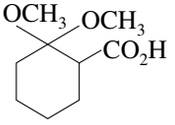
(III) $CH_2O \xrightarrow[(ii)\ H_2O]{(i)\ C_2H_5MgI} CH_3{-}CH_2{-}CH_2{-}OH$

NAR 1-propanol

(IV) $CH_2{=}CH{-}CH_3 \xrightarrow[\text{oxidation}]{\text{Neutral } KMnO_4}$

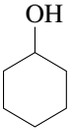
$CH_3{-}COOH + H{-}COOH$

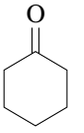
Acetic acid Formic acid

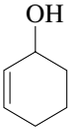
4. 

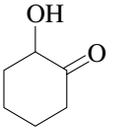
$\xrightarrow{H_3O^{\oplus}}$ (A) $\xrightarrow[\Delta]{}$ (B)

Product (B is)

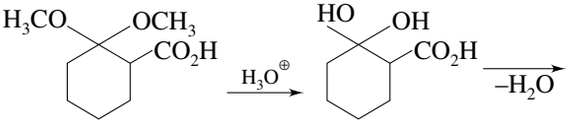
(1) 

(2) 

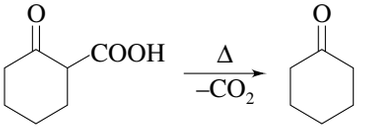
(3) 

(4) 

Sol. **[2]**



unstable



β keto acid

5. Dehydration of alcohol to alkene by heating with conc. H_2SO_4 the initiation step is ____ followed with _____ mechanism.

(1) Elimination of water, free radical
(2) Formation of an ester, free radical
(3) Protonation of alcohol, carbocation
(4) Protonation of alcohol, carbanion

Sol. **[3]**

$$R\text{–}OH \xrightarrow[H^{\oplus}]{\text{Conc. } H_2SO_4} R\text{–}\overset{\oplus}{O}\text{–}H_2 \longrightarrow R^{\oplus}$$

(Protonation) (Carbocation)

6. Ethylene glycol on treatment with Pl_3 mainly gives:
(1) Ethylene (2) Ethylene iodide
(3) Ethyl iodide (4) Ethane

Sol. **[1]**

$$\begin{matrix}CH_2\text{–}OH\\ |\\ CH_2\text{–}OH\end{matrix} \xrightarrow{PI_3} \begin{matrix}CH_2\text{–}I\\ |\\ CH_2\text{–}I\end{matrix} \xrightarrow{-I_2} \begin{matrix}CH_2\\ ||\\ CH_2\end{matrix}$$

unstable

7. In which of the following reactions, alcohol is formed as product gives positive iodoform test?

(1) $CH_3\text{–}\overset{O}{\overset{||}{C}}\text{–}CH_3 \xrightarrow[(ii)\ HOH/H^+]{(i)\ PhMgBr}$

(2) $CH_3\text{–}CH_2\text{–}CH{=}O \xrightarrow[(ii)\ HOH/H^+]{(i)\ MeMgBr}$

(3) $H\text{–}\overset{O}{\overset{||}{C}}\text{–}OEt \xrightarrow[(ii)\ HOH/H^+]{(i)\ PhMgBr\ (excess)}$

(4) $CH_3\text{–}\overset{O}{\overset{||}{C}}\text{–}OEt \xrightarrow[(ii)\ HOH/H^+]{(i)\ PhMgBr\ (excess)}$

Sol. **[2]**

$$CH_3\text{–}\overset{O}{\overset{||}{C}}\text{–}CH_3 \xrightarrow[H\ OH/H^+]{Ph\text{–}MgBr} CH_3\text{–}\overset{Ph}{\overset{|}{\underset{OH}{\underset{|}{C}}}}\text{–}CH_3 \xrightarrow{I_2|KOH} \text{–ve test}$$

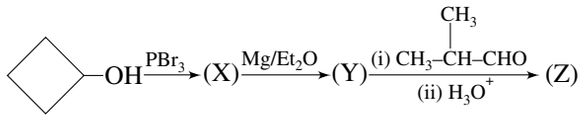
(tertiary alcohol)

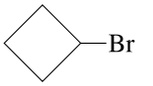
$$CH_3\text{–}CH_2\text{–}CH{=}O \xrightarrow[H\ OH/H^+]{MeMgBr} CH_3\text{–}CH_2\text{–}\underset{OH}{\underset{|}{CH}}\text{–}CH_3 \xrightarrow{I_2|KOH} \text{+ve test}$$

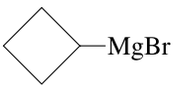
(Secondary alkanol)

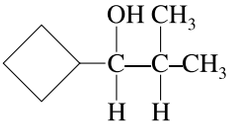
$$H\text{–}\overset{O}{\overset{||}{C}}\text{–}O\text{–}Et \xrightarrow[H\ OH/H^+]{Ph\text{–}MgBr} Ph\text{–}CH{=}O \xrightarrow[H\ OH/H^+]{Ph\text{–}MgBr} Ph\text{–}\underset{OH}{\underset{|}{CH}}\text{–}Ph \xrightarrow{I_2\ |\ KOH} \text{–ve test}$$

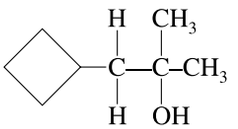
$$CH_3\text{–}\overset{O}{\overset{||}{C}}\text{–}O\text{–}Et \xrightarrow[H\ OH/H^+]{Ph\text{–}MgBr} CH_3\text{–}\overset{Ph}{\overset{|}{\underset{OH}{\underset{|}{C}}}}\text{–}Ph \xrightarrow{I_2|KOH} \text{–ve test}$$

8. 

(I) Y is 

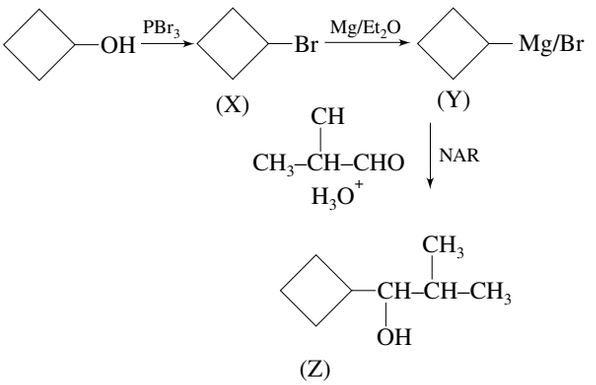
(II) Y is 

(III) Z is 

(IV) Z is 

Select the correct code for given reaction
(1) I and III (2) II and IV
(3) I and IV (4) II and III

Sol. **[4]**



9. $CH_3\text{–}\overset{18}{O}\text{–}\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}\text{–}CH_3 \xrightarrow{\text{conc. HI}}$

Product of above reaction is:

(1) $CH_3\text{–}I + CH_3\text{–}\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}\text{–}\overset{18}{O}H$

(2) $CH_3\text{–}\overset{18}{O}H + CH_3\text{–}\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}\text{–}I$

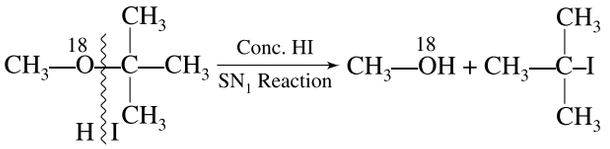
(3) $CH_3\text{–}\overset{18}{O}H + CH_3\text{–}\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}\text{–}OH$

(4) $CH_3–I + CH_3–\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}–I$

Sol. **[2]**

When one of the alkyl of ether is 3° alkyl then breaking of C–O bond takes place by S_N1 path.

In SN_1 reaction, breaking site towards the most stable carbocation



10. Consider the following sequence of reaction

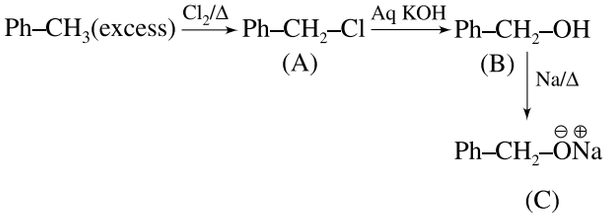
$PhCH_3(excess) + Cl_2 \xrightarrow{Heat} A \xrightarrow{aq.\ KOH} B \xrightarrow{Na} C$

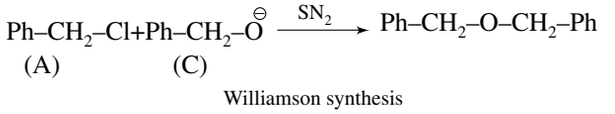
$A + C \xrightarrow{Heat} D$. Product D is:

(1) $PhCH_2OPh$ (2) $PhCH_2OCH_2Ph$

(3) $PhCH_2CH_2Ph$ (4) $Ph–CH_2–\overset{\displaystyle O}{\overset{\|}{C}}–Ph$

Sol. **[2]**





Williamson synthesis

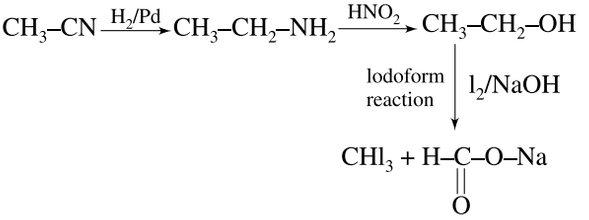
11. Identify the product C in the given reaction.

$CH_3–C\equiv N \xrightarrow{H_2/Pd} A \xrightarrow{HNO_2} B \xrightarrow{I_2/NaOH}$

(1) $CH_3–COOH$ (2) $CH_3–CH_2–NH–OH$

(3) $CH_3–\overset{\displaystyle O}{\overset{\|}{C}}–\overset{\ominus}{O}+CHI_3$ (4) CHI_3+HCOO^-

Sol. **[4]**

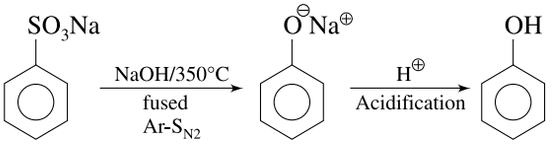


12. When sodium benzenesulphonate is fused with solid sodium hydroxide and subsequently acidified with dilute sulphuric acid, the product formed is:

(1) benzene (2) sodium phenoxide

(3) thiophenol (4) phenol

Sol. **[4]**



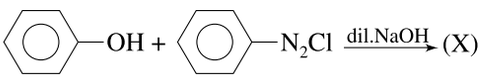
13. $Ph–\overset{\displaystyle O}{\overset{\|}{C}}–OH + EtOH \xrightarrow[\Delta]{H^\oplus}$ (P) major product, Product (P) is–

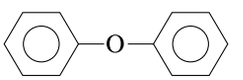
(1) $Ph–\overset{\displaystyle O^{18}}{\overset{\|}{C}}–O–Et$ (2) $Ph–\overset{\displaystyle O}{\overset{\|}{C}}–\overset{18}{O}–Et$

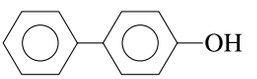
(3) $Ph–\overset{\displaystyle O}{\overset{\|}{C}}–Et$ (4) $Ph–\overset{18}{O}–\overset{\displaystyle O}{\overset{\|}{C}}–Et$

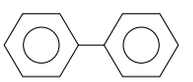
Sol. **[2]**

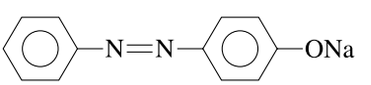
14. Consider the reaction:



(1) 

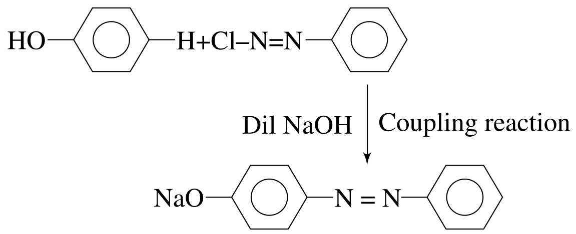
(2) 

(3) 

(4) 

Sol. **[4]**

Coupling reaction predominantly takes place at the *para* position.

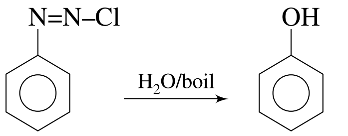


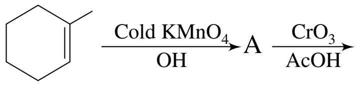
15. Benzenediazonium chloride can be converted into phenol by treating it with

(1) H_3PO_3, H_2O, CuCl (2) H_2O, heat

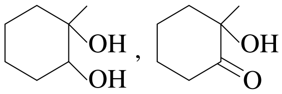
(3) Alcohol, heat (4) HBF_4, and $NaNO_2$/Cu

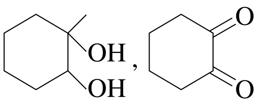
Sol. **[2]**

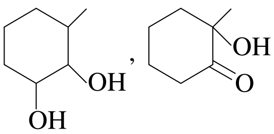


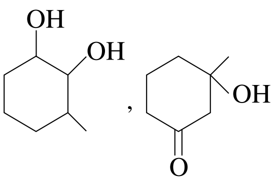
16. 

A and B are:

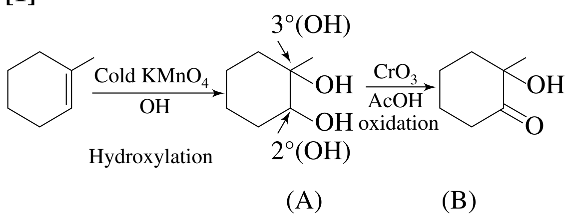
(1) 

(2) 

(3) 

(4) 

Sol. **[1]**



Oxidation of 3°-alcohol does not take place and 2°-alcohol oxidised into ketone.

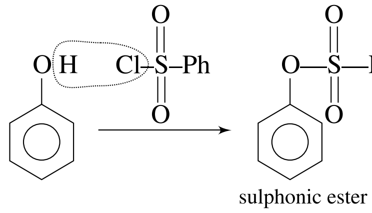
17. Phenol on reacting with Hinsberg's reagent gives:

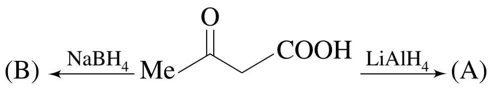
(1) Sulphone (2) Sulphanilic

(3) Sulphonic ester (4) Sulphonal

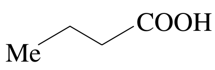
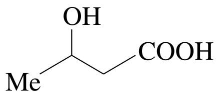
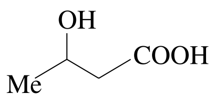
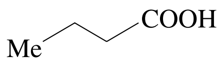
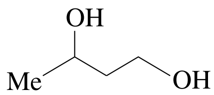
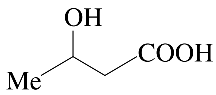
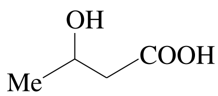
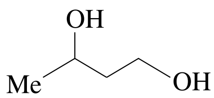
Sol. **[3]**

Benzene sulphonyl chloride (Ph–SO_2Cl) is known as Hinsberg reagent.



18. 

The products (A) and (B) are:

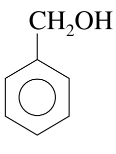
	(A)	**(B)**
(1)		
(2)		
(3)		
(4)		

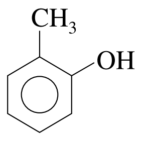
Sol. **[3]**

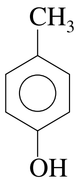
$NaBH_4$ is a weak reducing reagent. So it reduces only carbonyl group while reduction of –COOH group does not happen and it remains unaffected.

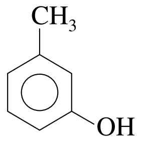
$LiAlH_4$ is strong reducing reagent; so it can reduce both >C=O and –COOH groups.

19. The structure of the compound that gives tribromo derivative on treatment with bromine water is:

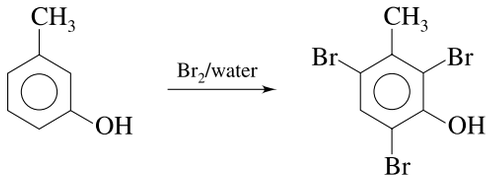
(1) 

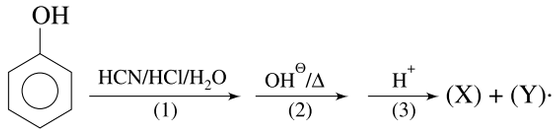
(2) 

(3) 

(4) 

Sol. **[4]**



20. 

X gives white turbidity with Lucas reagent instantly. X and Y both turb blue litmus solution red. Y can be:

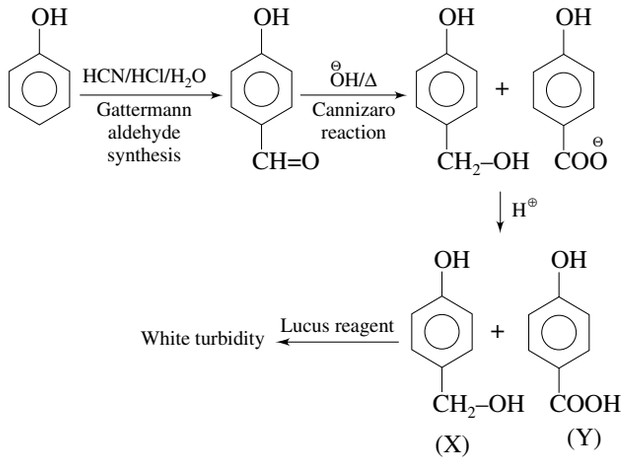
(1) *p*-Hydroxy benzoic acid

(2) *p*-Hydroxy benzaldehyde

(3) *m*-Hydroxy benzoic acid

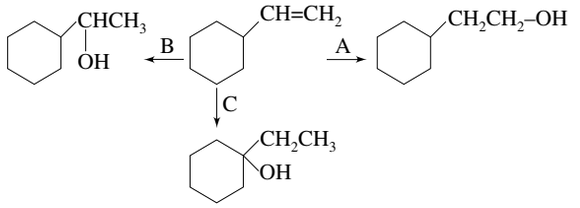
(4) *p*-Hydroxy benzyl alcohol

Sol. **[1]**



Both are phenolic so that (X) and (Y) give litmus test.

EXERCISE 1

1. 

Select schemes A, B, C, respectively, out of

I. Acid catalysed hydration

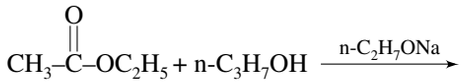
II. HBO

III. Oxymercuration–demercuration

(1) I in all cases (2) I, II, III

(3) II, III, I (4) III, I, II

2. The reaction



$CH_3COOC_3H_7(n) + C_2H_5OH$ is known as:

(1) Esterification

(2) Double decomposition

(3) Transesterification

(4) None of these

3. A compound 'X' with molecular formula C_3H_8O can be oxidised to a compound 'Y' with the molecular formula $C_3H_6O_2$, 'X' is most likely to be:

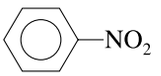
(1) Primary alcohol (2) Secondary alcohol

(3) Aldehyde (4) Ketone

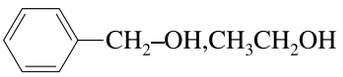
4. Which 'A' gives blue colour in the reaction?

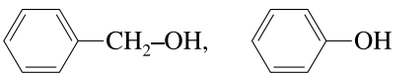
'A' $\xrightarrow[\text{(ii) NaOH}]{\text{(i) } HNO_2}$ blue colour

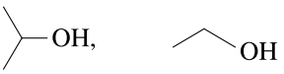
(1) $CH_3CH_2NO_2$ (2) $(CH_3)_2CHNO_2$

(3) $(CH_3)_3CNO_2$ (4) 

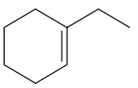
5. Which of the following pairs cannot be distinguished by using Lucas reagent?

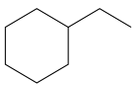
(1) 

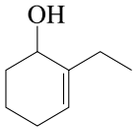
(2) 

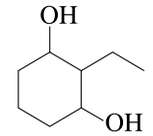
(3) 

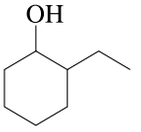
(4) 

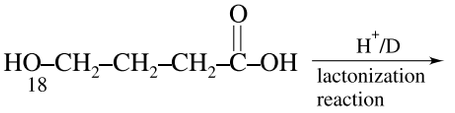
6.  $\xrightarrow{SeO_2}$ A.A is

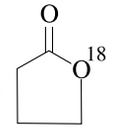
(1) 

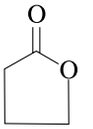
(2) 

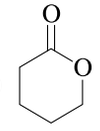
(3) 

(4) 

7. 

(1) 

(2) 

(3) 

(4) None

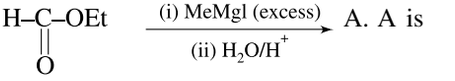
8. $A + Ac_2O \longrightarrow (B)$

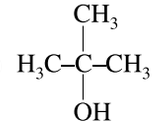
(acetic anhydride)

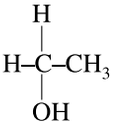
Molecular formula of A increases by $C_8H_8O_4$. Number of OH group present in A are:

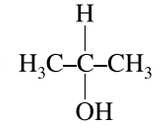
(1) 3 (2) 4

(3) 5 (4) 6

9.  A. A is

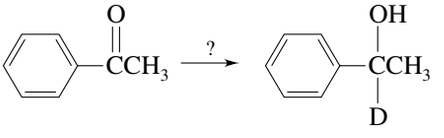
(1) 

(2) 

(3) 

(4) $CH_3–CH=O$

10. Which of the following reagents would carry out of the following transformation ? (D = ^2H)



(1) $NaBD_4$ in CH_3OH (2) $LiAlH_4$, then D_2O

(3) ($NaBD_4$ in CH_3OD (4) $LiAlD_4$, then D_2O

11. Methyl propionate, $CH_3CH_2COOCH_3$, is heated with aqueous H_2SO_4 in ^{18}O labelled water. When the equilibrium is achieved, the labelled oxygen will be present in:

(1) methyl alcohol

(2) Propionic acid

(3) unchanged methyl propionate

(4) both propionic acid and methyl propionate

12. $\underset{\text{Ester(X)}}{C_4H_8O_2} \xrightarrow[\text{(ii) HOH/HCl}]{\text{(i) } CH_3MgBr} \underset{\text{Alcohol(Y)}}{C_4H_{10}O}$

Alcohol (Y) gives Lucas test immediately. Thus, (X) and (Y) are, respectively:

(1) $CH_3COOC_2H_5$; $(CH_3)_3(COH)$

(2) $HCOOC_3H_7$; $C_2H_5CH(CH_3)OH$

(3) $C_2H_5COOCH_3$; $(C_2H_5)_3COH$

(4) $HCOOC_3H_7$; $CH_3(CH_2)_3OH$

13. The enzymes A, B and C in the reaction sequence are:

$$(C_6H_{10}O_5)_n \xrightarrow{A} C_{12}H_{22}O_{11} \xrightarrow{B} C_6H_{12}O_6 \xrightarrow{C} C_2H_5OH$$

(1) Invertase, Maltase, Zymase

(2) Diastase, Maltase, Zymase

(3) Maltase, Zymase, Invertase

(4) Diastase, Zymase, Maltase

14. A carbon compound A forms B with sodium metal and again A forms C with PCl_5, but B and C form diethyl ether. Therefore A, and B and C are:

(1) C_2H_5OH, C_2H_5ONa, C_2H_5Cl

(2) C_2H_5Cl, C_2H_5ONa, C_2H_5OH

(3) C_2H_5OH, C_2H_6, $C_2H_5Cl_2$

(4) C_2H_5OH, C_2H_5Cl, C_2H_5ONa

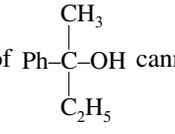
15. In order to obtain diethyl ether from ethanol and sulphuric acid, the latter is taken:

(1) In equal amount of sulphuric acid

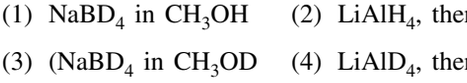
(2) In slightly lesser amount of sulphuric acid

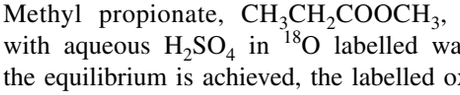
(3) In excess amount of sulphuric acid

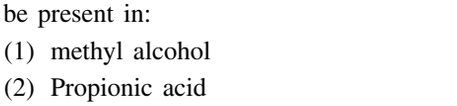
(4) In far lesser amount of sulphuric acid

16. The synthesis of  cannot be achieved by:

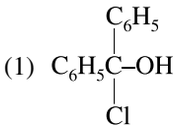
(1)

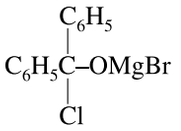
(2) 

(3) 

(4) 

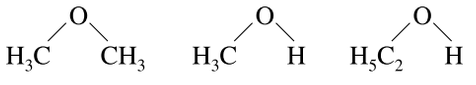
17. Which of the following is the final product in the reaction between benzoyl chloride and phenyl magnesium bromide?

(1) 

(2) 

(3) C_6H_5COOH (4) $(C_6H_5)_3COH$

18. The order of solubility of

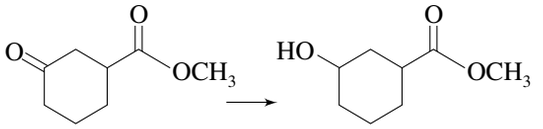


(I) (II) (III)

in water is:

(1) I > II > III (2) I < II < III

(3) II > III > I (4) II > I > III

19. 

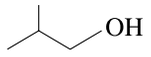
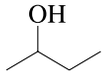
Above conversion can be achieved by–

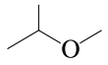
(1) $LiAlH_4$ (2) $NaBH_4$

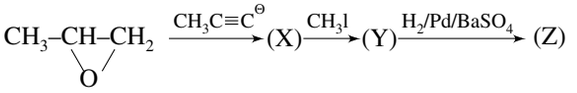
(3) H_3O^+ (4) PCC

20. (A) $\xrightarrow[C_4H_{10}O]{CrO_3/H^{\oplus}}$ (B) $\xrightarrow{NaOI}$ CHI_3+ Salt of acid

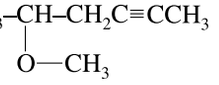
Reactant (A) is:

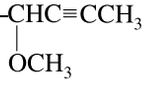
(1)  (2) 

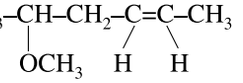
(3)  (4)

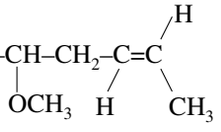
21. 

Which one in not correct

(1) Y is 

(2) Y is 

(3) Z is 

(4) Z is 

22. Which of the following is the best method for making isopropyl methyl ether?

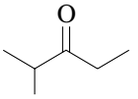
(1) $CH_3I + (CH_3)_2CHOH \longrightarrow$

(2) $CH_3I + (CH_3)_2CHO^- \longrightarrow$

(3) $(CH_3)_2CHI + CH_3O^- \longrightarrow$

(4) $(CH_3)_2CHCl + CH_3OH \longrightarrow$

23. Which sequence of steps describes the best synthesis of 2-methyl-3-pentanone?



(1) (1) 1-Propanol + $(CH_3)_2CHMgBr$, diethyl ether
(2) H_3O^+
(3) PCC, CH_2Cl_2

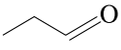
(2) (1) 1-Propanol + $Na_2Cr_2O_7$, H_2SO_4, H_2O, heat
(2) $SOCl_2$
(3) $(CH_3)_2CHCl$, $AlCl_3$

(3) (1) 1-Propanol + PCC, CH_2Cl_2
(2) $(CH_3)_2CHLi$, diethyl ether
(3) H_3O^+
(4) $Na_2Cr_2O_7$, H_2SO_4, H_2O, heat

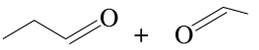
(4) (1) 2-Propanol + $Na_2Cr_2O_7$, H_2SO_4, H_2O, heat
(2) $CH_3CH_2CH_2Li$, diethyl ether
(3) H_3O^+
(4) PCC, CH_2Cl2

24. $CH_3 - CH_2 - O - \underset{\underset{CH_3}{|}}{C} = CH_2 \xrightarrow{H_3O^{\oplus}}$ Product are

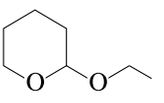
(1)  + EtOH

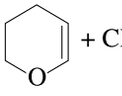
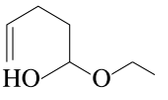
(2)  + EtOH

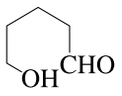
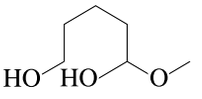
(3)  + EtOH

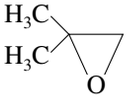
(4) 

25. The major product formed in the reaction is:



(1)  + CH_3CH_2OH (2) 

(3)  (4) 

26.  A, A is

(1) CH_3CHCH_2OH (2) $CH_3CH_2CH_2CH_2OH$

(3) $(CH_3)_3C-OH$ (4) No reaction

27. Major (B) $\xleftarrow[CH_3ONa]{CH_3OH}$ $CH_3-\underset{\diagdown O \diagup}{C}-CH_2$ $\xleftarrow[H^+]{H_2O^{18}}$ (A) major A and B are:

(1) $CH_3-C(CH_3)(OH)-CH_2(^{18}OH)$, $CH_3-C(CH_3)(OH)-CH_2(OCH_3)$

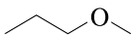
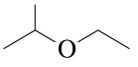
(2) $CH_3-C(CH_3)(OH)-CH_2(OH)$, $CH_3-C(CH_3)(OH)-CH_2(OH)$

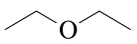
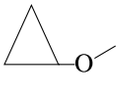
(3) $CH_3-C(CH_3)(OH)-CH_2(OH)$, $CH_3-C(CH_3)(OH)-CH_2(^{18}OH)$

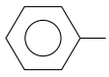
(4) $CH_3-C(CH_3)(OH)-CH_2(^{18}OH)$, $CH_3-C(CH_3)(OMe)-CH_2(OH)$

28. $C_4H_{10}O$ → (i) Na Metal → No H_2 gas evolved; (ii) Cl_2/hv → 3-monochloro poducts; (iii) Lucas reagent → –ve test

Compound is:

(1)  (2) 

(3)  (4) 

29.  $\xrightarrow{H_3O^+}$ P + Q

What is false about this reaction–

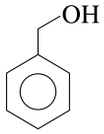
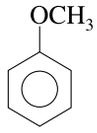
(1) one compound is phenol which is less acidic than other compound

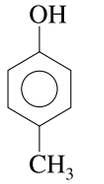
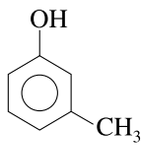
(2) one compound is phenol and other is methanol

(3) reactant is anisole

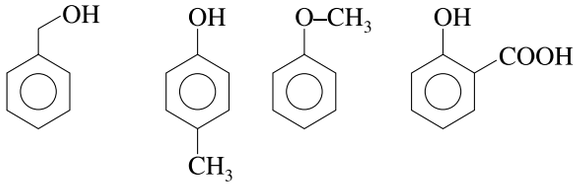
(4) this reaction occur through SN^2 reaction

30. A compound of molecular formula C_7H_8O is insoluble in water and dilutes sodium bicarbonate but dissolves in dilute aqueous sodium hydroxide and gives a characteristic colour with aqueous $FeCl_3$. On treatment with bromine water, it readily gives precipitate of $C_7H_5OBr_3$. The structure of 'A' is:

(1)  (2) 

(3)  (4) 

31. Which of the following can give purple colour with neutral $FeCl_3$?



(I) (II) (III) (IV)

(1) II and IV (2) I and III

(3) II and III (4) III and IV

32. *Ortho*-nitrophenol is steam volatile, whereas *para*-nitrophenol is not. This is due to

(1) the presence of intramolecular hydrogen boding in o-nitrophenol.

(2) the presence of intermolecular hydrogen bonding in o-nitrophenol.

(3) the presence of intermolecular hydrogen bonding in p-nitrophenol.

(4) None of these.

33. Phenol cannot be converted into salicylic acid by heating with:

(1) CO_2 (under pressure) and alkali

(2) CCl_4 and alkali

(3) $CHCl_3$ and alkali

(4) HCN/HCl, followed by oxidation

34. 4-Hydroxybenzenesulphonic acid is treated with bromine water. The product formed is:

(1) 2, 4, 6-tribromophenol

(2) 3, 5-dibromo-4-hydroxybenzenesulphonic acid

(3) 3-bromo-4-hydroxybenzenesulphonic acid

(4) 2, 6-dibromophenol

35. In the Liebermann nitroso reaction, changes in the colour of phenol occur as:

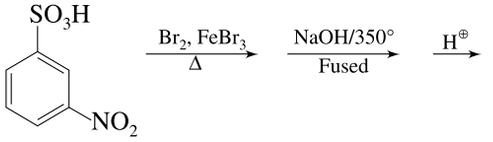
(1) Brown or red-green-red-deep blue

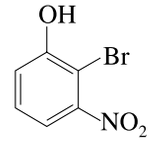
(2) Red-deep blue-green

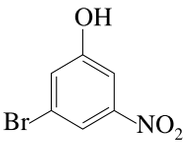
(3) Red-brown-white

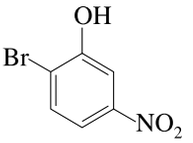
(4) White-red-green

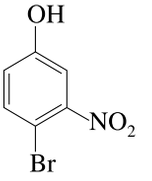
36. Which of the following is the major product from given sequence?



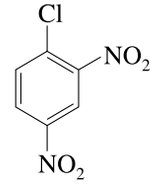
(1) 

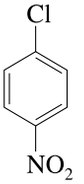
(2) 

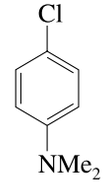
(3) 

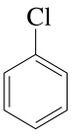
(4) 

37. Which of the following would undergo most rapid hydrolysis with aqueous NaOH to furnish the corresponding hydroxyl derivatives?

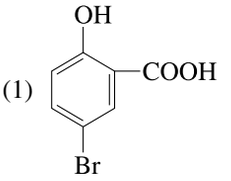
(1) 

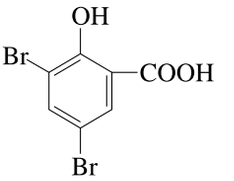
(2) 

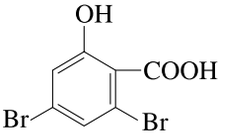
(3) 

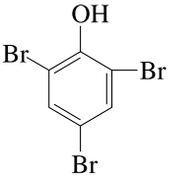
(4) 

38. The bromination of salicylic with bromine water gives

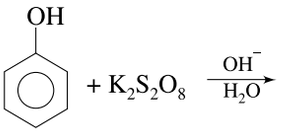
(1) 

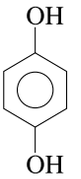
(2) 

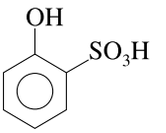
(3) 

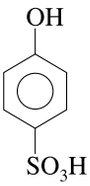
(4) 

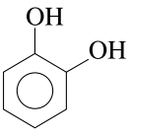
39. Identify the nature of product of in the following reaction:

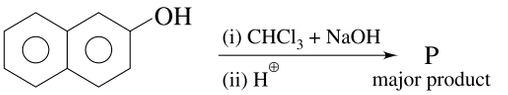


(1) 

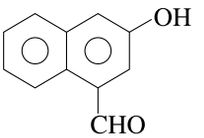
(2) 

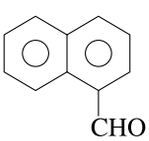
(3) 

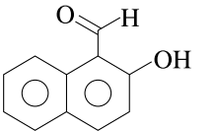
(4) 

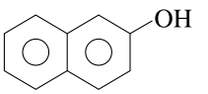
40. 

Identify the structure of 'P'

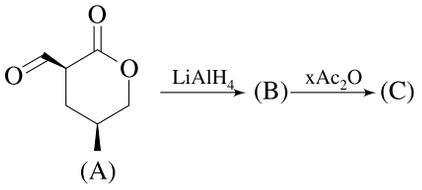
(1) 

(2) 

(3) 

(4) 

EXERCISE 2

1. 

(I) x = 3

(II) A will show geometrical isomerism

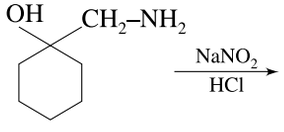
(III) B is optically active

(IV) C is optically inactive

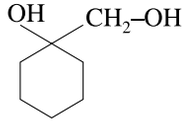
Select correct statement

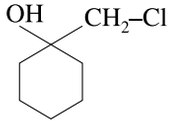
(1) (I), (II), (IV) (2) (I), (II), (III)

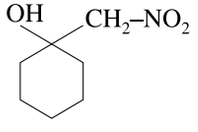
(3) (II), (III), (IV) (4) (I), (II), (III), (IV)

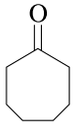
2. 

A; A (major product) is:

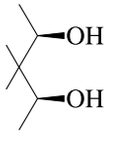
(1) 

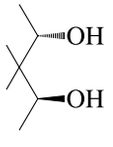
(2) 

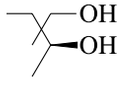
(3) 

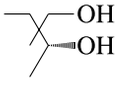
(4) 

3. A chiral $C_7H_{16}O_2$ diol is oxidised by PCC in CH_2Cl_2 to an achiral $C_7H_{12}O_2$ compound. Which of the following would satisfy these facts?

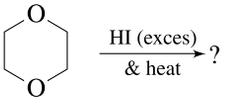
(1) 

(2) 

(3) 

(4) 

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

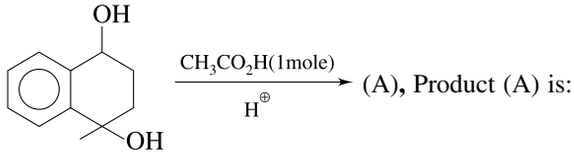


(1) $2CH_3CH_2I$

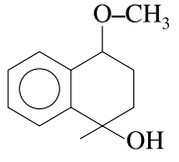
(2) $2ICH_2CH_2OH$

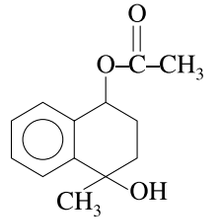
(3) $2ICH_2CH_2I$

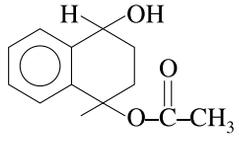
(4) $CH_3CH_2I+CH_3CH_2OH$

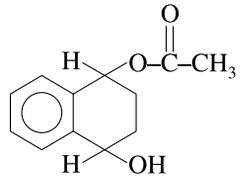
5. 

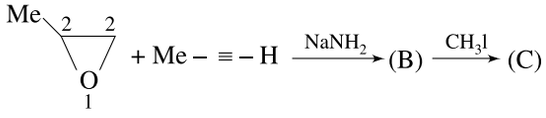
(A), Product (A) is:

(1) 

(2) 

(3) 

(4) 

6. 

2-Methyl oxirane

Give the product (C) in the above reaction

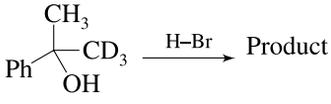
(1) 2-Methoxy hex-4-yne

(2) 4-Methoxy hex-2-yne

(3) 5-Methoxy hex-2-yne

(4) None of these

7. Which describes the best stereochemical aspects of the following reaction?



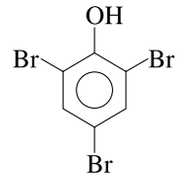
(1) Inversion of configuration occurs at the carbon undergoing substitution.

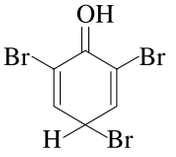
(2) Retention of configuration occurs at the carbon undergoing substitution.

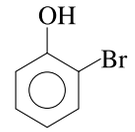
(3) Racemisation occurs at the carbon undergoing substitution.

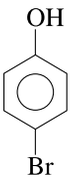
(4) The carbon undergoing substitution is not sterogenic.

8. What is the structure of the major product when phenol is treated with bromine water?

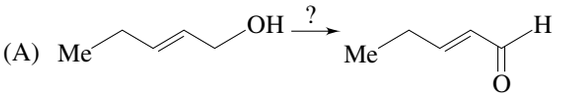
(1) 

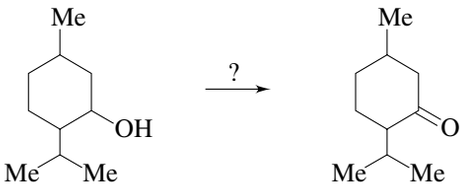
(2) 

(3) 

(4) 

9. Suggest a suitable oxidising reagent for the following conversions:

(A) 

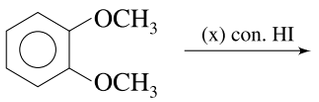
(B) 

(1) MnO_2 in (A) and CrO_3 (in glacial acetic acid) in (B)

(2) CrO_3 in (A) and MnO_2 in (B)

(3) both are correct

(4) both are incorrect

10. 

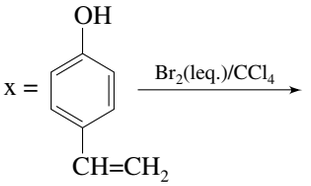
X = moles of HI consumed.

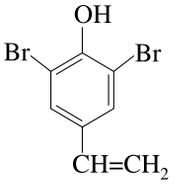
Value of x is:

(1) 2 (2) 4

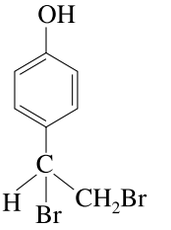
(3) 5 (4) 6

11. Observe the following reaction carefully. Select the correct answer regarding the major product formed and the relative reactivity of compound X with respect to ethene for the following reaction.

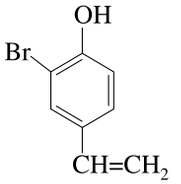


(1) 

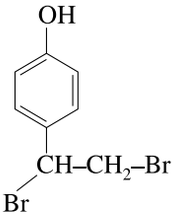
Much less reactive than ethene

(2) 

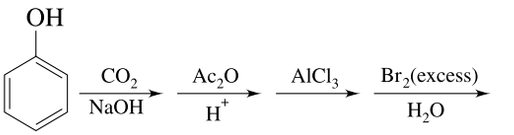
Much more reactive than ethene

(3) 

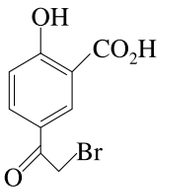
Much less reactive than ethene

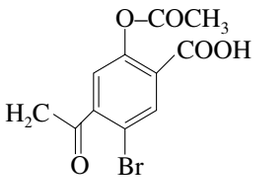
(4) 

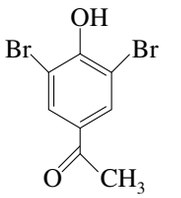
Less more reactive than ethene

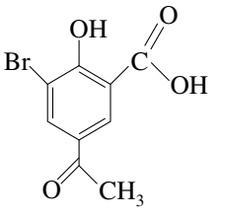
12. 

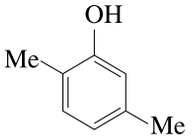
Final product is:

(1) 

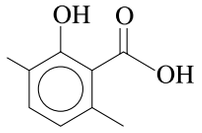
(2) 

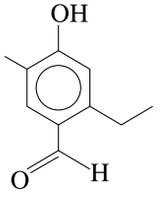
(3) 

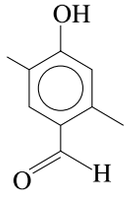
(4) 

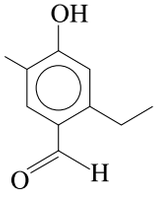
13.  ‘P’, the product

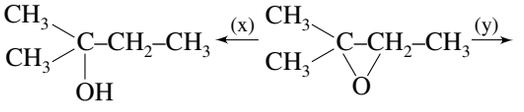
‘P’ is–

(1) 

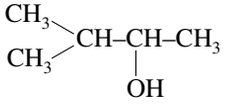
(2) 

(3) 

(4) 

14. 

3° alchol



2° alchol

Find missing reagents

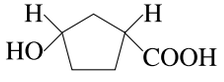
(1) x = $LiAlH_4$, y = $NaBH_4$

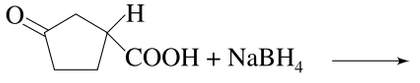
(2) x = $LiAlH_4/AlCl_3$, y = $LiAlH_4$

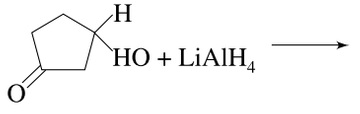
(3) x = $LiAlH_4$, y = $LiAlH_4/AlCl_3$

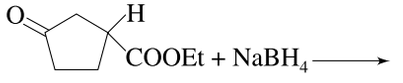
(4) x = H_2/Ni, y = H_2/Pt

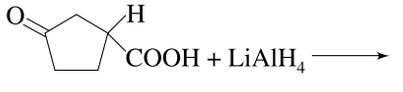
15. The given compound is prepared by–



(1) 

(2) 

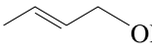
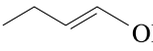
(3) 

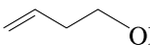
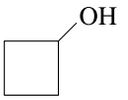
(4) 

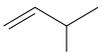
16. Compounds X and Y both have the same molecular formula C_4H_8O, and they give the following results with some characteristic tests:

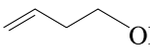
Tests	**Compounds X**	**Compound Y**
Bromine	Decolourise	No reaction
Na Metal	Bubbles	No reaction
Chromic acid	Orange to green	No reaction
Lucas reagent	Slow reaction	No reaction

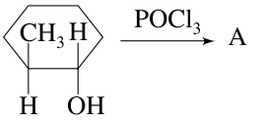
Which of the following structures for X and Y are consistent with the test results?

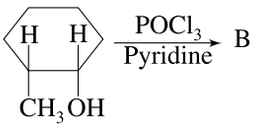
(1) X =  Y = 

(2) X =  Y = 

(3) X =  ; Y = 

(4) X =  Y = 

17. Reaction I: 

Reaction II: 

Products A and B are respectively

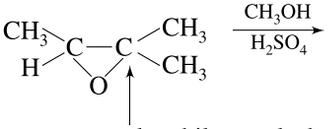
(1) A =  ; B = 

(2) A =  = B

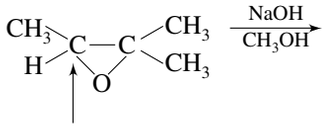
(3) A =  ; B = 

(4) A =  = B

18. Which is/are correct Statements?

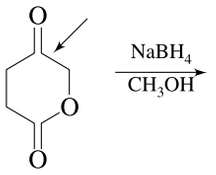
(A) 

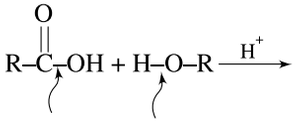
nucleophile attacks here when epoxy linkage is cleaved

(B) 

Nucleophile attacks here

(C) This is only affected in reduction to 2° alcohol

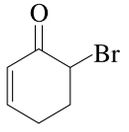


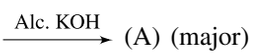
(D) 

These bonds are affected in esterification

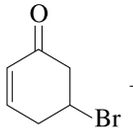
(1) A and D (2) A and B

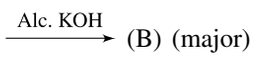
(3) A, B and C (4) A, B, C and D

19. Reaction (I) 

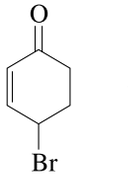


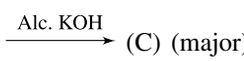
(A) (major)

Reaction (II) 



(B) (major)

Reaction (III) 



(C) (major)

Product obtained in above reactions (I), (II) & (III) is:

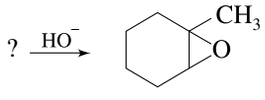
(1) A = B, but C is different

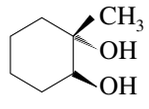
(2) A = C, but B is different

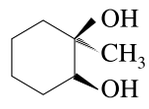
(3) B = C, but A is different

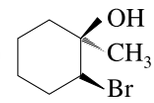
(4) A = B = C all product are identical

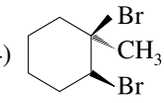
20. The best choice of reactant(s) for the following conversion is:



(1) 

(2) 

(3) 

(4) 

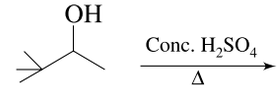
21. In the reaction, $CH_3CH_2ONa + CH_3CH_2OSO_2CH_3 \xrightarrow[\text{heat}]{\text{THF}}$ the product formed is:

(1) $CH_3CH_2OCH_3$

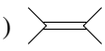
(2) $CH_3CH_2OCH_2CH_3$

(3) $CH_3CH_2OSO_2OCH_2CH_3$

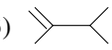
(4) $CH_3CH_2OSO_2OCH_3$

22. 

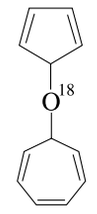
Major product?

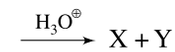
(1) 

(2) 

(3) 

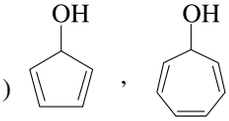
(4) None of these

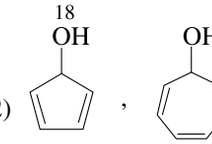
23. 

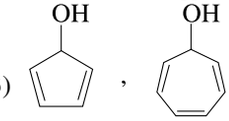


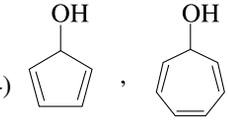
X + Y

The products X and Y are

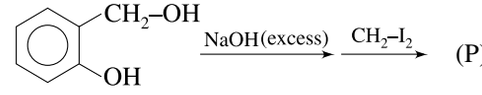
(1) 

(2) 

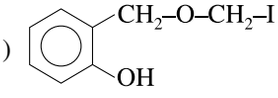
(3) 

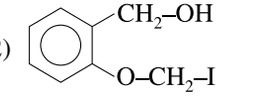
(4) 

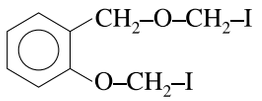
24. The product 'P' of the following reaction is:

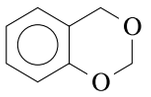


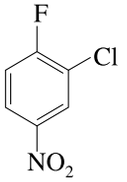
(P)

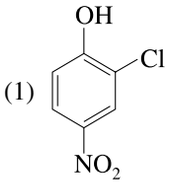
(1) 

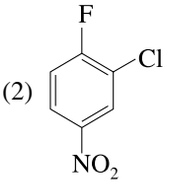
(2) 

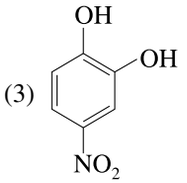
(3) 

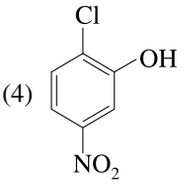
(4) 

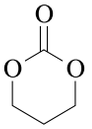
25.  $\xrightarrow[\Delta]{KOH}$ Y; Identify Y in this reaction.

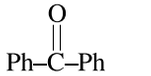
(1) 

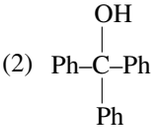
(2) 

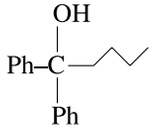
(3) 

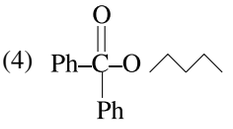
(4) 

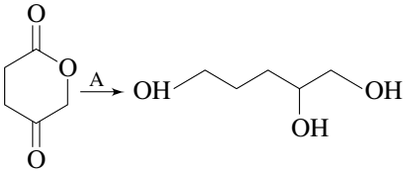
26. PhMgBr + (excess)  $\xrightarrow{H^+}$ (A). Product (A) is:

(1) 

(2) 

(3) 

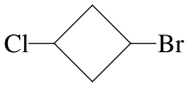
(4) 

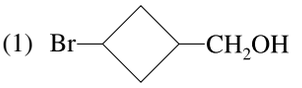
27. 

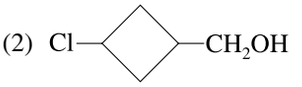
Reagent A used in this change is:

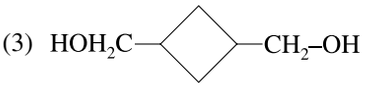
(1) Sn/HCl (2) $LiAlH_4$

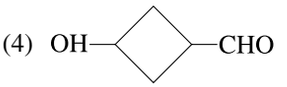
(3) $NaBH_4$ (4) HI/P_4

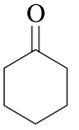
28.  $\xrightarrow[1\text{ mole}]{Mg/ether}$ $\xrightarrow[H^\oplus]{HCHO}$ A, A is

(1) 

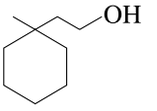
(2) 

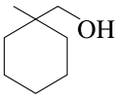
(3) 

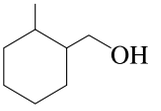
(4) 

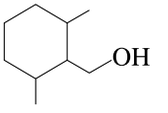
29.  + CH_3MgBr $\xrightarrow{H^\oplus/H_2O}$ P $\xrightarrow{KBr+H_2SO_4}$

Q $\xrightarrow[Ether]{Mg}$ R $\xrightarrow[H^\oplus/H_2O]{HCHO}$ S, S is

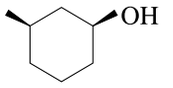
(1) 

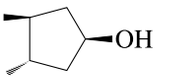
(2) 

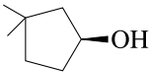
(3) 

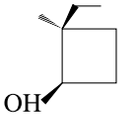
(4) 

30. A $C_7H_{14}O$ optically active alcohol is oxidised by Jones' reagent (H_2CrO_4) to an optically inactive (achiral) ketone. Which of the following compounds meets these facts?

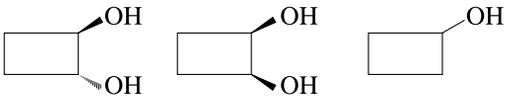
(1) 

(2) 

(3) 

(4) 

31. What is the order of solubility of the following in water?

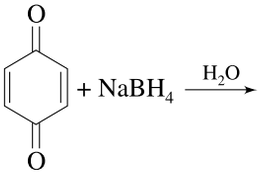


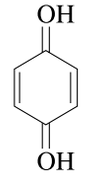
I II III

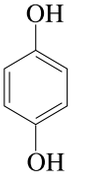
(1) I < II < III (2) III < II < I

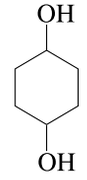
(3) III < I < II (4) II < I < III

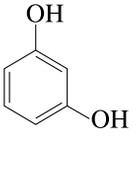
32. What is the major product of the following reaction?



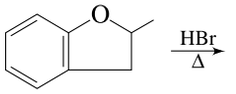
(1) 

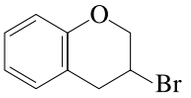
(2) 

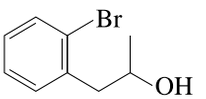
(3) 

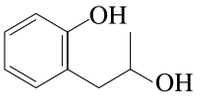
(4) 

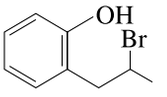
33. The major organic product formed in the following reaction is



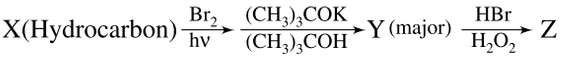
(1) 

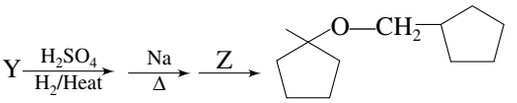
(2) 

(3) 

(4) 

34. Consider the following roadmap reaction:

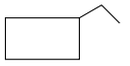


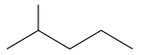


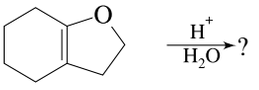
The most probable structure of X is

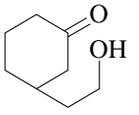
(1) 

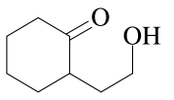
(2) 

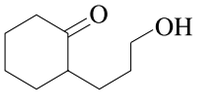
(3) 

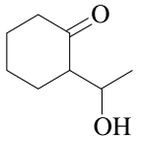
(4) 

35. 

(1) 

(2) 

(3) 

(4) 

EXERCISE 3

One and More Than One Option Correct Type Question

1. C_2H_5Br can be converted into $C_2H_5–O–C_2H_5$ by:

(1) Reacting by C_2H_5ONa

(2) Heating with moist Ag_2O

(3) Heating with dry Ag_2O

(4) Treating with C_2H_5MgBr

2. Which of the following statements is correct about the transesterification reaction, catalysed by

$H_3O^{\oplus}$ (H_2SO_4 or dry HCl) or $RO^{\ominus}$ (EtONa)?

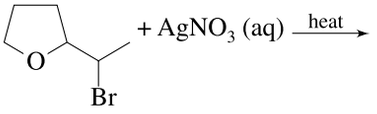
(1) Alcohol (PrOH) is taken in excess to shift the equilibrium to R.H.S.

(2) It involves tetrahedral intermediate in which the hybridisation of C of the (C = O) group changes from sp^2 to sp^3

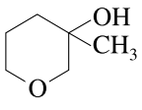
(3) Isotopic oxygen is present in the new alcohol ($Et\overset{*}{O}H$) formed

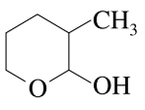
(4) Rate of transesterification is dependent on the concentration of ester only.

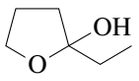
3. In the following reaction.

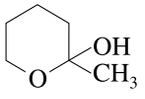


The possible substitution product (s) is/are

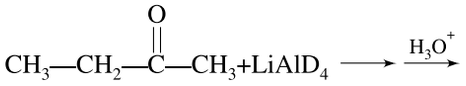
(1) 

(2) 

(3) 

(4) 

4. In the reaction given below,



The correct statement regarding the outcome of the above reaction is/are

(1) A pure enantiomer of alcohol is formed

(2) Racemic mixture of alcohol is formed

(3) Product alcohol has deuterium attached to oxygen

(4) Product alcohol has deuterium attached to carbonyl-carbon atom

5. Which of the following is true statement regarding reaction of *cis* and *trans*-2-hexene with CH_3OH/H^+

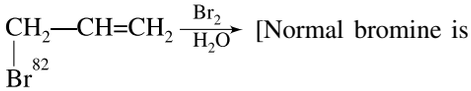
(1) Both react at same rate

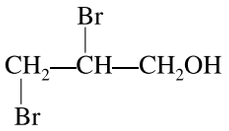
(2) *Cis* isomer reacts faster than *trans* isomer

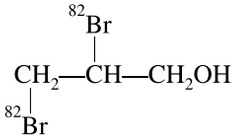
(3) Both cis and *trans* isomers give mixture of positional isomers as the major product

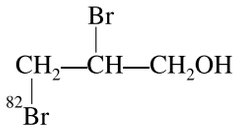
(4) No reaction is possible

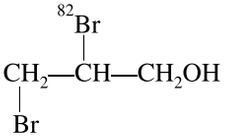
6. Upon treatment with bromine water, allyl bromide gives chiefly primary alcohol $BrCH_2CHBrCH_2OH$. What are the expected primary alcohols in the following reaction?



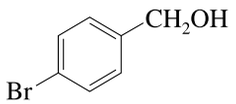
(1) 

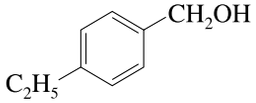
(2) 

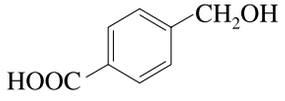
(3) 

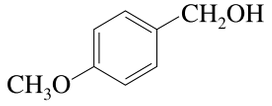
(4) 

7. Alcohols given below that behaves like 1°-aliphatic alcohol in Lucas test is/are

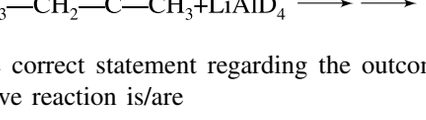
(1) 

(2) 

(3) 

(4) 

8. Consider the following reaction,



The correct statement(s) concerning X and Y is/are

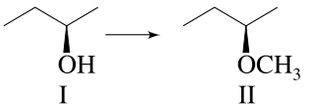
(1) Both form immediate turbidity with HCl in the presence of $ZnCl_2$

(2) Both change colour of $CrO_3 - H_2SO_4$

(3) X gives yellow solid with $NaOH/I_2$

(4) X decolourises Br_2-CCl_4 solution forming $C_6H_{12}OBr_2$

9. Consider the following reaction



The correct statements(s) concerning the above transformation is/are

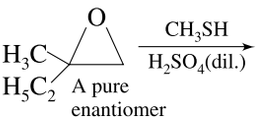
(1) If I is treated with Na followed by addition of CH_3I gives II with the retention of configuration

(2) If I is treated with TsCl followed by the addition of CH_3ONa gives II with inversion of configuration

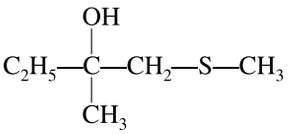
(3) If I is first heated with concentrated H_2SO_4 followed by the addition of CH_3OH in dil. H_2SO_4 gives racemic mixture of II

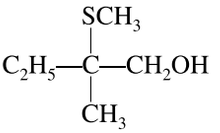
(4) If I is heated with concentrated H_2SO_4 followed by the treatment with $(CH_3COO)_2Hg—CH_3OH$ and finally reducing the mercurinium intermediate with $NaBH_4$ gives a pure enantiomer of II

10. Consider the reaction given below,



The correct statement regarding the above reaction is/are

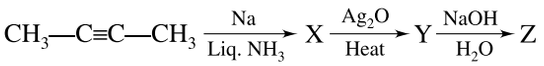
(1) The major product is 

(2) The major product is 

(3) The product would be a single enantiomer

(4) The product would consist of a racemic mixture

11. In the reaction below,



The correct statement concerning the above reaction is/are

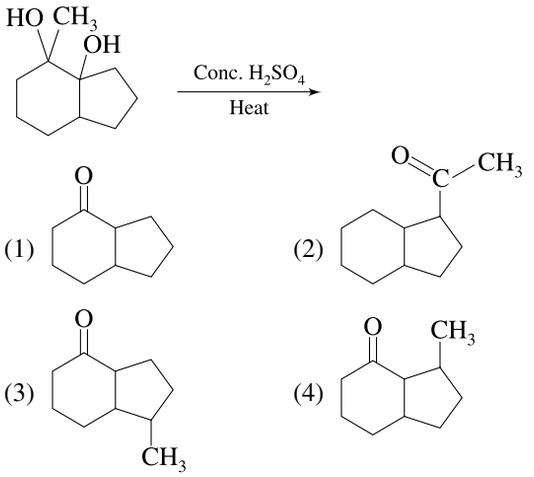
(1) Y is a racemic mixture while Z is achiral

(2) Both Y and Z are racemic mixture

(3) A diastereomer of Y gives racemic Z

(4) X shows diastereomerism but not enantiomerism

12. In the following rearrangement, possible product(s) is/are



13. 3-methyl-3-hexanol can be prepared by the reaction of

(1) CH_3MgBr and 3-hexanone followed by hydrolysis

(2) C_2H_5MgBr and 2-pentanone followed by hydrolysis

(3) propyl-MgBr + 2-butanone followed by hydrolysis

(4) C_4H_9MgBr and propanone followed by hydrolysis

Statement Type Question

(1) If both Statement-I and Statement-II are correct and Statement-II is the correct explanation for Statement-I

(2) If both Statement-I and Statement-II are correct and Statement-II is not the correct explanation for Statement-I

(3) If Statement-I is correct and Statement-II is incorrect

(4) If Statement-I is incorrect and Statement-II is correct

14. Statement-I: Phenolic compounds give characteristic colours with neutral $FeCl_3$.

Statement-II: It is the property of all the enolic compounds.

15. Statement-I: 3-Methyl-2-butanol is more reactive than 2-butanol in acid catalysed dehydration to alkene.

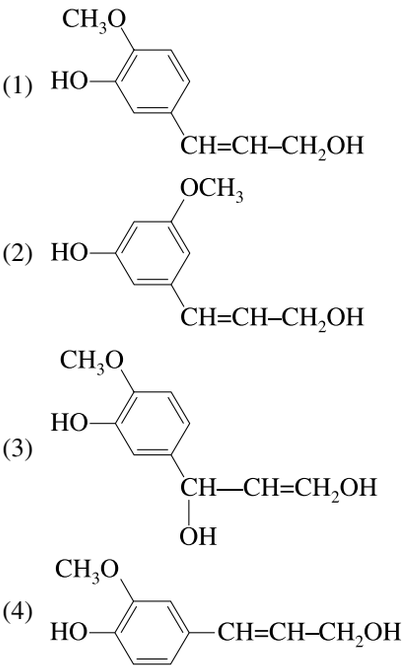
Statement-II: 3-methyl-2-butanol forms more stable carbocation than 2-butanol during dehydration reaction.

Comprehension Type Question

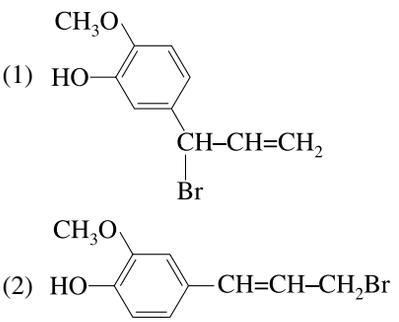
Passage based questions (Q. 16–18)

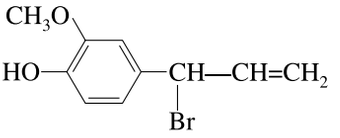
An organic compound $X(C_{10}H_{12}O_3)$ is not soluble in water or $NaHCO_3$. A solution of Br_2 in CCl_4 is decolourised by X forming $C_{10}H_{12}O_3Br_2$. X on controlled ozonolysis followed by the treatment with $(CH_3)_2S$ gives $Y(C_8H_8O_3)$ and $C_2H_4O_2$. Y can also be obtained by reaction between *ortho* methoxy phenol with $CHCl_3$ in KOH solution followed by acid hydrolysis.

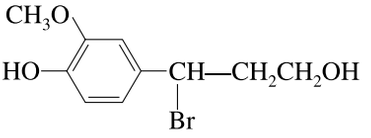
16. What is the correct structure of X?



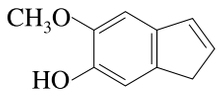
17. If X is treated with cold HBr, the major product would be

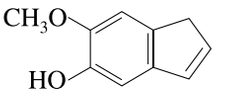


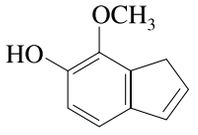
(3) 

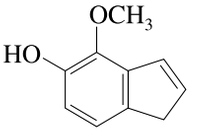
(4) 

18. What would be the major product if X is treated with cold concentrated H_2SO_4?

(1) 

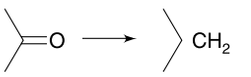
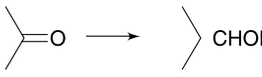
(2) 

(3) 

(4) 

Column Matching Type Questions

19. Match the statements given in Column-I and Column-II

Column-I	Column-II
(a) 	(p) $LiAlH_4$
(b) H–CH = O → CH_3CH_2OH	(q) Zn-Hg/conc. HCl
(c) 	(r) DIBAL-H
(d) 	(s) CH_3MgBr

(1) a → p; b → q; c → r; d → s
(2) a → q; b → s; c → p; d → r
(3) a → p; b → q; c → s; d → r
(4) a → r; b → s; c → q; d → p

20. Match the reagents given in Column-I with the appropriate items given in Column-II

Column-I	Column-II
(a) Conc. HCl–$ZnCl_2$	(p) Reducing agent
(b) $LiAlH_4$	(q) Grignard reagent
(c) pyridinium chlorochromate	(r) Oxidising agent
(d) Ethyl magnesium bromide	(s) Lucas reagent

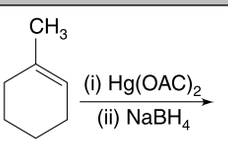
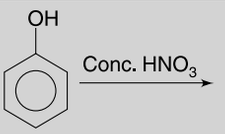
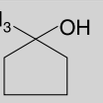
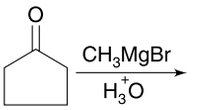
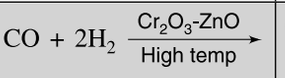
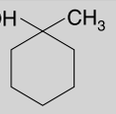
(1) a → s; b → r; c → p; d → q
(2) a → s; b → p; c → r; d → q
(3) a → p; b → s; c → q; d → r
(4) a → s; b → q; c → p; d → r

21. Match the pairs of compounds in Column-I with the appropriate Column-II. Distinguishing test in Column-II

Column-I	Column-II
(a) Methanol and ethane-1, 2-diol	(p) Lucas test
(b) O-cresol and Benzyl alcohol	(q) Iodoform test
(c) n-butyl alcohol and iso-butyl alcohol	(r) Litmus test
(d) 2-Pentanol and 3-pentanol	(s) Periodic acid test

(1) A → r, B → p, C → s; D → q
(2) A → s, B → r, C → q; D → p
(3) A → s, B → r, C → p; D → q
(4) A → r, B → s, C → p; D → q

22. Make the correct match of the following from List-I and List-II.

List-I		List-II	
(A)		(P)	Picric Acid
(B)		(Q)	
(C)		(R)	CH_3OH
(D)		(S)	

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

23. Make the correct match of the following from List-I and List-II.

List-I		List-II	
(A)	Ethyl alcohol	(P)	$FeCl_3$ Test
(B)	Picric acid	(Q)	Iodoform Test
(C)	Glycerol	(R)	Lucas Test
(D)	Isopropyl alcohol	(S)	HIO_4

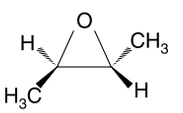
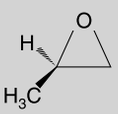
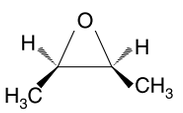
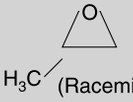
(1) A → Q, B → P, C → S, D → R

(2) A → P, B → Q, C → S, D → R

(3) A → Q, B → P, C → R, D → S

(4) A → R, B → S, C → P, D → Q

24. Match the reactant from Column I with the reaction(s) from Column II and mark the correct option from the codes given below.

Column I		Column II	
i.		**p.**	$\xrightarrow[H_2O]{NaOH}$ Racemic mixture
ii.		**q.**	$\xrightarrow[H_2O]{NaOH}$ Pure, single enantiomer
iii.		**r.**	$\xrightarrow[H_2O]{NaOH}$ Meso isomer
iv.	 (Racemic)	**s.**	$\xrightarrow{CH_3MgBr}$ $\xrightarrow{H_2O}$ Racemic mixture

Codes:

	i	ii	iii	iv
(1)	r, s	q	p, s	p, s
(2)	p	q	r	s
(3)	q	r	s	p
(4)	q, p	s	p	r

25. Match the column I with Column II and mark the correct option from the codes given below.

Column I		Column II	
i.	1-butanol	**p.**	Treatment with H^+/H_2O gives racemic mixture
ii.	2-butanol	**q.**	Changes the colour of acidic $K_2Cr_2O_7$
iii.	(+)-3-methyl-3-hexanol	**r.**	Gives turbid solution with $ZnCl_2$/Conc. HCl at room temperature
iv.	(–)-2-ethyl oxirane	**s.**	With $LiAlH_4$. gives another compound from column II.

Codes:

	i	ii	iii	iv
(1)	p, q	p, q, r	p, r	s
(2)	q	r	p	q
(3)	p, s	r	p	q
(4)	p, q	r	s	p

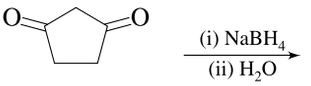
Single Digit Integer Type Question

26. In the reaction given below,

$$CH_3—CH_2—\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}=CH—CH_3 + CO + H_2 \xrightarrow{Co_2(CO)_8} \xrightarrow[H_2]{Cu\text{-}Zn}$$

How many different products are expected?

27. In the following reaction how many different diols, are formed?



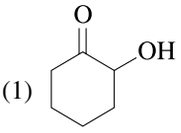
28. An alcohol $X(C_4H_{10}O_3)$ is chiral and absorbs two moles of HIO_4 per mole of X. How many stereoisomers exist for X?

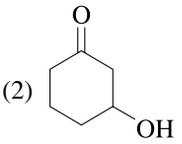
29. When 2-ethyl-3-metyl-1-pentene is treated with CH_3OH in H_2SO_4, how many different methoxy ethers would be formed in significant amount?

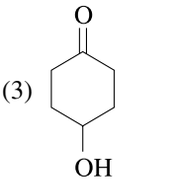
30. An organic compound $A(C_{10}H_{18}O_8)$ on treatment with excess of CH_3COCl gives a fully acetylated product whose molar mass is found to be 518 g/mol. How many hydroxyl functional groups are present in A?

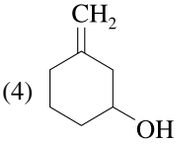
EXERCISE 4

1. Maximum dehydration takes place that of **[AIEEE-2002]**

(1) 

(2) 

(3) 

(4) 

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

(1) Dipolar character of ethers

(2) Alcohols having resonance structures

(3) Intermolecular hydrogen bonding in ethers

(4) Intermolecular hydrogen bonding in alcohols

3. During dehydration of alcohols to alkenes by heating with concentrated H_2SO_4 the initiation step is **[AIEEE-2003]**

(1) Protonation of alcohol molecule

(2) Formation of carbocation

(3) Elimination of water

(4) Formation of an ester

4. Among the following compounds which can be dehydrated very easily is **[AIEEE-2004]**

(1) $CH_3CH_2CH_2CH_2CH_2OH$

(2) $CH_3CH_2CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$

(3) $CH_3CH_2\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}CH_2CH_3$

(4) $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2OH$

5. For which of the following parameters the structural isomer C_2H_5OH and CH_3OCH_3 would be expected to have the same values? **[AIEEE-2004]**

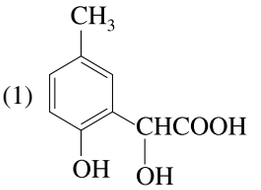
(1) Heat of vaporisation

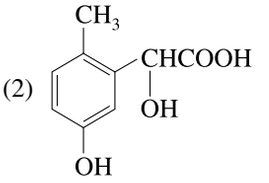
(2) Vapour pressure at the same temperature

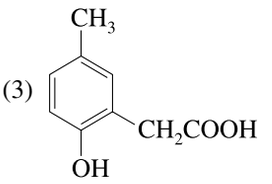
(3) Boiling points

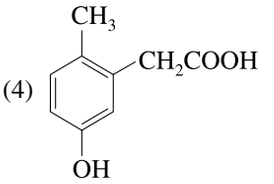
(4) Gaseous densities at the same temperature and pressure

6. 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]**

(1) 

(2) 

(3) 

(4) 

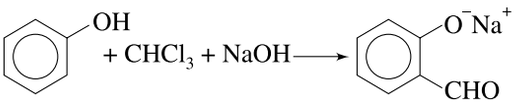
7. HBr reacts with $CH_2 = CH - OCH_3$ under anhydrous conditions at room temperature to give– **[AIEEE-2005]**

(1) $BrCH_2CHO$ and CH_3OH

(2) $BrCH_2–CH_2–OCH_3$

(3) $H_3C–CHBr–OCH_3$

(4) CH_3CHO and CH_3Br

8. 

The electrophile involved in the above reaction is **[AIEEE-2006]**

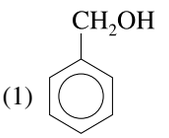
(1) dichlorocarbene ($:CCl_2$)

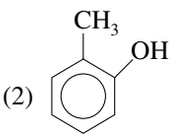
(2) trichloromethyl anion $\overset{\ominus}{C}Cl_3$

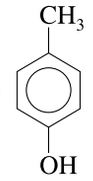
(3) formyl cation ($\overset{\oplus}{C}HO$)

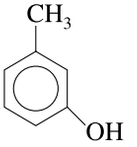
(4) dichloromethyl cation ($\overset{\oplus}{C}HCH_2$)

9. The structure of the compound that gives a tribromo derivative on treatment with bromine water :is: **[AIEEE-2006]**

(1) 

(2) 

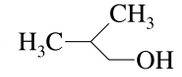
(3) 

(4) 

10. Among the following the one that gives positive iodoform test upon reaction with I_2 NaOH is **[AIEEE-2006]**

(1) $CH_3CH_2CH(OH)CH_2CH_3$

(2) $C_6H_5CH_2CH_2OH$

(3) 

(4) $PhCHOHCH_3$

11. Acid catalysed hydration of alkenes except ethene leads to the formation of **[AIEEE-2006]**

(1) mixture of secondary and tertiary alcohols

(2) mixture of primary and secondary alcohols

(3) secondary or tertiary alcohol

(4) primary alcohol

12. In the following sequence of reactions, **[AIEEE-2007]**

$$CH_3CH_2OH \xrightarrow{P+I_2} A \xrightarrow[ether]{Mg} B \xrightarrow{HCHO} C \xrightarrow{H_2O} D$$

the compound D is

(1) butanol (2) n-butyl alcohol

(3) n-propyl alcohol (4) propanol

13. Phenol, when it first reacts with concentrated sulphuric acid and then with concentrated nitric acid, gives **[AIEEE-2008]**

(1) *o*-nitrophenol (2) *p*-nitrophenol

(3) nitrobenzene (4) 2, 4, 6-trinitrophenol

14. 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]**

(1) HCHO (2) CH_3COCH_3

(3) CH_3COOH (4) CH_3OH

15. The major product obtained on interaction of phenol with sodium hydroxide and carbon dioxide is– **[AIEEE-2009]**

(1) Salicyladehyde (2) Salicyclic acid

(3) Phthalic acid (4) Benzoic acid

16. From amongst the following alcohols the one that would react fastest with conc. HCl and anhydrous $ZnCl_2$, is– **[AIEEE-2010]**

(1) 1-Butanol (2) 2-Butanol

(3) 2-Methylpropan-2-ol (4) 2-Methylpropanol

17. Consider the following reaction **[AIEEE-2011]**

$C_2H_5OH + H_2SO_4 \rightarrow$ Product

Among the following, which one cannot be formed as a product under any conditions?

(1) Ethylene (2) Acetylene

(3) Diethyl ether (4) Ethyl-hydrogen sulphate

18. Thermosetting polymer, Bakelite is formed by the reaction of phenol with **[AIEEE-2011]**

(1) CH_3CHO (2) HCHO

(3) HCOOH (4) CH_3CH_2CHO

19. Reagent used to convert allyl alcohol to acrolein is: **[JEE Main Online-2012]**

(1) MnO_2 (2) $KMnO_4$

(3) OsO_4 (4) H_2O_2

20. An unknown alcohol is treated with the "Lucas reagent" to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts fastest and by what mechanism- **[JEE Main-2013]**

(1) secondary alcohol by S_N2

(2) Tertiary alcohol by S_N2

(3) Secondary alcohol by S_N1

(4) Tertiary alcohol by S_N1

21. Rate of dehydration of alcohols follows the order- **[JEE Main Online-2013]**

(1) $2° > 1° > CH_3OH > 3°$

(2) $3° > 2° > 1° > CH_3OH$

(3) $2° > 3° > 1° > CH_3OH$

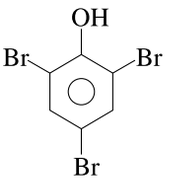
(4) $CH_3OH > 12° > 2° > 3°$

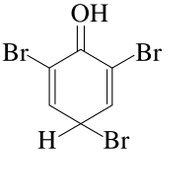
22. An ether (A), $C_5H_{12}O$, when heated with excess of hot concentrated HI produced two alkyl halides which when treated with NaOH yielded compounds (B) and (C). Oxidation of (B) and (C) gave a propanone and an ethanoic acid respectively. The IUPAC name of the ether (A) is- **[JEE Main Online-2013]**

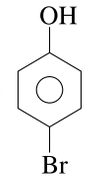
(1) 2-ethoxypropane (2) ethoxypropane

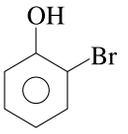
(3) methoxybutane (4) 2-methoxybutane

23. What is the structure of the major product when phenol is treated with bromine water: **[JEE Main Online-2013]**

(1) 

(2) 

(3) 

(4) 

24. Amongst the following alcohols which would react fastest with conc. HCl and $ZnCl_2$?

[JEE Main Online-2013]

(1) Pentanol (2) 2-Methylbutanol

(3) 2-Pentanol (4) 2-Methyl butan-2-ol

25. The reaction of phenol with benzoyl chloride to give phenyl benzoate is known as:

[JEE Main Online-2013]

(1) Claisen reaction

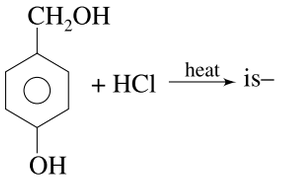
(2) Schotten–Baumann reaction

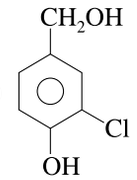
(3) Reimer–Tiemann reaction

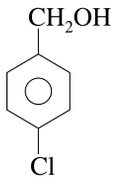
(4) Gatterman–Koch reaction

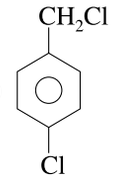
26. The major product in the following reaction

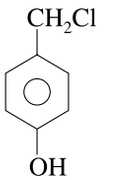
[JEE Main Online-2013]



(1) 

(2) 

(3) 

(4) 

27. Phenol on heating with $CHCl_3$ and NaOH gives salicylaldehyde. The reaction is called

[JEE main Online-2013]

(1) Reimer–Tiemann reaction

(2) Claisen reaction

(3) Cannizzaro reaction

(4) Hell-Volhard-Zelinsky reaction

28. The most suitable reagent of the conversion of $R—CH_2—OH \longrightarrow R—CHO$ is

(1) $KMnO_4$

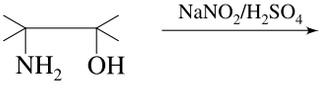
(2) $K_2Cr_2O_7$

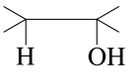
(3) CrO_3

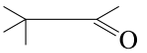
(4) PCC (Pyridinium chlorochromate)

29. The major product of reaction

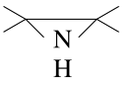
[JEE main Online-2014]



(1) 

(2) 

(3) 

(4) 

30. Allyl phenyl ether can be prepared by heating:

[JEE main Online-2014]

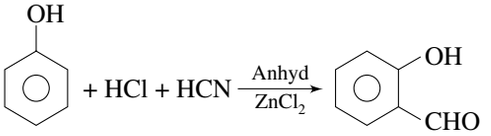
(1) $C_6H_5Br + CH_2=CH–CH_2–ONa$

(2) $CH_2=CH–CH_2–Br + C_6H_5ONa$

(3) $C_6H_5–CH=CH–Br + CH_3–ONa$

(4) $CH_2=CH–Br + C_6H_5–CH_2–ONa$

31. The following reaction **[JEE main Online-2014]**



Is known as:

(1) Perkin reaction

(2) Gattermann–Koch formylation

(3) Kolbe's reaction

(4) Gattermann reaction

32. Which one of the following statements is not correct? **[JEE main Online-2014]**

(1) Alcohols are weaker acids than water

(2) Acid strength of alcohols decrease in the following order

$RCH_2OH > R_2CHOH > R_3COH$

(3) Carbon–oxygen bond length in methanol, CH_3OH is shorter than that of C–O bond length in phenol

(4) The bond angle  in methanol is 108.9°

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

[JEE main Online-2014]

(1) Red, colourless, blue (2) Red, blue, colourless

(3) Colourless, red, blue (4) Red, blue, violet

34. Phthalic acid reacts with resorcinol in the presence of concentrated H_2SO_4 to give: **[JEE main Online-2014]**

(1) Phenolphthalein (2) Alizarin

(3) Coumarin (4) Fluorescein

35. Williamson synthesis of ether is an example of: **[JEE main Online-2014]**

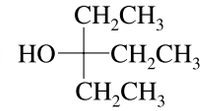
(1) Nucleophilic addition

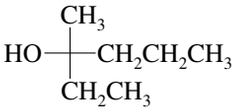
(2) Electrophilic addition

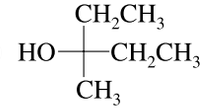
(3) Electrophilic substitution

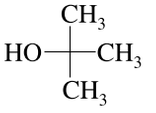
(4) Nucleophilic substitution

36. CH_3MgBr (excess) + Ethyl ester $\rightarrow$ which can be formed as product **[IIT-2003]**

(1) 

(2) 

(3) 

(4) 

37. The best method to prepare cyclohexene from cyclohexanol is by using **[IIT-2005]**

(1) Conc. HCl + $ZnCl_2$ (2) Conc. H_3PO_4

(3) HBr (4) Conc. HCl

38. When phenyl magnesium bromide reacts with tert. butanol, which of the following is formed? **[IIT-2005]**

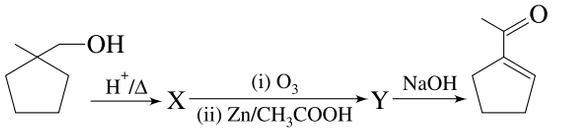
(1) Tert. butyl methyl ether

(2) Benzene

(3) Tert. butyl benzene

(4) Phenol

39. Consider the given reaction, **[IIT-2005]**



Identify X and Y.

40. The increasing order of boiling points of the following mentioned alcohols is **[IIT-2006]**

I. 1, 2-dihydroxy benzene

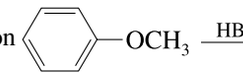
II. 1, 3-dihydroxy benzene

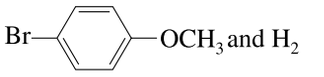
III. 1, 4-dihyroxy benzene

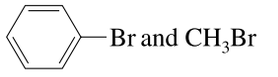
IV. Hydroxy benzene

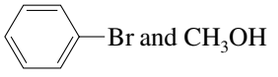
(1) I < II < III < IV (2) I < II < IV < III

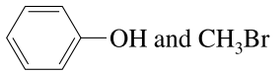
(3) IV < I < II < III (4) IV < II < I < III

41. In the reaction  the products are- **[IIT-2010]**

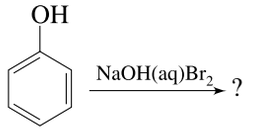
(1) 

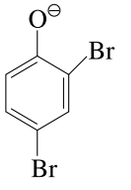
(2) 

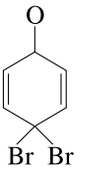
(3) 

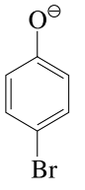
(4) 

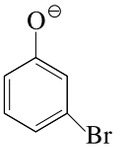
42. In the reaction intermediate (s) is (are) **[IIT-2010]**



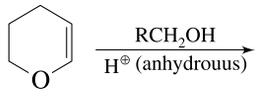
(1) 

(2) 

(3) 

(4) 

43. The major product of the following reaction is **[IIT-2011]**

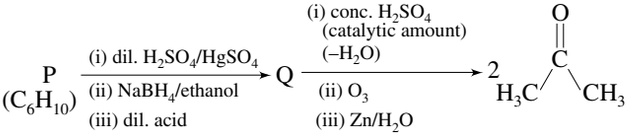


(1) A hemiacetal (2) An acetal

(3) An ether (4) An ester

Passage: (Q.44 to Q.45)

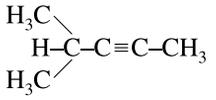
An acyclic hydrocarbon P, having molecular formula C_6H_{10}, gave acetone as the only organic product through the following sequence of reactions, in which Q is an intermediate organic compound, **[IIT-2011]**

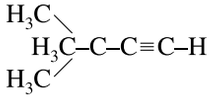


44. The structure of compound P is–

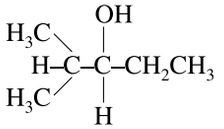
(1) $CH_3CH_2CH_2CH_2–C\equiv C–H$

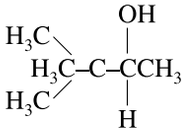
(2) $H_3CH_2C–C\equiv C–CH_2CH_3$

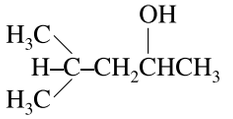
(3) 

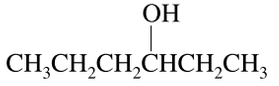
(4) 

45. The structure of compound Q is

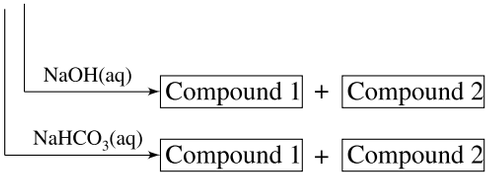
(1) 

(2) 

(3) 

(4) 

46. Identify the binary mixture(s) that can be separated into individual compounds, by differential extraction, as shown in the given scheme. **[IIT-2012]**



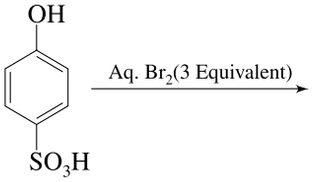
(1) C_6H_5OH and C_6H_5COOH

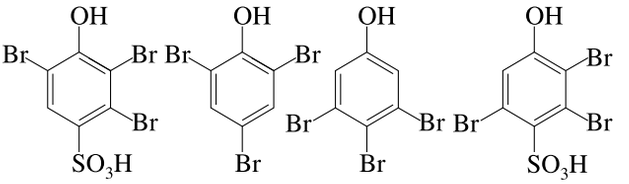
(2) C_6H_5COOH and $C_6H_5CH_2OH$

(3) $C_6H_5CH_2OH$ and C_6H_5OH

(4) $C_6H_5CH_2OH$ and $C_6H_5CH_2COOH$

47. The major product(s) of the following reaction is (are) **[JEE Advance-2013]**



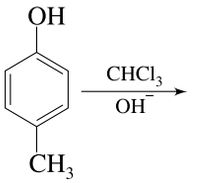


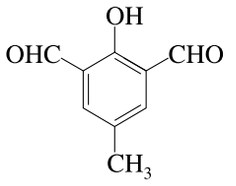
(P) (Q) (R) (S)

(1) P (2) Q

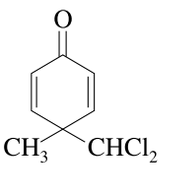
(3) R (4) S

48. In the following reaction, the product(s) formed **[JEE Advance-2013]**

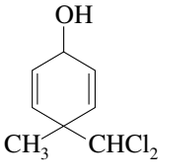




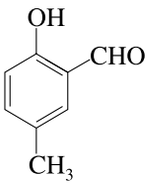
(P)



(Q)



(R)

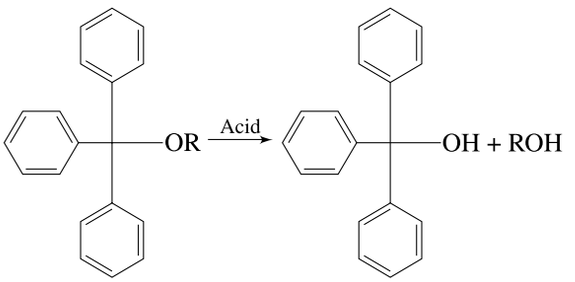


(S)

(1) P (major) (2) Q (minor)

(3) R (minor) (4) S (major)

49. The acidic hydrolysis of ether x shown below is fastest when **[IIT-2014]**



X

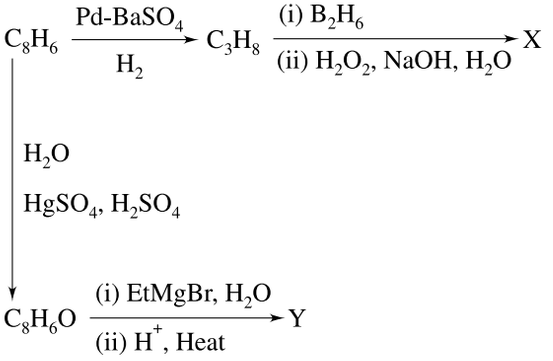
(1) One phenyl group is replaced by a methyl group

(2) One phenyl group is replaced by a *para*-methoxyphenyl group

(3) Two phenyl groups are replaced by two *para*-methoxyphenyl groups

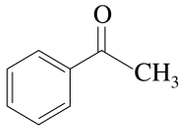
(4) No structural change is made of X

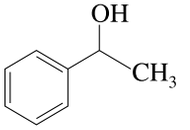
Passage for Q. Nos. (50 and 51)

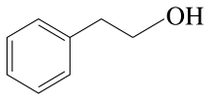


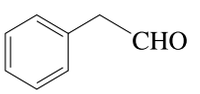
[IIT-2015]

50. Compound X is

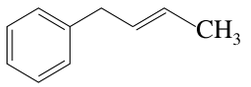
(1) 

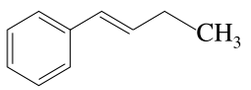
(2) 

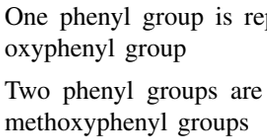
(3) 

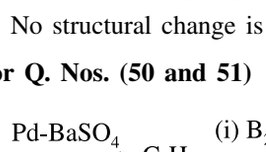
(4) 

51. The major compound Y is

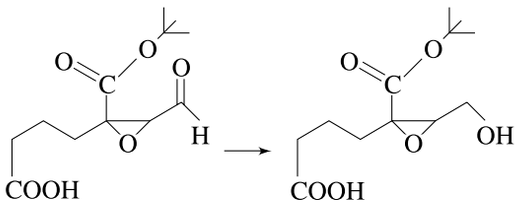
(1) 

(2) 

(3) 

(4) 

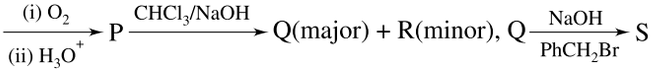
52. Reagent(s) which can be used to bring about the following transformation is (are)



(1) $LiAlH_4$ in $(C_2H_5)_2O$ (2) BH_3 in C_2H_5OH

(3) $NaBH_4$ in C_2H_5OH (4) Raney Ni/H_2 in THF

53. The correct statement(s) about the following reaction sequence is (are) Cummene (C_9H_{12})



(1) R is steam volatile

(2) Q gives dark violet colouration with 1% aqueous $FeCl_3$ solution

(3) S gives yellow precipitate with 2, 4-dinitrophenylhydrazine

(4) S gives dark violet colouration with 1% aqueous $FeCl_3$ solution

ANSWER KEY

EXERCISE # 1

1. (3)	2. (3)	3. (1)	4. (2)	5. (4)
6. (2)	7. (1)	8. (2)	9. (3)	10. (1)
11. (2)	12. (1)	13. (2)	14. (1)	15. (3)
16. (4)	17. (4)	18. (3)	19. (2)	20. (2)
21. (2)	22. (2)	23. (3)	24. (1)	25. (3)
26. (3)	27. (1)	28. (2)	29. (1)	30. (4)
31. (1)	32. (1)	33. (3)	34. (1)	35. (2)
36. (2)	37. (2)	38. (4)	39. (1)	40. (2)

EXERCISE # 2

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

EXERCISE # 3

1. (1,3)	2. (1,2,3)	3. (2,3)	4. (2,4)	5. (1,3)
6. (3,4)	7. (1,3)	8. (1,4)	9. (1,2,3)	10. (2,3)
11. (1,3,4)	12. (1,2)	13. (1,2,3)	14. (1)	15. (1)
16. (*)	17. (*)	18. (*)	19. (*)	20. (*)
21. (*)	22. (*)	23. (*)	24. (1)	25. (*)
26. (*)	27. (*)	28. (*)	29. (*)	30. (*)

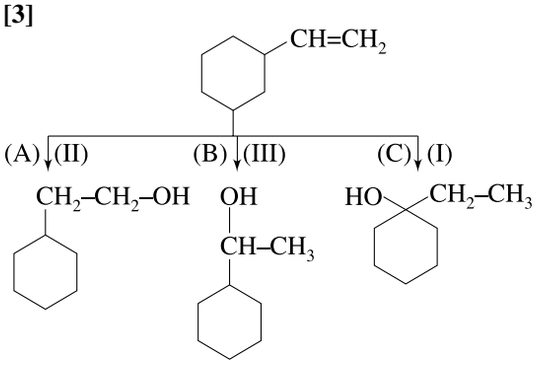
EXERCISE # 4

1. (2)	2. (4)	3. (1)	4. (3)	5. (4)
6. (3)	7. (4)	8. (1)	9. (4)	10. (4)
11. (3)	12. (3)	13. (4)	14. (3)	15. (2)
16. (3)	17. (2)	18. (2)	19. (1)	20. (4)
21. (2)	22. (1)	23. (1)	24. (4)	25. (2)
26. (4)	27. (1)	28. (4)	29. (2)	30. (2)
31. (4)	32. (3)	33. (2)	34. (4)	35. (4)
36. (4)	37. (2)	38. (2)	39. (*)	40. (3)
41. (4)	42. (1,2,3)	43. (2)	44. (4)	45. (2)
46. (2,4)	47. (2)	48. (2,4)	49. (3)	50. (3)
51. (4)	52. (3)	53. (2,3)		

HINT AND SOLUTION

EXERCISE # 1

1. [3]



2. [3]

Fact

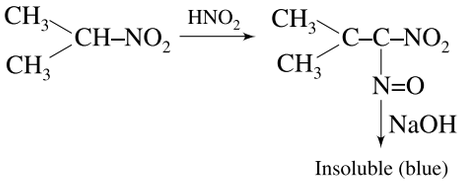
3. [1]

$$C_3H_8O \xrightarrow{[O]} C_3H_6O_2$$

Primary alcohol (X) → carboxylic acid (Y)

4. [2]

Victor Mayer test



Insoluble (blue)

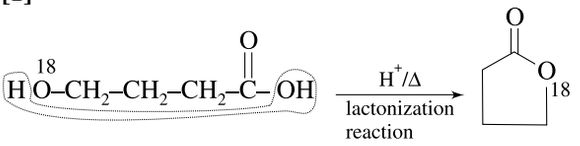
5. [4]

Both enol and 1° alcohol gives negative test with Lucas reagent at room temprature.

6. [2]

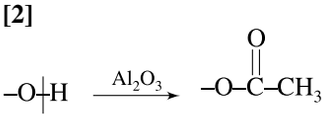
With SeO_2, oxidation at allylic position takes place

7. [1]



Intramolecular esterification

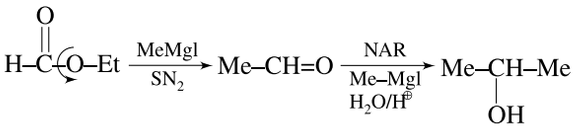
8. [2]



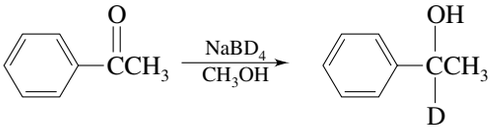
1 OH increase molecular formula → C_2H_2O

$$\text{No of } -OH = \frac{C_8H_8O}{C_2H_2O} = 4$$

9. [3]

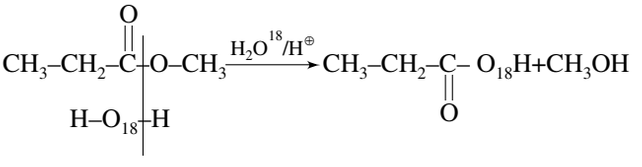


10. [1]



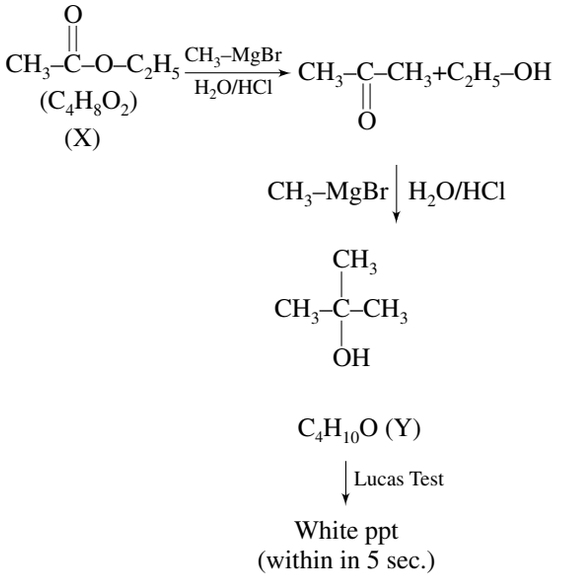
(Nucleophilic addition takes place)

11. [2]



12. [1]

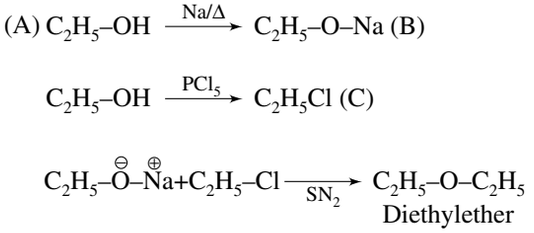
Since Y will give white ppt immediately with Lucas reagent, hence it must be 3° alcohol so that (X) is alkyl alkanoate.



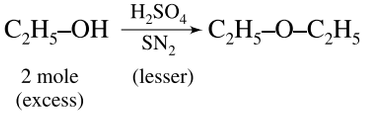
13. [2]

Theory based

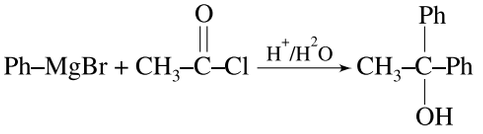
14. [1]



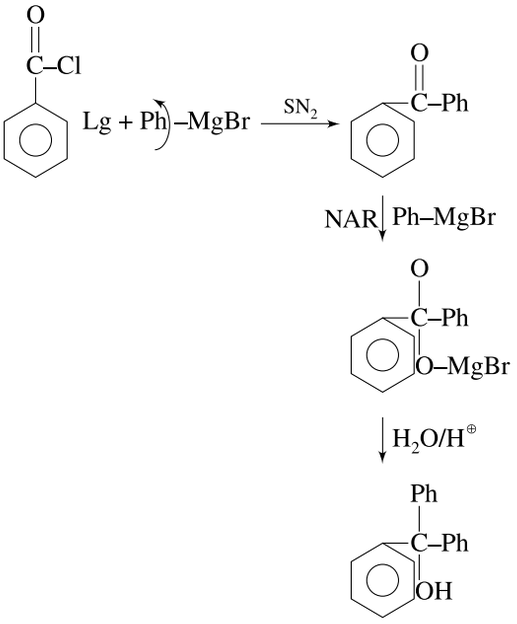
15. [3]



16. [4]



17. [4]



18. [3]

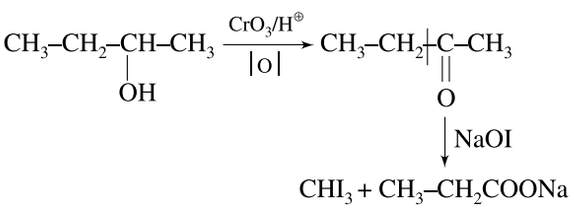
(Refer key concept)

19. [2]

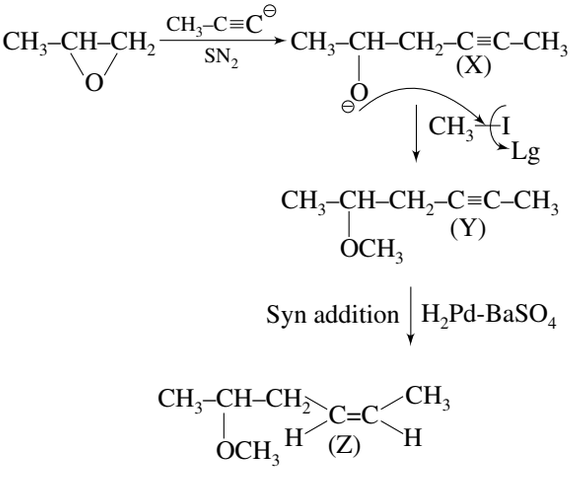
$NaBH_4$ do not reduce ester. It reduces only > C=O in > CH – OH.

20. [2]

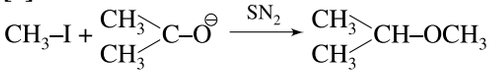
Formation of CHI_3 with NaOI, proves that (B) must be methyl ketone like R–C(=O)–CH_3



21. [2]

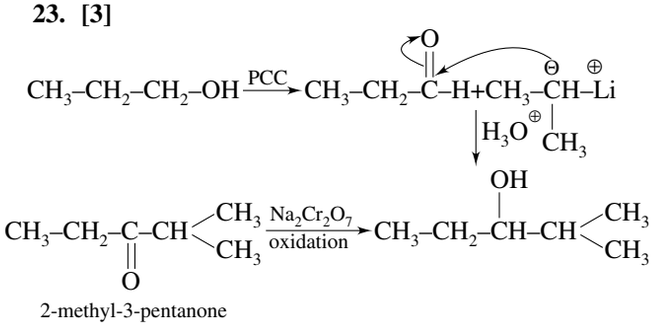


22. [2]



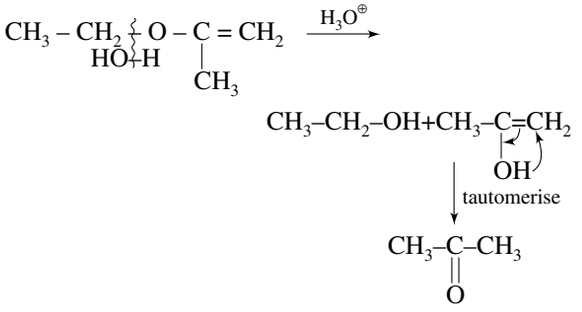
Methyliodide (best for SN_2) — Isopropylmethyl ether

23. [3]

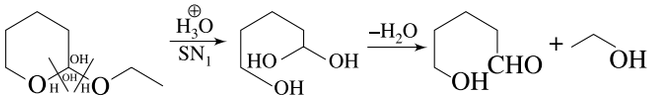


2-methyl-3-pentanone

24. [1]



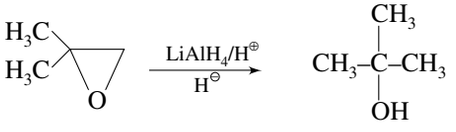
25. [3]



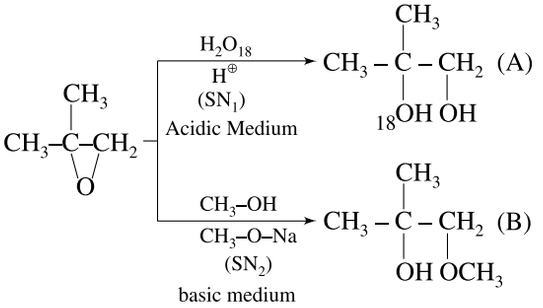
26. [3]

$LiAlH_4 \rightarrow Li^+ + \overset{\oplus}{Al}H_4 \rightarrow AlH_3 + H^{\ominus}$

In alkaline medium nucleophilic attack from less steric side takes plance.



27. [1]



$\rightarrow$ In acidic medium, SN_1 reaction is favoured, i.e., nucleophile approach towards most sterically hindered site

$\rightarrow$ In alkaline media, SN_2 reaction is favoured, i.e., Nucleophile approach towards least sterically hindered site

28. [2]

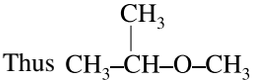
$C_4H_{10}O \Rightarrow C_nH_{2n+2}O$ (alcohol/ether)

The given reaction indicates that

(i) no alcohol, i.e., only ether

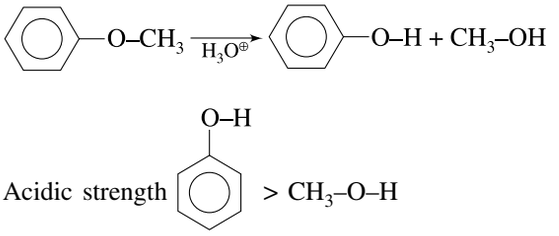
(ii) type of H = 3

(iii) no alcohol

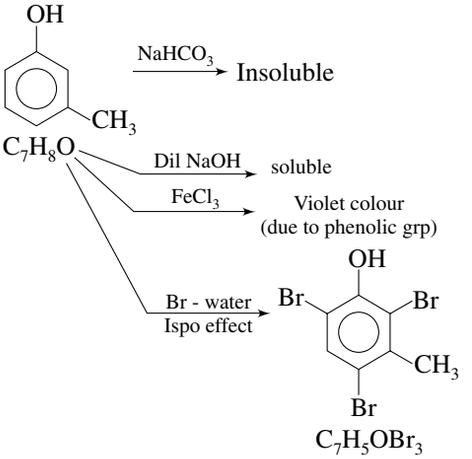
Thus 

(Type of H = 3)

29. [1]



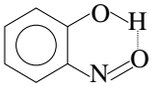
30. [4]



31. [1]

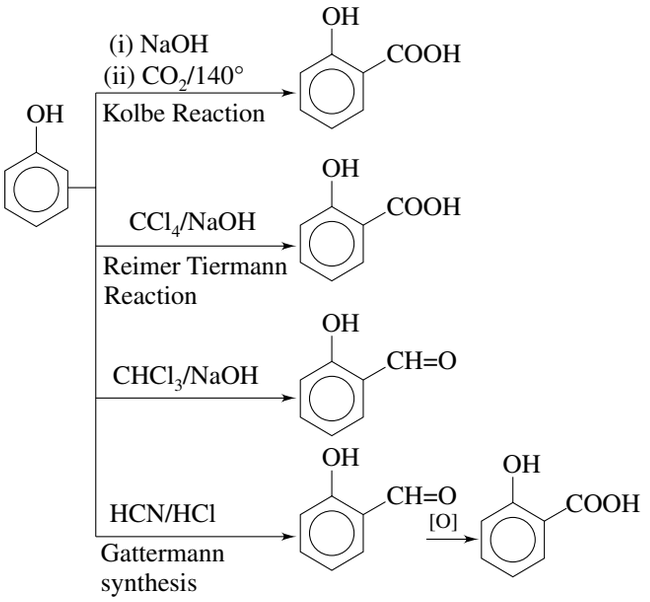
Substances containing phenolic group give purple colour with $FeCl_3$

32. [1]

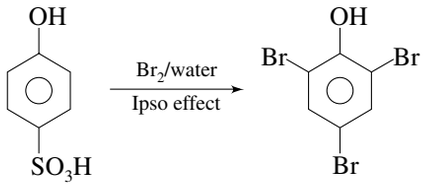


Intramolecular H-bond boiling point $\downarrow$ volatile nature

33. [3]



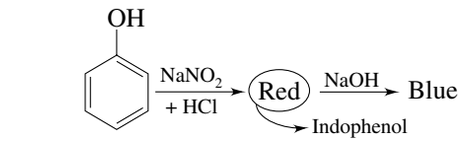
34. [1]

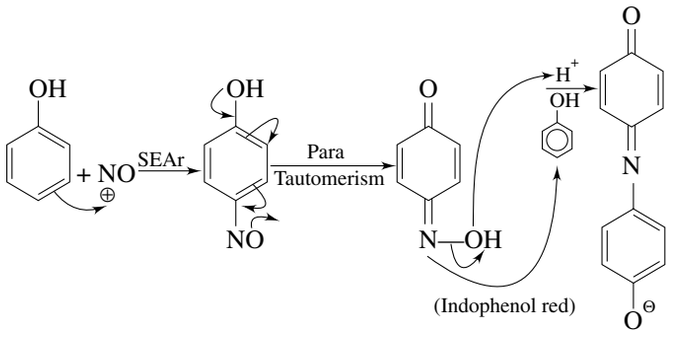


2, 4, 6-tribromophenol

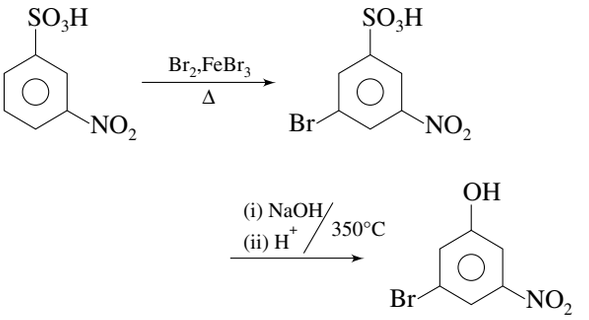
Ipso substitution means replacement of any functional group (good leaving group) which already exist in benzene.

35. [2]





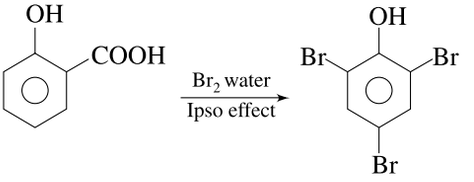
36. [2]



37. [1]

Rate of Ar–SN_2 reaction ∝ (EWG) De-activating power

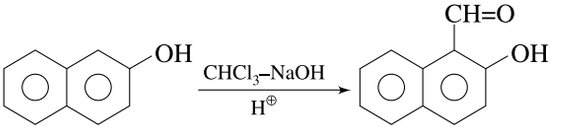
38. [4]



39. [1]

Elb's persulphate oxidation reaction

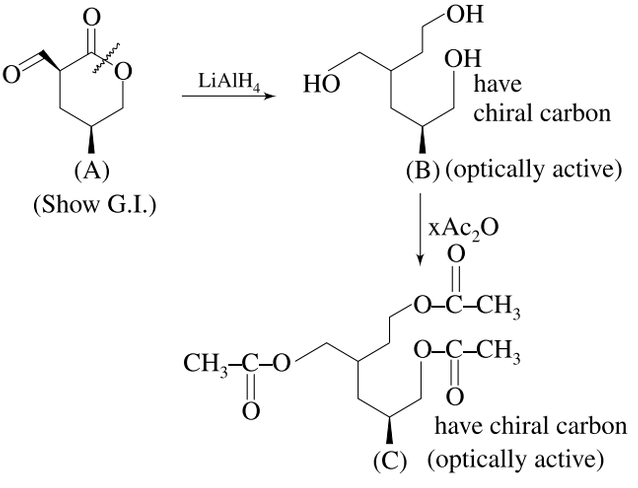
40. [2]



Reimer-Tieman Reaction

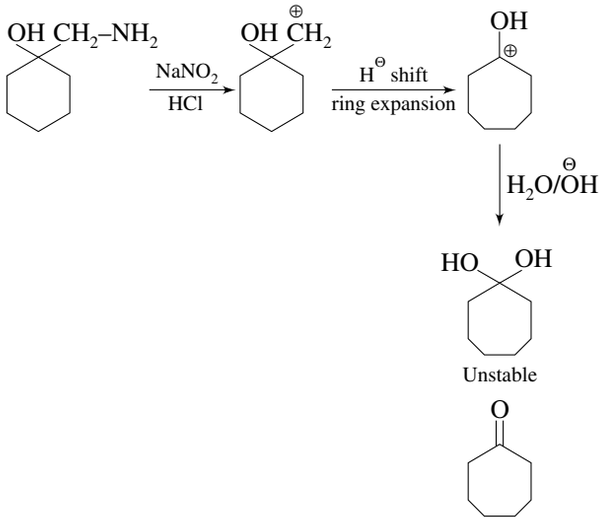
EXERCISE # 2

1. [2]

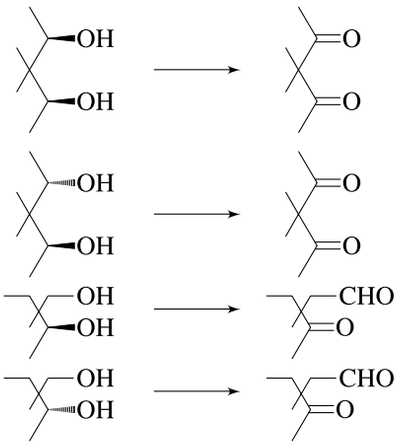


→ x = 3(because 3 OH group present)

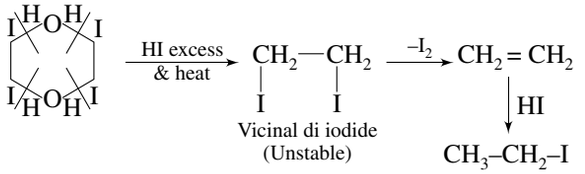
2. [4]



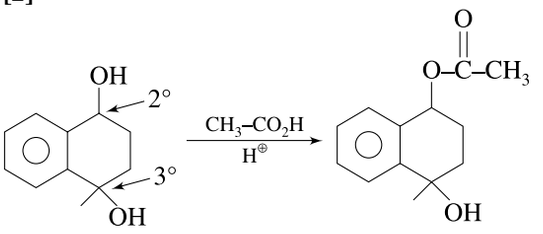
3. [2]



4. [1]

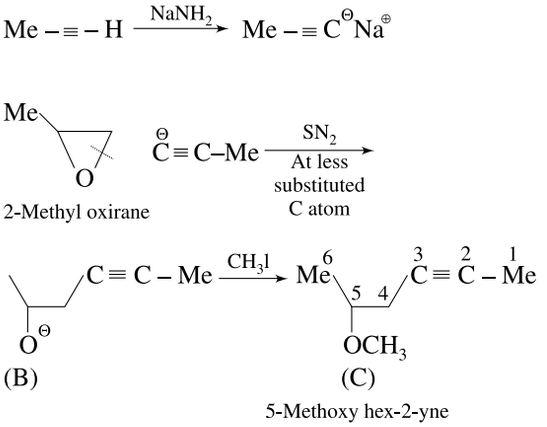


5. [2]

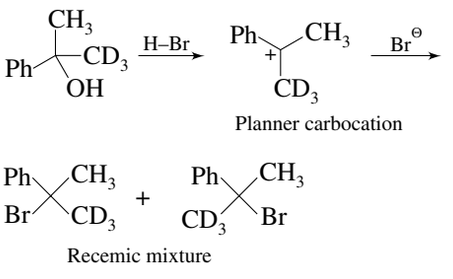


Rate of esterification $\propto \frac{1}{\text{steric hindrance}}$

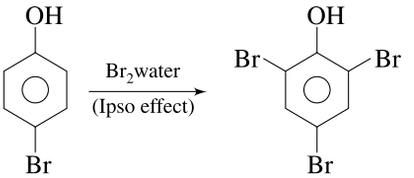
6. [3]



7. [3]



8. [1]

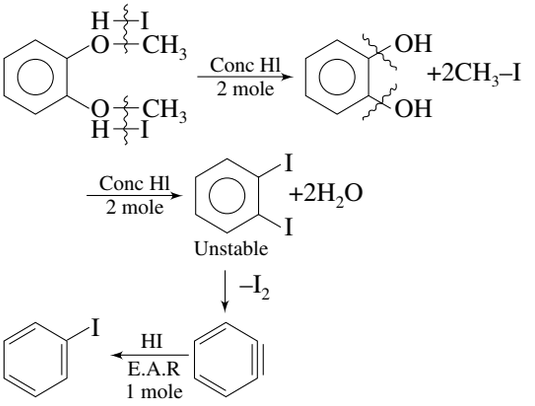


9. [1]

$\rightarrow$ Oxidation at allylic position achieved by MnO_2

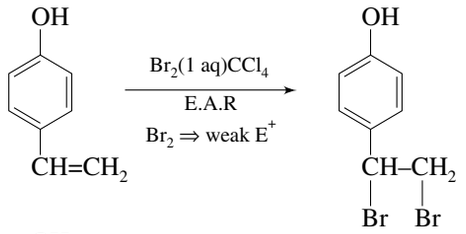
$\rightarrow$ Oxidation of ordinary alcohol achieved by CrO_3

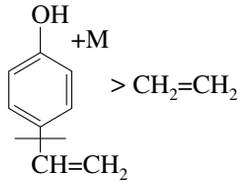
10. [3]



Total mole HI (consumed) = 5

11. [2]

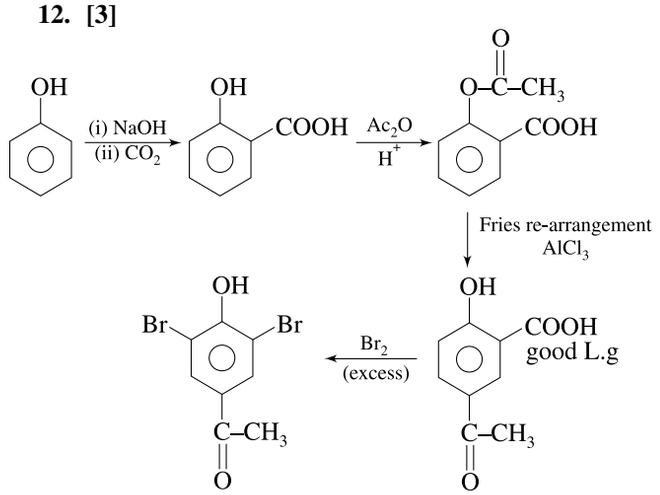




Due of +M and –I effect of –OH, e-density of C = C increases at para position.

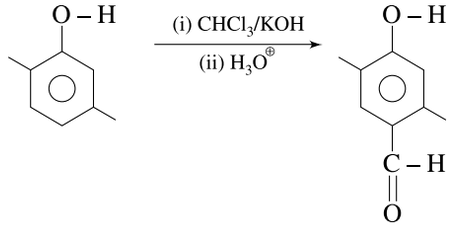
Hence (x) more reactive than ethene.

12. [3]

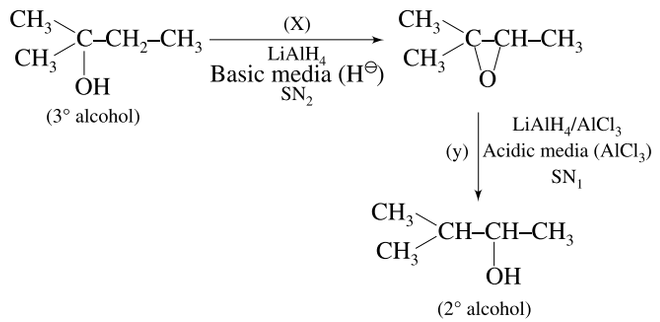


13. [3]

This is Riemer–Tiemann reaction



14. [3]



15. [1]

$NaBH_4$ is weak reducing agent so that only carbonyl group will be reduced.

16. [4]

Test	**x**	**y**
Br_2	Unsaturated	Saturated
Na Metal	alcohol	ether
Chromic acid	oxidation	no oxidation
Lucas reagent	1°alcohol	ether

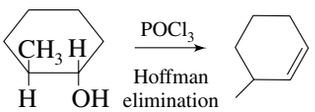
with the above reactions possible structure of

X $\Rightarrow$ Unsaturated primary alcohol &

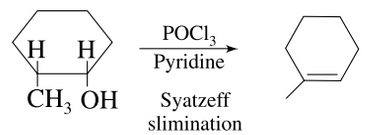
Y $\Rightarrow$ Saturated ether

17. [3]

Reaction I:

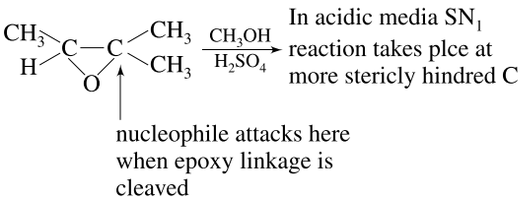


Reaction II:

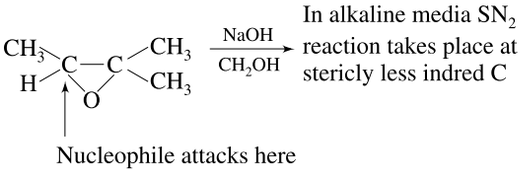


18. [4]

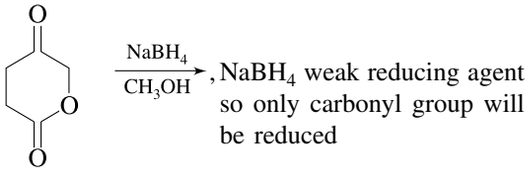
(A)



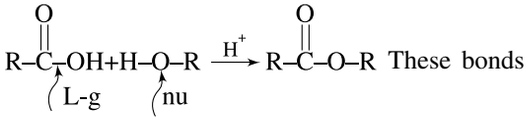
(B)



(C)



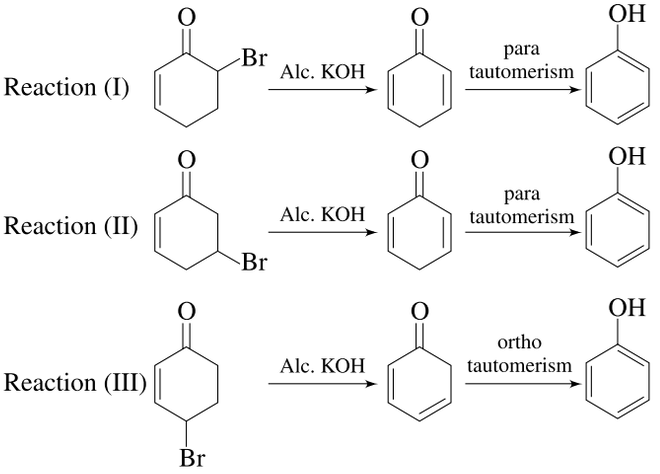
(D)



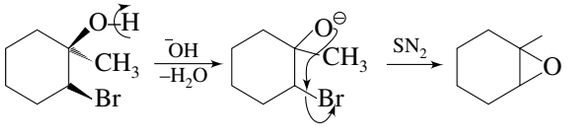
are affected in esterification

Thus, all four statements are correct

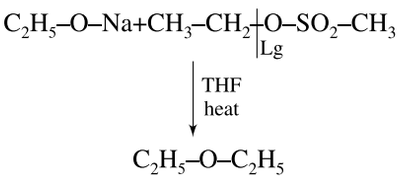
19. [4]



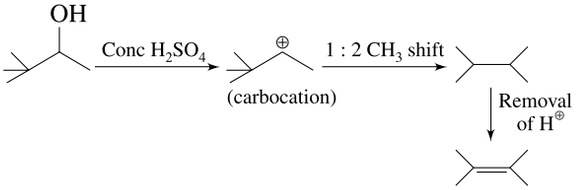
20. [3]



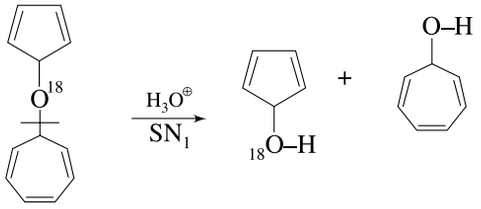
21. [2]



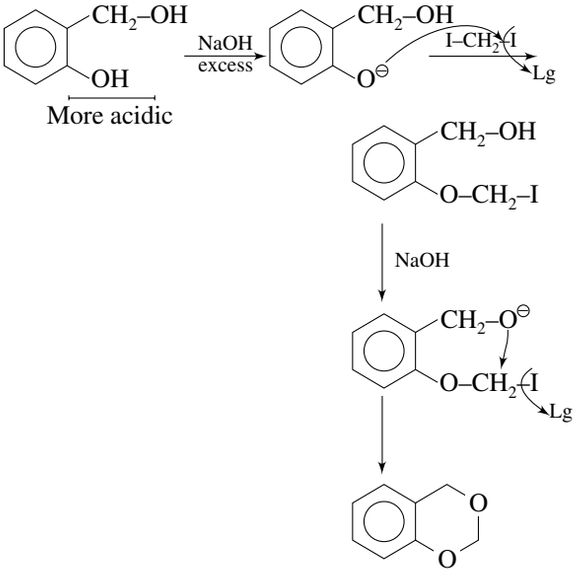
22. [1]



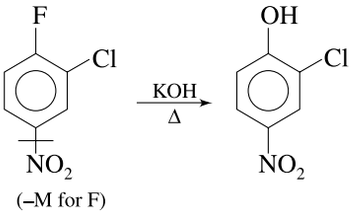
23. [2]



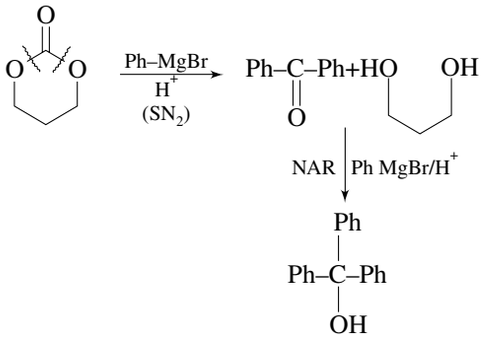
24. [4]



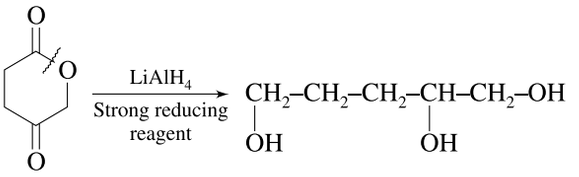
25. [1]



26. [2]

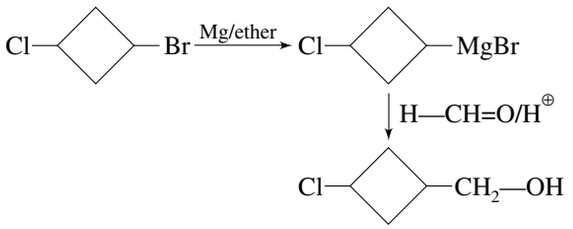


27. [2]

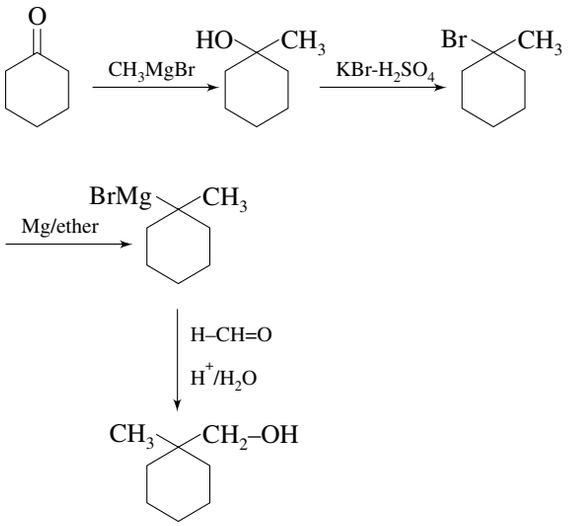


28. [2]

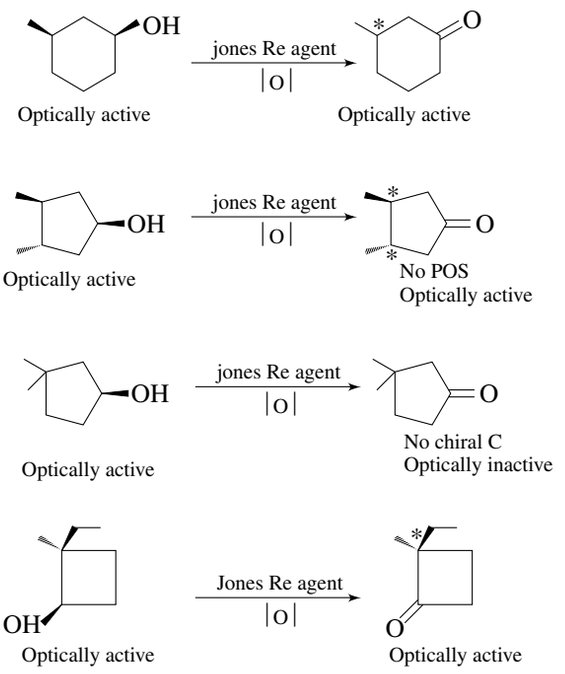
→ R Br more reactive than R Cl



29. [2]



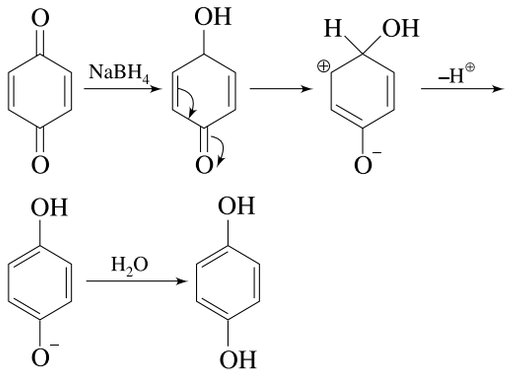
30. [3]



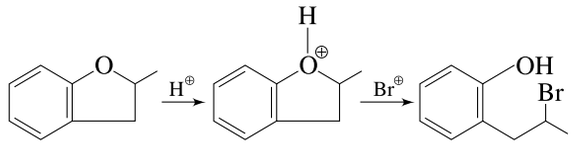
31. [2]

Dihydric alcohols are always more soluble in water than monohydric alcohol. Between (I) and (II), (I) is more soluble as it forms intermolecular H-bonds with water while (II) forms intramolecular H-bonds which decreases its ability to form intermolecular H-bonds with water.

32. [2]

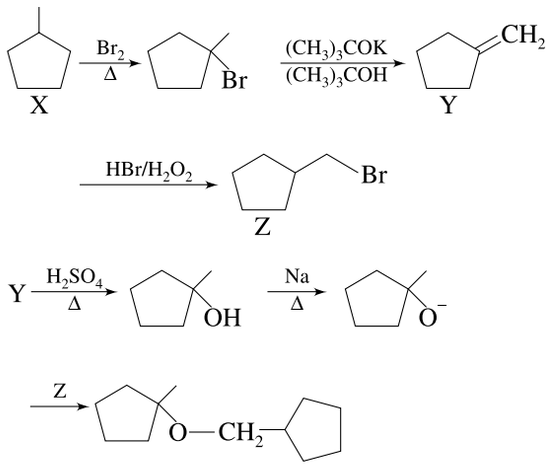


33. [4]

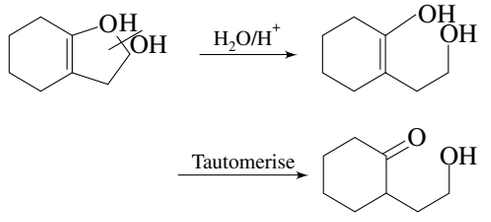


Phenolic —OH does not undergo further substitution.

34. [2]



35. [2]



EXERCISE # 3

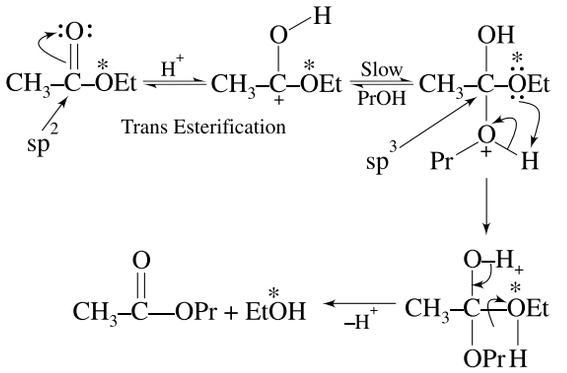
1. [1,3]

$C_2H_5–Br \xrightarrow{C_2H_5ONa} C_2H_5–O–C_2H_5$

$C_2H_5–Br \xrightarrow{\text{dry } Ag_2O} C_2H_5–O–C_2H_5–+2AgBr$

2 Mole

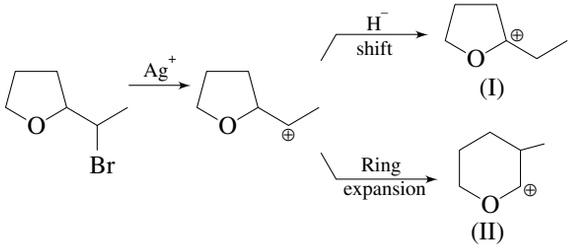
2. [1,2,3]



Trans Esterification follow Le-chaterlier principle in which for forward reaction PrOH is taken in excess and for backward reaction EtOH is taken in excess.

In the slow step formation of tetrahedral intermediate it means it having vanderwall repulsion.

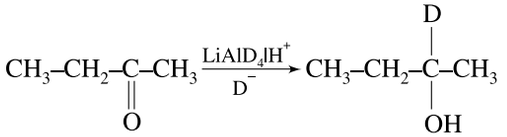
3. [2,3]



(I) and (II) undergo nucleophilic attack by H_2O giving the desired products.

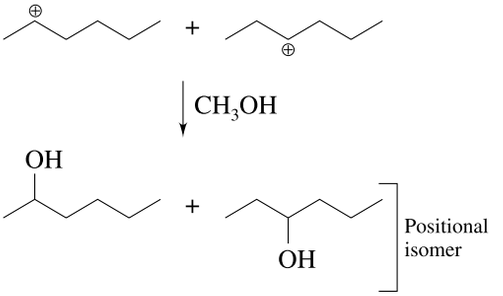
4. [2,4]

Deutride (D^-) addition at planar carbonyl carbon occur from both side of plane with equal probability giving racemic mixture of alcohols, Also, deuterium is attached to carbonyl carbon atom only.

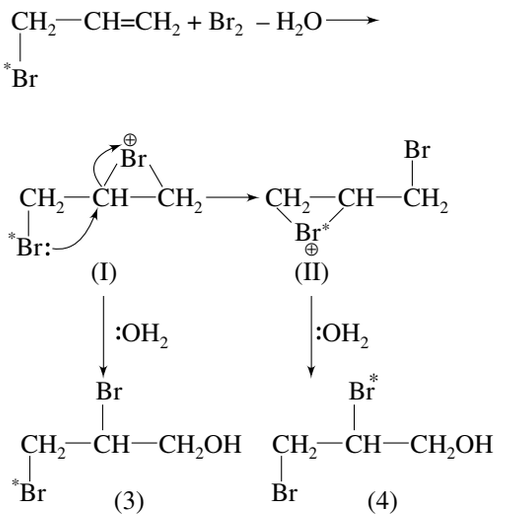


5. [1,3]

Both *cis* and *trans* 2-hexene forms the same carbocation, hence react at same rate.



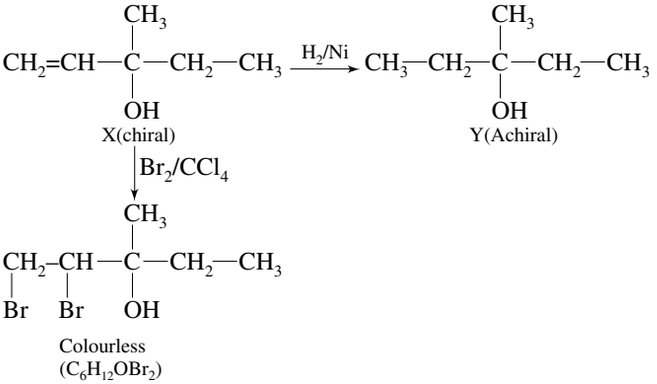
6. [3, 4]



7. [1, 3]

Option (1) and (3) have electron withdrawing groups, destabilises carbocation, do not form turbidity with Lucas reagent at room temperature like primary alcohols. Option (2) and option (4) have electron donating groups, stabilise benzylic carbocation, form immediate turbidity with Lucas reagent like 2° and 3° alcohols.

8. [1, 4]



X neither oxidised by chromic acid nor gives iodoform.

9. [1, 2, 3]

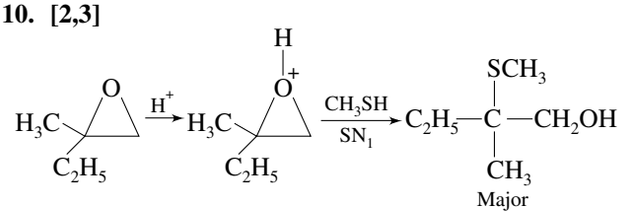
(1) Reaction does not involve breaking of bonds to chiral carbon, hence retention of configuration.

(2) With TsCl, —OTs is formed with retention of configuration. Subsequent reaction with CH_3O-Na involves S_N2 reaction, hence inversion of configuration takes place.

(3) With conc. H_2SO_4, alkene is formed. Alkene in the next step reacts via carbocation intermediate, hence racemic product is obtained.

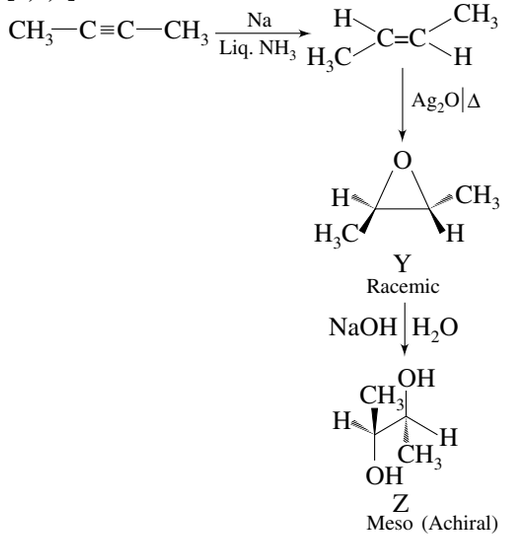
(4) Racemic mixture would be obtained.

10. [2,3]

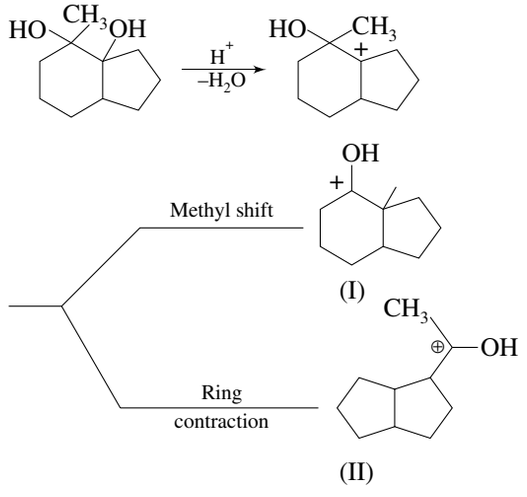


In acidic medium, SN_1 reaction favourable

11. [1,3,4]

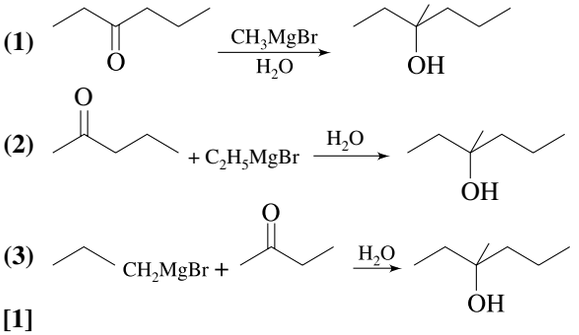


12. [1,2]



(I) on deprotonation gives (1) while (II) on deprotonation (2)

13. [1,2,3]



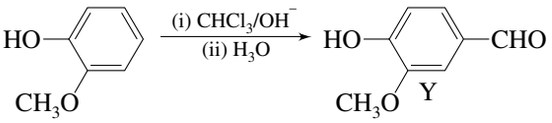
14. [1]

Theory based

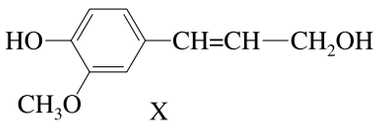
15. [1]

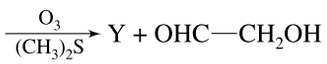
Acid catalysed dehydration of alcohols proceeds via carbocation intermediates. Hence, greater the stability of carbocation, greater is the reactivity of corresponding alcohols.

16. [4]

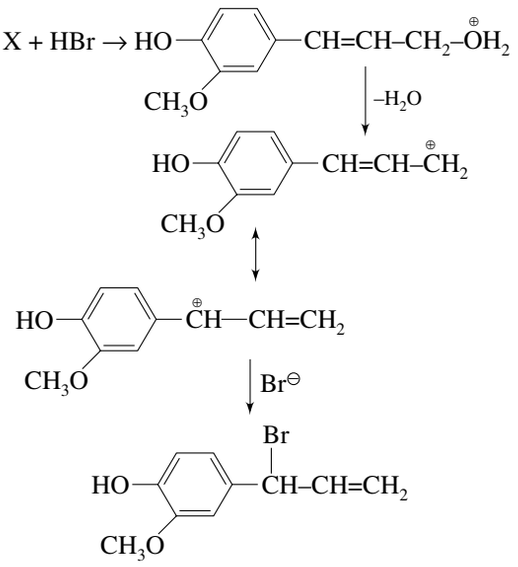


Also, Y is an ozonolysis product of X.

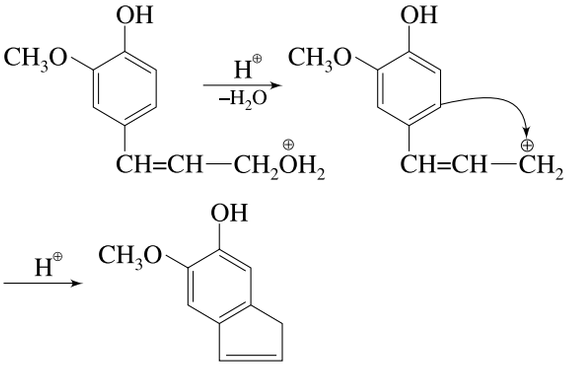




17. [3]



18. [1]



19. [2]

a → q (Clemmenson reduction)

b → s (NAR)

c → p (reduction by $LiAlH_4$)

d → r (specific reduction of ester)

20. [2]

Theory based

21. [3]

(A) Vicinal diol cleaved by HIO_4

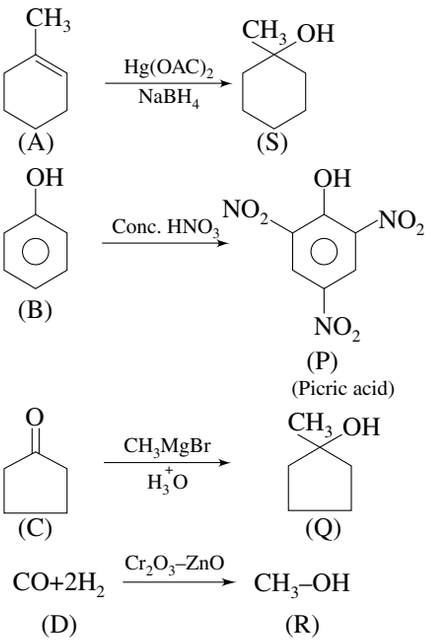
(B) Benzyl alcohol is neutral towards litmus paper

(C) Lucas test achieved via SN1,

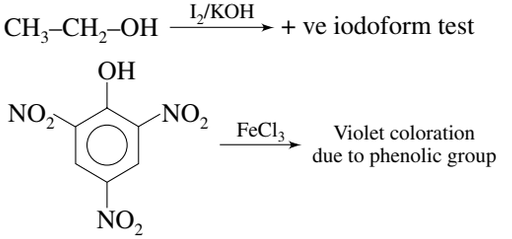
reactivity of SN1 ∝ stability of $-\overset{|}{\underset{|}{C^+}}$

(D) Only $R–\underset{\underset{OH}{|}}{CH}–CH_3$ type gives positive iodoform test

22. [2]

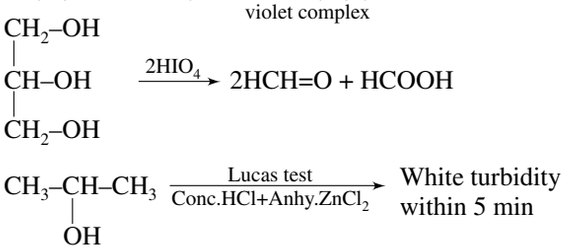


23. [1]



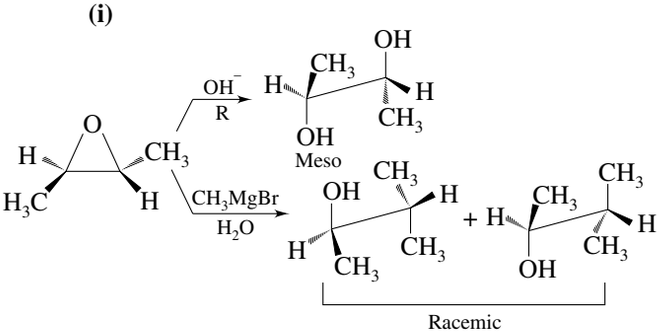
Phenol gives a violet-coloured water soluble complex with ferric chloride. The complex formed is a coordination compound in which iron is hexavalent.

$$6C_6H_5OH + FeCl_3 \rightarrow \underset{\text{violet complex}}{[Fe(OC_6H_5)_6]^{3-}} + 3H^+ + 3HCl$$

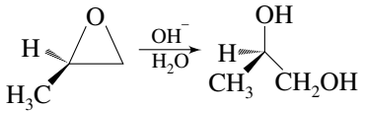


24. [1]

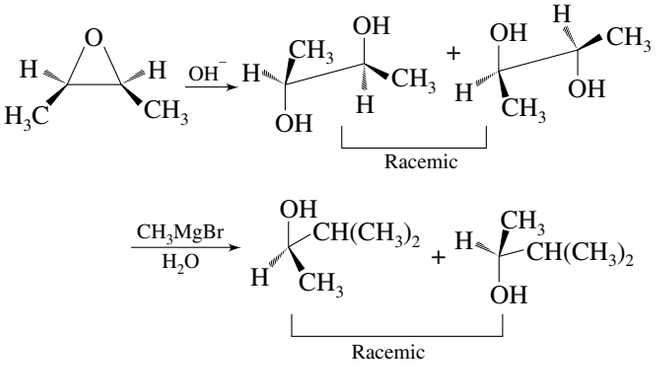
(i)



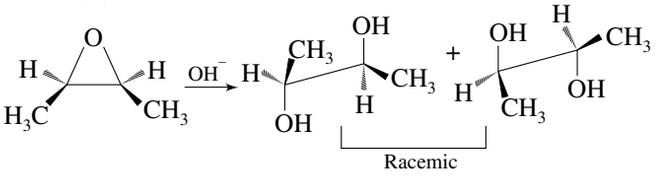
(ii)



(iii)

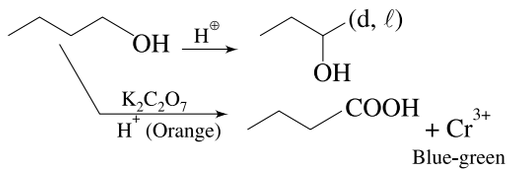


(iv)

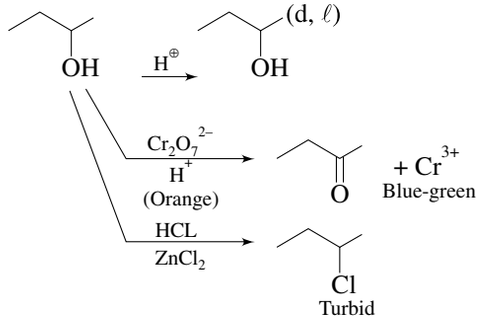


25. [1]

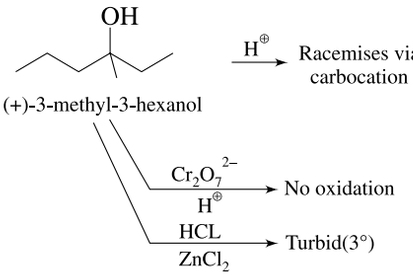
(i)



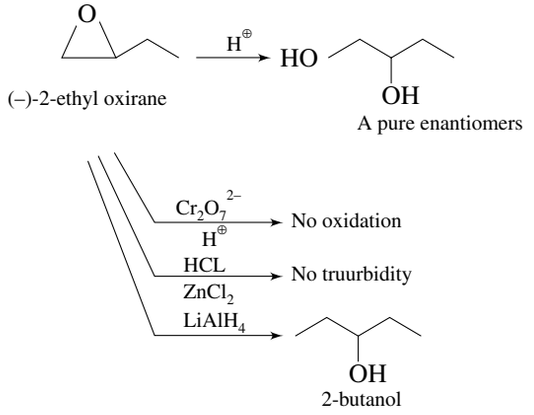
(ii)



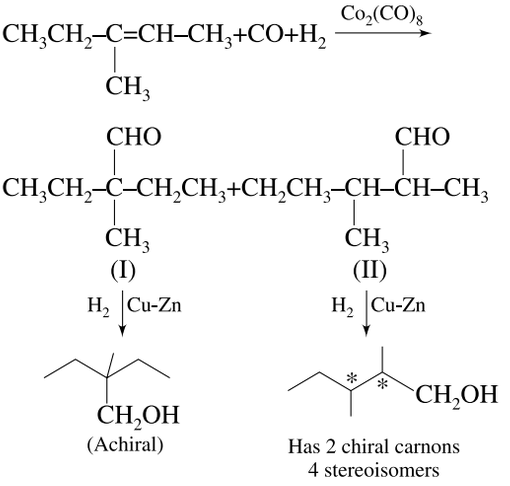
(iii)



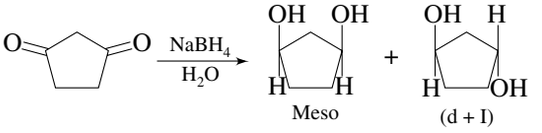
(iv)



26. [5]

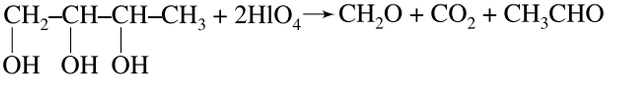


27. [3]



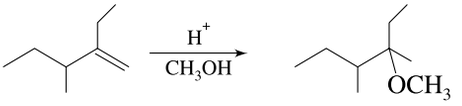
28. [4]

X satisfying the given criteria is



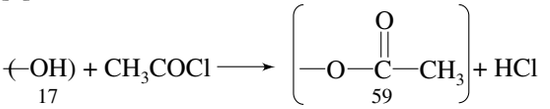
Since, X has two chiral carbon so that four optically active isomers exist.

29. [4]



Has two chiral carbons, here total four stereoisomers

30. [6]



Mass gain due to incorporation of one acetyl group = 59 – 17 = 42

Net mass gain due to acetylation = 518 – 266 = 252

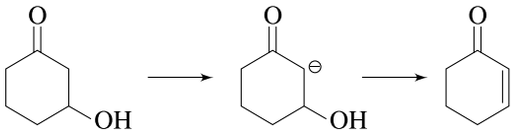
Hence, six hydroxyl groups (6 × 42 = 252) were present.

EXERCISE # 4

1. [2]

In Presence of > C = O group dehydration takes places according to E_{1CB} reaction

Rate of $E_{1CB} \propto$ stability of carbanion



Resonance stable carboanion

2. [4]

Alcohol has polar H which makes intermolecular H-bonding possible. Ether is non-polar, hence has no H-bonding. Lack of H-bonding in ether makes it more volatile than alcohol.

3. [1]

Protonation of —OH is first step. It involves conversion of poor leaving group (—OH) into good leaving group ($—\overset{+}{O}H_2$).

4. [3]

Rate of dehydration $\propto$ stability of carbocation

5. [4]

Gas equation

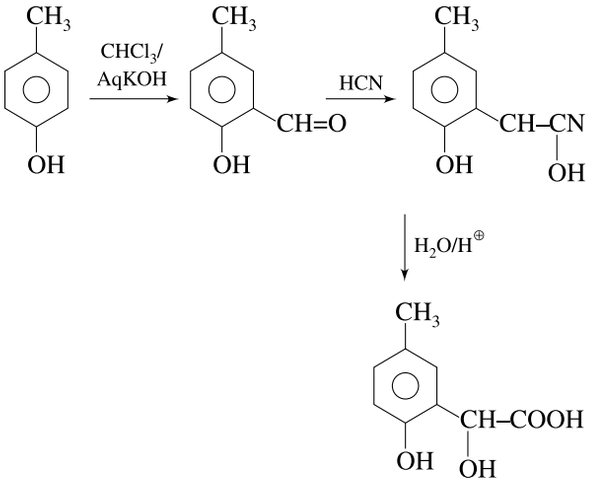
$PV = nRT$

$P = \frac{w}{mv} RT$

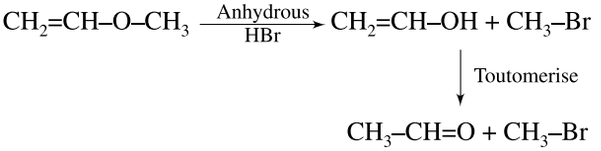
$P = \frac{\rho}{m} RT$

$\because P \propto \rho$

6. [3]



7. [4]

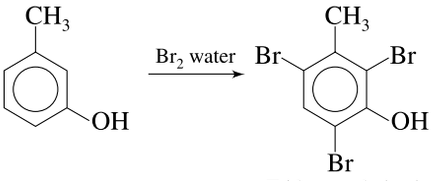


8. [1]

$CHCl_3 + KOH \rightarrow \ddot{C}Cl_2 + KCl + H2O$

Dichlorocarbene

9. [4]

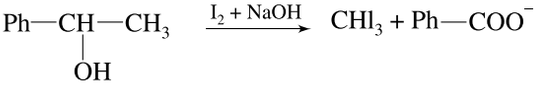


Tri bromo derivative

10. [4]

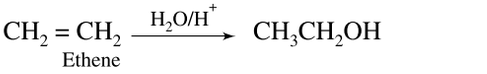
For positive iodoform test, alcohol molecule must have $CH_3—\underset{\underset{OH}{|}}{CH}—$ group

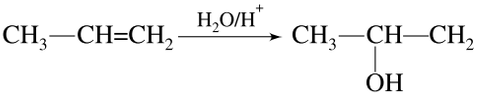
Thus, iodoform test is given by only (4) $Ph—\underset{\underset{OH}{|}}{CH}—CH_3$ while others will not give this test.



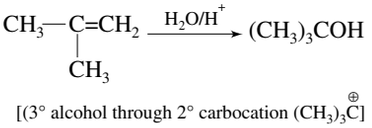
11. [3]

Hydration of ethane gives 1° alcohol (ethanol) while all other alkenes give either 2° or 3° alcohols.

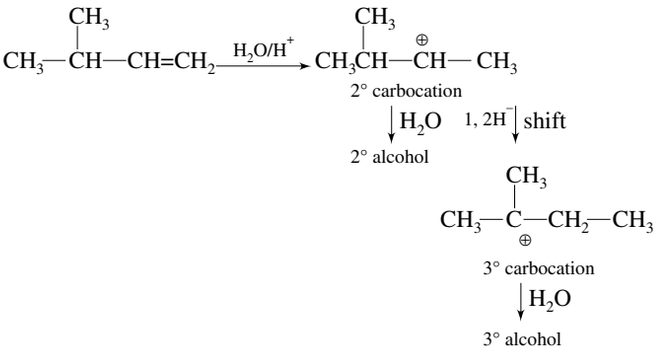




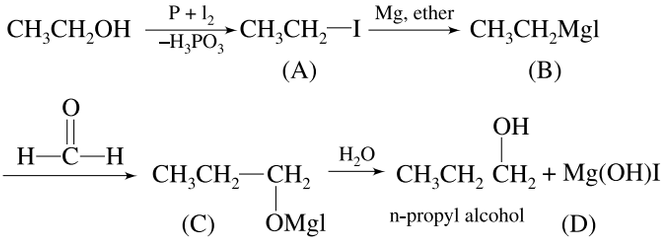
[(2° alcohol through 2° carbocation $CH_3\overset{\oplus}{C}HCH_3$)]



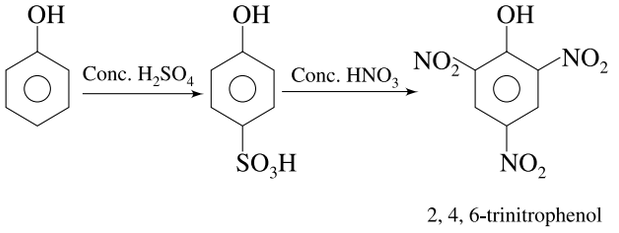
[(3° alcohol through 2° carbocation $(CH_3)_3\overset{\oplus}{C}$]



12. [3]

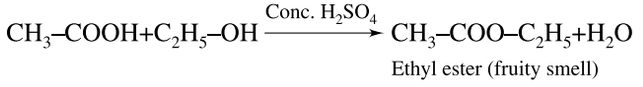


13. [4]



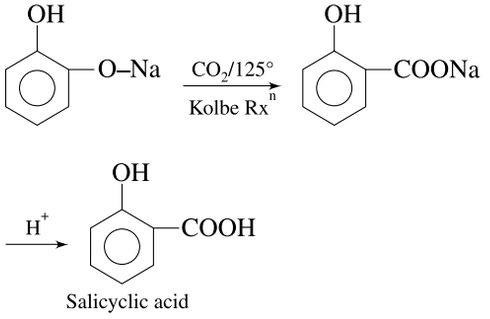
2, 4, 6-trinitrophenol

14. [3]



Ethyl ester (fruity smell)

15. [2]

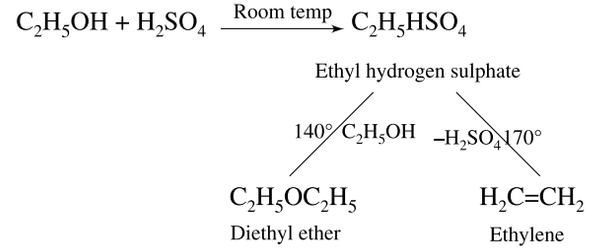


Salicyclic acid

16. [3]

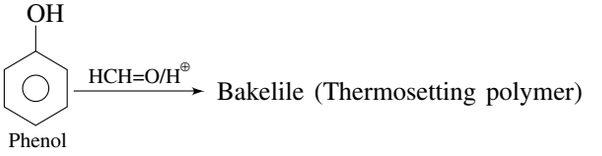
The reaction of alcohol with conc. HCl and anhydrous $ZnCl_2$ follows S_N1 pathway, so greater the stability of carbocation formed faster sis the reaction 2-methylpropan-2-ol gives 3° carbocation. Hence, it reacts rapidly with conc. HCl and anhydrous $ZnCl_2$ (Lucas reagent).

17. [2]



Option (1), (3) and (4) may be formed but option (2) is never formed.

18. [2]

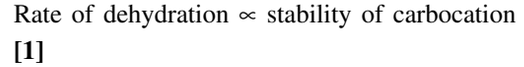


Phenol

Bakelile (Thermosetting polymer)

19. [1]

By the use of MnO_2 oxidation of only allylic alcohol takes place.



20. [4]

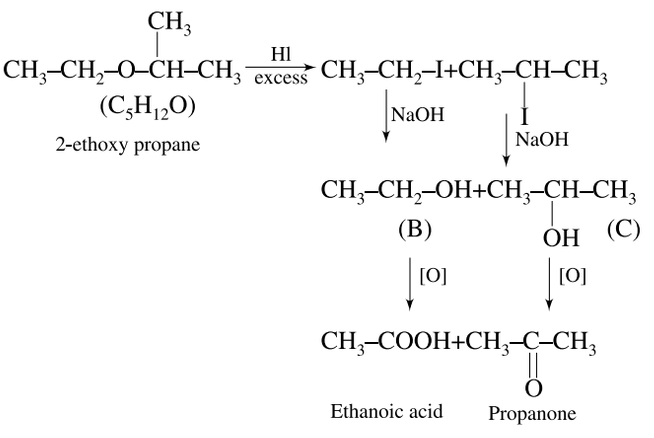
The reaction of alcohol with Lucas reagent is mostly S_N1 reaction and the rate of reaction is directly proportional to the stability of carbocation formed in the reaction.

Since, 3° R—OH forms 3° carbocation (most stable) hence, it will react fastest by S_N1 reaction.

21. [2]

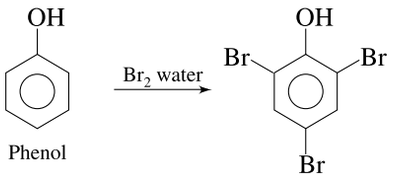
Rate of dehydration $\propto$ stability of carbocation

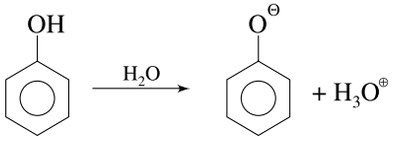
22. [1]



Ethanoic acid Propanone

23. [1]



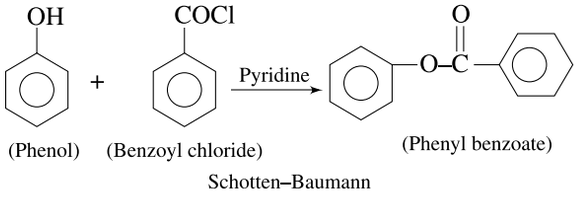


So that Ar-SE reaction takes places at all *o*/*p* position.

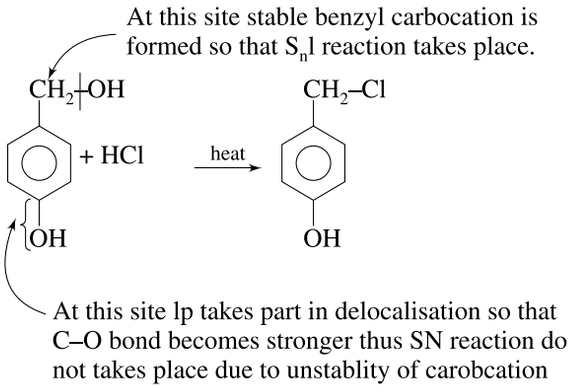
24. [4]

The reaction of alcohol with conc. HCl and anhydrous $ZnCl_2$ follows S_N1 pathway, so greater the stability of carbocation formed faster sis the reaction 2-methyl butan-2-ol gives 3° carbocation. Hence, it reacts rapidly with conc. HCl and anhydrous $ZnCl_2$ (Lucas reagent).

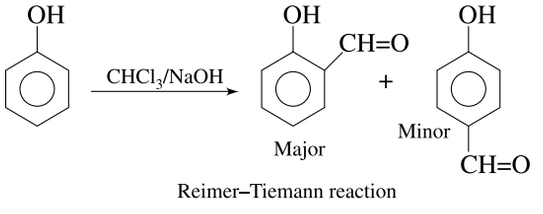
25. [2]



26. [4]



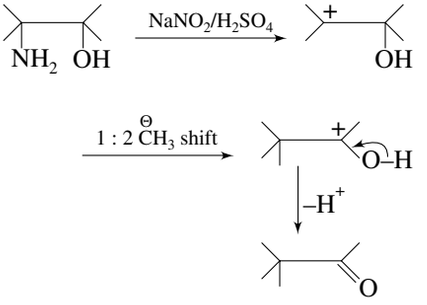
27. [1]



28. [4]

Mild oxidising agents like PCC (Pyridinium chlorochromate are particularly used for the conversion of $R—CH_2OH \longrightarrow R—CHO$

29. [2]



30. [2]

$CH_2=CH–CH_2–Br + C_6H_5ONa \longrightarrow$

$CH_2=CH–CH_2–\ O–C_6H_5$

Allyl bromide gives resonating stable allyl carbocation so it easily gives SN reaction.

31. [4]

Given reaction is known as Gattermann reaction.

32. [3]

Acidic strength $\propto -I \propto \dfrac{1}{+I}$

- $\underset{+I}{R}–OH < H–OH$ So option (1) is correct
- +I Power ($R_3–C– > R_2–CH– > R–CH_2–$) So option (2) is correct.
- Bond length of single bond $\propto \dfrac{1}{\text{Resonance}}$

  C–O bond of phenol involve in resonance bond length decreases.

  So that C–O ($CH_3–OH$) > C–O(Ph–OH) hence option (3) is incorrect.
- Bond angle of sp^3 hybridised atom ≈ 109°.

33. [2]

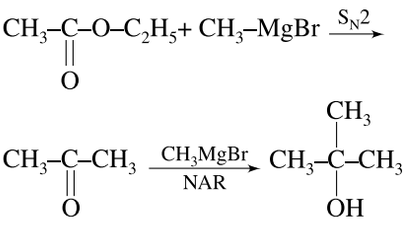
34. [4]

35. [4]

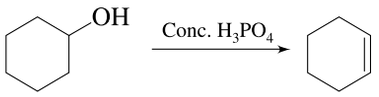
$R–X + R'–O^\ominus \xrightarrow{S_N2} R–O–R'$

Nucleophilic substitution

36. [4]



37. [2]



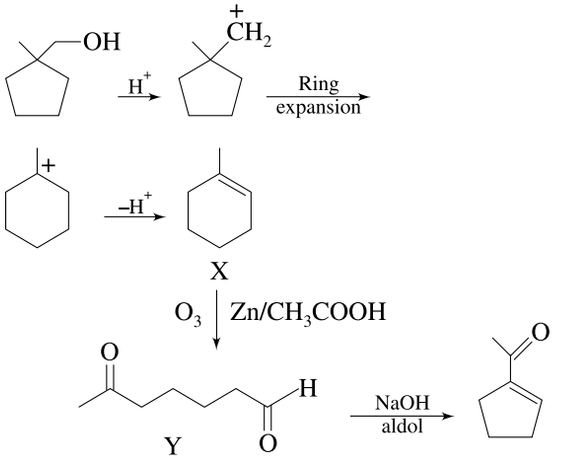
Concentrated H_3PO_4 solution does not involve any substitution product while with others, substitution product are also formed

38. [2]

$$C_6H_5MgBr + (CH_3)_3COH \longrightarrow C_6H_6 + Mg\,[(CH_3)_3CO]Br$$

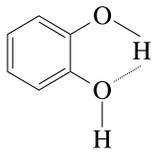
(Benzene)

39.



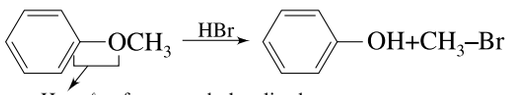
40. [3]

All dihydroxy benzene will have higher boiling points than monohydroxy benzene Also, among dihydroxy benzenes, 1, 2-di-hydroxy benzene has lowest boiling point due to intramolecular H-bonding.



Intramolecular H-bonding in

41. [4]



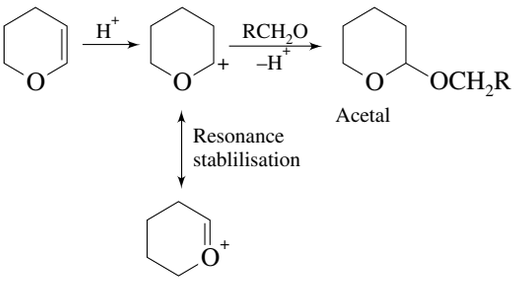
Here ℓp of oxygen de-localised so S_N2 reaction do not takes place

42. [1,2,3]

Since OH group is activating group so that negative charge is developed at *ortho* and para position during resonance.

Hence (1), (2) and (3) are the intermediate obtained during mechanism.

43. [2]

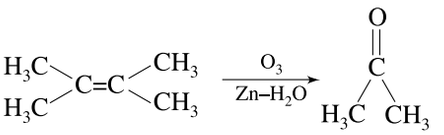


44. [4]

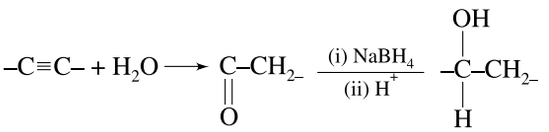
45. [2]

(44 to 45)

The final ozonolysis product indicates that the alkene before ozonolysis is

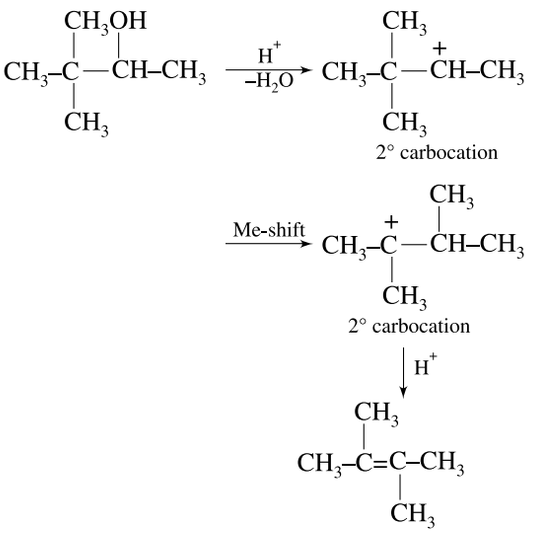


Also P(C_6H_{16}) has two degree of unsaturation and oxymercuration–demercuration hydration indicates that it is an alkyne. As alkyne, on hydration, gives a carbonyl compound which on reduction with $NaBH_4$ gives a 2° alcohol.

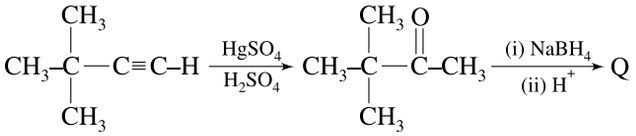


2° alcohol

The secondary alcohol that can give above shown alkene on acid catalysed dehydration is



44.



45. Explained in the beginning.

46. [2,4]

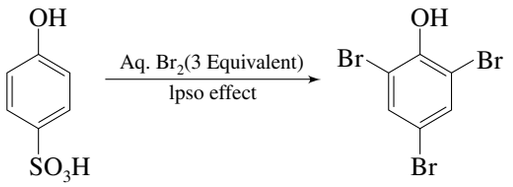
(1) Both phenol and benzoic acid forms salt with NaOH, hence this mixture can't be separated.

(2) Benzoic acid forms salt with NaOH while benzyl alcohol does not, hence the mixture can be separated using NaOH. Also, benzoic acid forms salt with $NaHCO_3$ but benzyl alcohol does not, hence $NaHCO_3$ can be used for separation.

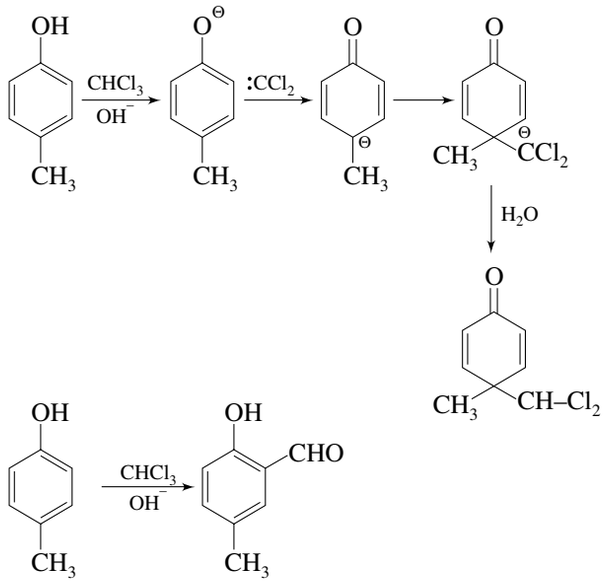
(3) Neither benzyl alcohol nor phenol forms salt with $NaHCO_3$, mixture cannot be separated using $NaHCO_3$.

(4) $C_6H_5CH_2COOH$ forms salt with NaOH, C_6H_5-CH_2OH does not, hence NaOH. $C_6H_5CH_2COOH$ forms salt with $NaHCO_3$. $C_6H_5CH_2OH$ does not, hence mixture can be separated using $NaHCO_3$.

47. [2]



48. [2,4]

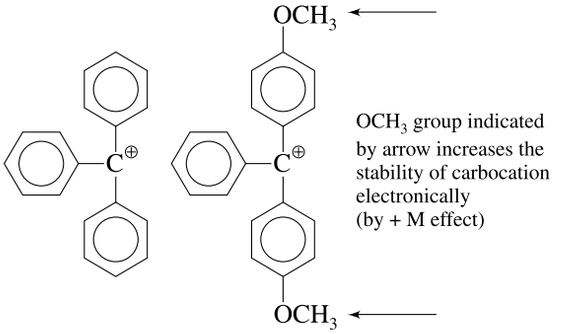


49. [3]

This problem can be solved by using the concept of stability of carbocation and S_N1 reaction.

When two phenyl groups are replaced by two para methoxy group, carbocation formed will be more stable.

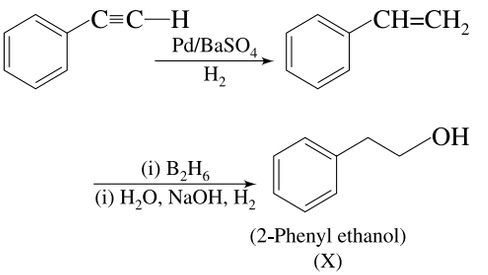
As the stability of carbocation formed increases, rate of acidic hydrolysis increases.



More stable carbocation

50. [3]

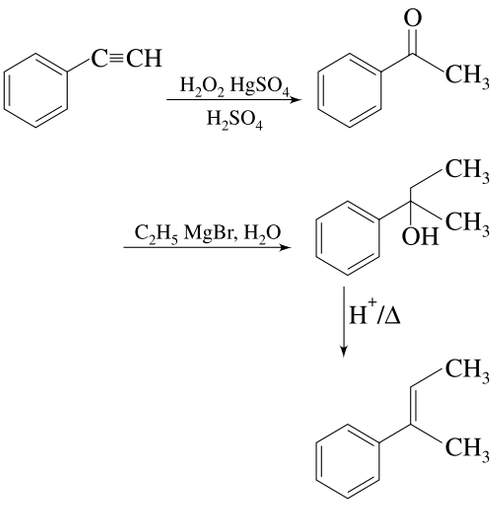
The reaction condition indicates that starting compound is phenyl acetylene.



(2-Phenyl ethanol)
(X)

Hydroboration oxidation brings about anti-Markownikoff's hydration of alkene.

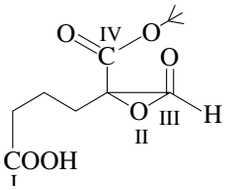
51. [4]



52. [3]

Only –CHO group is to be reduced to $-CH_2OH$

It can be done using $NaBH_4$ in C_2H_5OH.



(1) $LiAlH4/(C_2H_5)_2O$ reduces I, II and III into $-CH_2OH$, and IV into diol.

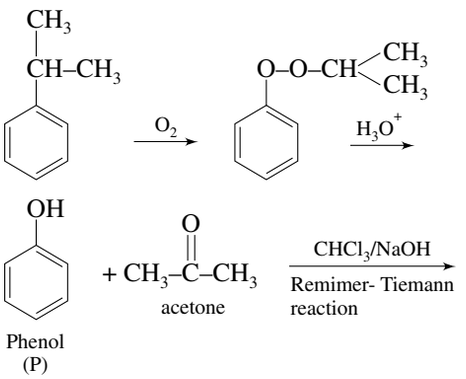
(2) BH_3/THF show same properties as (1).

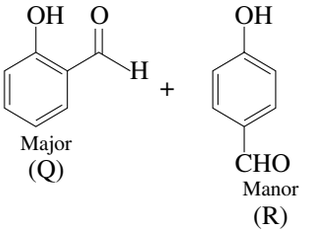
(3) $NaBH_4/C_2H_5OH$ reduces III into $-CH_2OH$

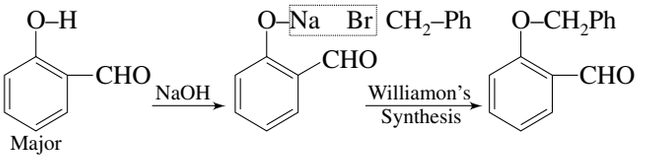
(4) Raney nickel, same as (1) and (2),

Thus (3) is correct reagent.

53. [2, 3]







(Q) (S)

(1) R is not steam volatile, but Q is steam volatile thus, incorrect.

(2) Q has enolic group; thus it gives violet colour with 1% aqueous $FeCl_3$ solution thus, correct.

(3) S has Carbonyl group hence, gives yellow precipitate with 2,4-DNP thus, correct.

(4) S does not give colour with $FeCl_3$ thus, incorrect