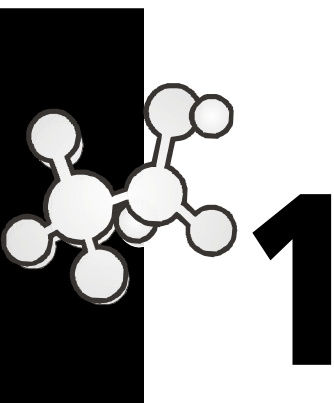
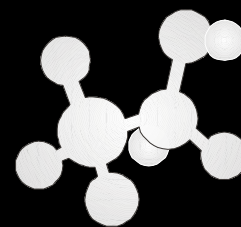


Class XII



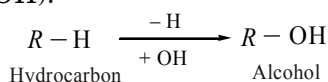
Alcohols, Phenols and Ethers



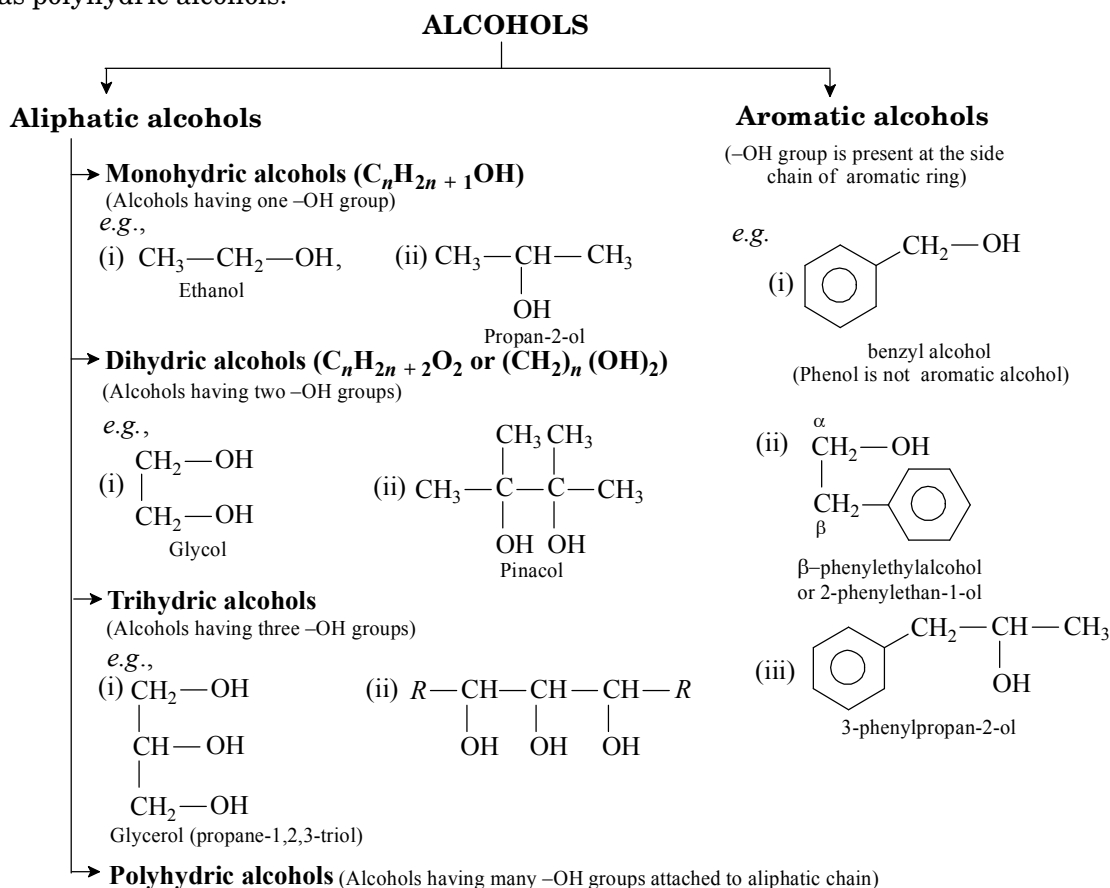
- General methods of preparation, properties, reactions and uses.
- Alcohols : Identification of primary, secondary and tertiary alcohols; mechanism of dehydration.
- Phenols : Acidic nature, electrophilic substitution reactions : halogenation, nitration, sulphonation and Reimer-Tiemann reaction.
- Ethers : Structure

ALCOHOLS

- Alcohols are regarded as hydroxy derivatives of hydrocarbons. These are formed by the replacement of one, two or more hydrogen atoms of a hydrocarbon by a corresponding number of hydroxyl groups (–OH).

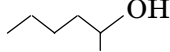


- The compounds in which hydroxyl group is attached to a saturated carbon atom are called as alcohols. The compounds in which a hydroxyl group is attached to an unsaturated carbon atom of a double bond are called as **enols**. The saturated carbon may be that of an alkyl, alkenyl or benzyl group. However, if a hydroxyl group is attached to a benzene ring, the compound is called as phenol.
- Alcohols are further classified according to the number of hydroxyl groups present in their molecules. Monohydric alcohols contain one hydroxyl group, dihydric two, trihydric three, respectively. However, alcohols containing two or more hydroxyl groups are generally called as polyhydric alcohols.



NOMENCLATURE

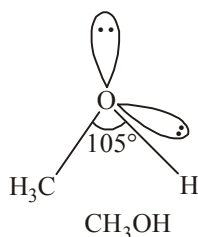
During writing the IUPAC name of alcohols 'e' of alkane is replaced by '-ol'. Thus it is alkanol. Let us consider some structures and their IUPAC names and nature of alcohol.

- $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{OH}$ 1° alcohol • $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{OH}$ 1° alcohol
Propanol-1 or propan-1-ol 2-Methylpropanol-1
- $\text{CH}_3-\underset{\text{CH}_3}{\overset{\text{OH}}{\text{C}}}-\text{CH}_2-\text{CH}_3$ 3° alcohol • $\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{OH}$ 2° alcohol
2-Methylbutanol-2 Hex-4-yn-2-ol
- $\text{CH}_2=\text{CH}-\underset{\text{OH}}{\text{CH}}-\text{CH}_3$ 2° alcohol • $\text{CH}_3-\underset{\text{OH}}{\overset{\text{H}_3\text{C}}{\text{C}}}-\underset{\text{OH}}{\overset{\text{CH}_3}{\text{C}}}-\text{CH}_3$ 3° alcohol
But-3-en-2-ol 2,3-Dimethylbutane-2,3-diol
- $\text{CH}_3-\text{CH}_2-\underset{\text{H}_3\text{C}}{\overset{\text{CH}_3}{\text{C}}}-\underset{\text{C}_2\text{H}_5}{\text{CH}}-\text{OH}$ 3° alcohol • $\text{C}_6\text{H}_5-\underset{\text{OH}}{\overset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\text{CH}_3$ 3° alcohol
4,4-Dimethylhexanol-3 2-Phenylbutanol-2
-  2° alcohol
Hexanol-2

Alcohols can be considered as derivatives of hydrocarbons in which one hydrogen is replaced by hydroxyl (-OH) group and thus have the general formula $\text{C}_n\text{H}_{2n+1}\text{OH}$ (monohydric alcohols only).

Structure

In alcohols, both carbon and oxygen atoms are sp^3 hybridised. Two of the four sp^3 hybridised orbitals of oxygen get involved in formation of σ -bond with hydrogen and carbon respectively whereas rest of the two sp^3 hybridised orbitals contain lone pairs of electrons. C-O-H bond angle is found to be as 105° (rather than normal tetrahedral angle of 109.5°). Deviation from normal angle can be explained on the basis of greater lone pair - lone pair repulsion than bond pair - lone pair repulsion.



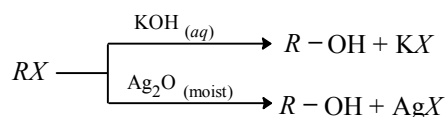
Note

- The C-O-H bond angle in phenol is approx the same (109°) as in methanol but the carbon-oxygen bond length in phenol is, however, slightly less (136 pm) than in methanol. This is due to (i) resonance as a result of which carbon-oxygen bond acquires some double bond character because of conjugation of the lone pair of electrons of oxygen with the benzene ring and (ii) sp^2 -hybridised state of carbon of which oxygen is attached.
- Phenol, has a smaller dipole moment (1.54 D) than methanol. This is due to the reason that the C-O bond in phenol is *less polar* due to the *electron-withdrawing effect* of the benzene ring while in methanol, C-O bond is more polar due to *electron-donating effect* of the CH_3 group.
- Due to this dipolar nature, alcohols and phenols form intermolecular hydrogen bonds.

GENERAL METHODS OF PREPARATION

1. Hydrolysis of alkyl halides

Alkyl halides on hydrolysis with either aqueous KOH or moist Ag₂O yield alcohols.



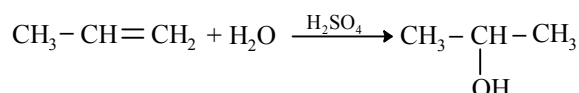
This reaction is useful with reactants that do not undergo E2 elimination readily. It is therefore used for the synthesis of alcohols from alkyl halides that are primary in nature.

2. Hydration of alkenes

Hydration of alkenes can be carried out directly or indirectly.

(i) Direct hydration

Direct addition of water to an alkene is an acid catalysed process in which addition takes place according to Markownikoff's rule.



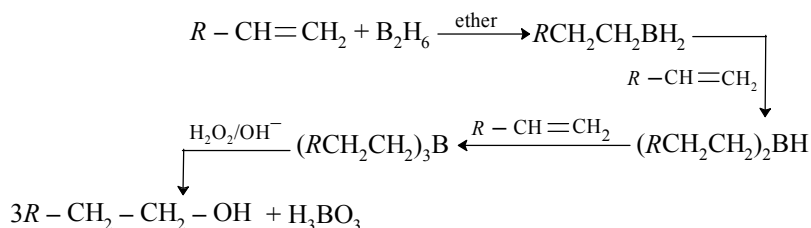
Reaction mechanism involves intermediate carbocation formation, hence rearrangement may occur.

(ii) Indirect hydration

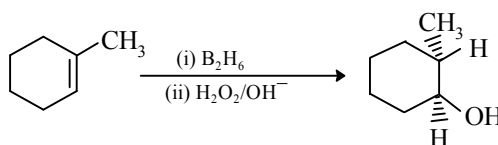
Indirect hydration can be carried out by following methods.

(a) Hydroboration-oxidation

Alkenes on reaction with diborane in an inert solvent like ether or THF form an intermediate alkyl boranes which on oxidation with hydrogen peroxide (alkaline) yield alcohols. Reaction ultimately results in **anti-Markownikoff's addition** of water.

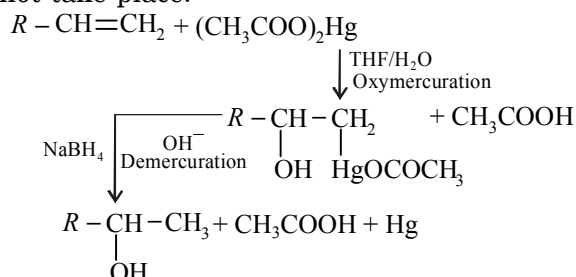


Reaction takes place by concerted mechanism and no carbocation is involved as an intermediate. Hence rearrangement does not take place, and reaction is completed by *syn*-addition (stereospecific).



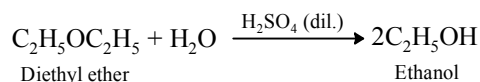
(b) Oxymercuration-demercuration

Alkenes on reaction with mercuric acetate form intermediate mercury compound which on reduction with sodium borohydride gives alcohols. Addition takes place according to **Markownikoff's rule**. Reaction does not involve intermediate carbocation, hence rearrangement does not take place.



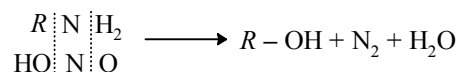
3. From ethers

Ethers on heating with dilute sulphuric acid under pressure yield alcohols.



4. From primary amines

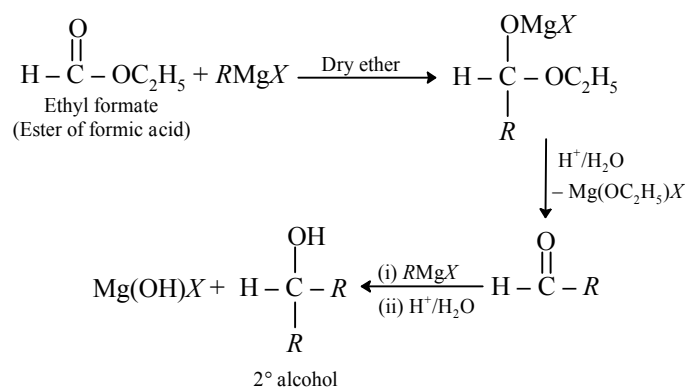
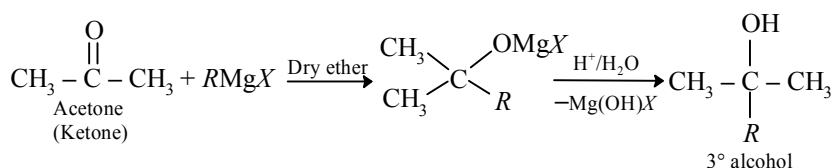
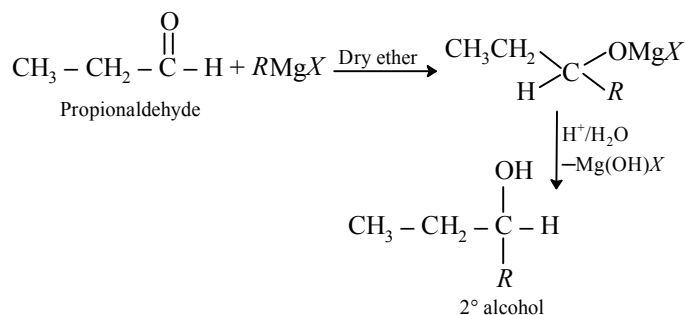
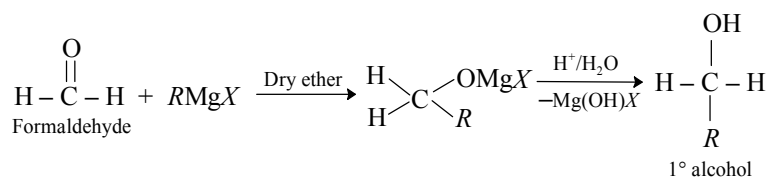
Primary amines yield alcohols by the action of nitrous acid.

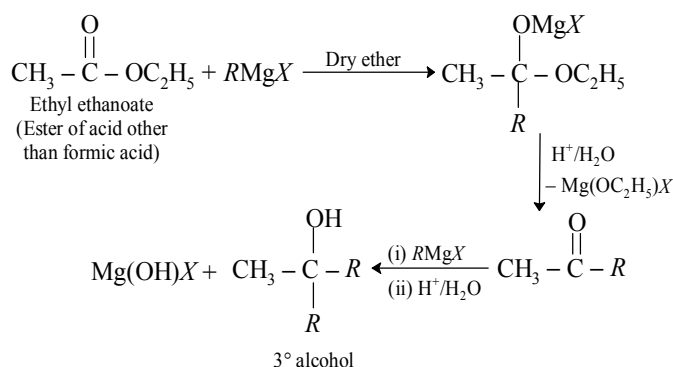


5. Action of Grignard reagent

Grignard reagent reacts with aldehydes, ketones or esters to give addition compounds which on hydrolysis yield alcohols.

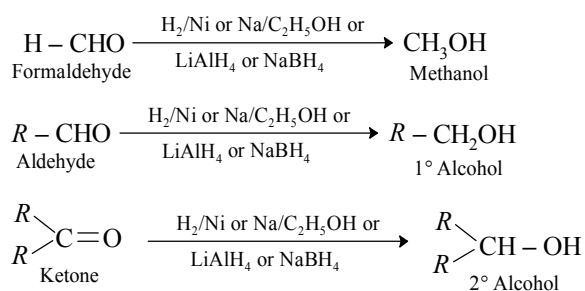
Formaldehyde gives primary alcohol, aldehydes other than formaldehyde yield secondary alcohols. Ketones yield tertiary alcohols and esters of formic acid give secondary alcohols whereas esters of acids other than formic acid give tertiary alcohols.



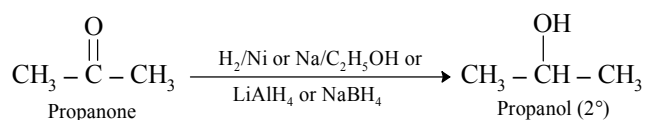


6. Reduction of aldehydes and ketones

Aldehydes and ketones can be reduced to corresponding alcohols by catalytic hydrogenation or by action of sodium on ethanol or by action of complex metal hydrides such as lithium aluminium hydride (LiAlH_4) or sodium borohydride (NaBH_4).

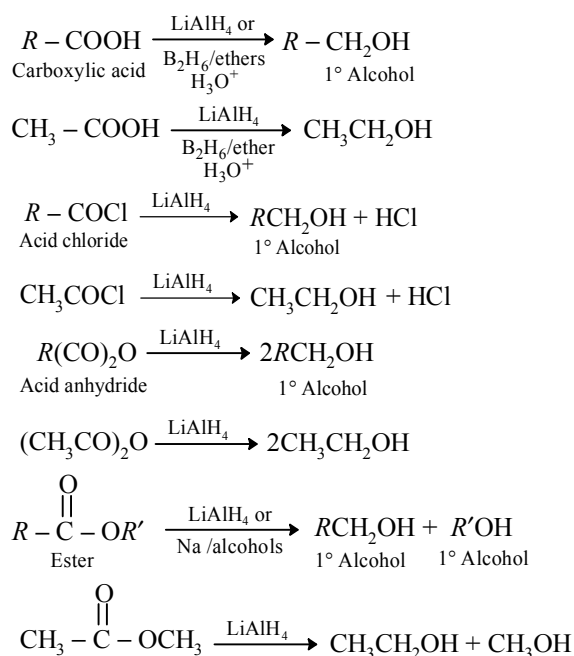


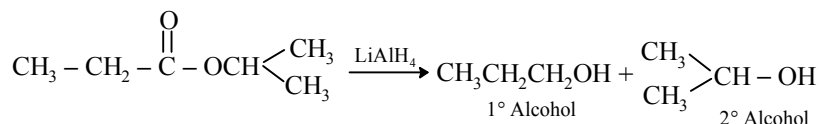
e.g.,



7. Reduction of carboxylic acids and esters

Carboxylic acids and their derivatives can be reduced to corresponding alcohols with strong reducing agents such as LiAlH_4 .



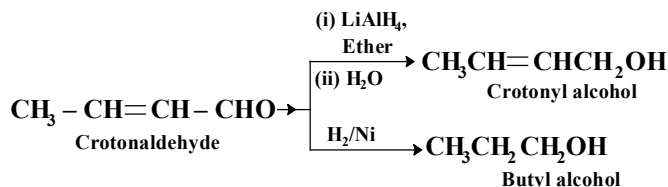


Reduction of carbonyl compounds and esters to alcohols by using alcoholic sodium is called **Bouveault-Blanc reduction**.

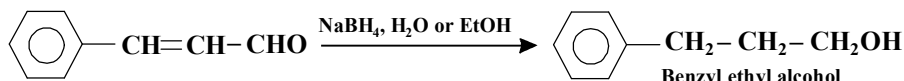


Note

- Lithium aluminium hydride (LiAlH_4) and sodium borohydride (NaBH_4) are highly specific reducing agents. They reduce a wide variety of groups without attacking the double bond of the compound if present. For example,

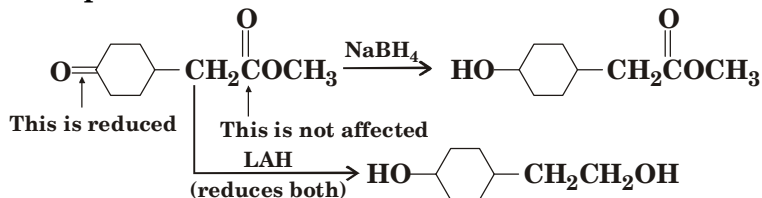


- However if a phenyl group is attached to the β -carbon atom of α, β -unsaturated carbonyl compound, double bond is also reduced.

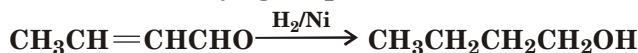


Cinnamic aldehyde Benzyl ethyl alcohol

- NaBH_4 is also selective in reducing more reactive carbonyl group. Keto part of ester is not reduced.



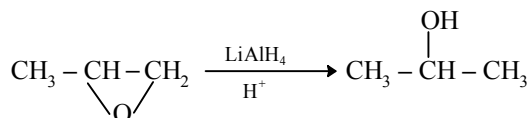
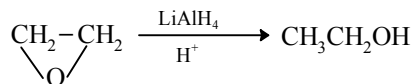
- Catalytic hydrogenation reduces carbon-carbon double bond as well as carbonyl group.



8. From epoxides

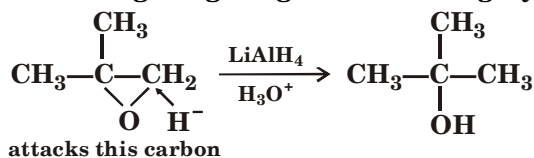
(i) Reduction

Epoxides can also be reduced with LiAlH_4 into alcohols.



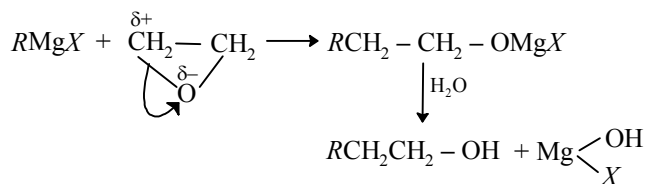
Note

Hydride (a base) selectively attacks the less alkylated carbon of the epoxide ring so giving the more highly alkylated alcohol.



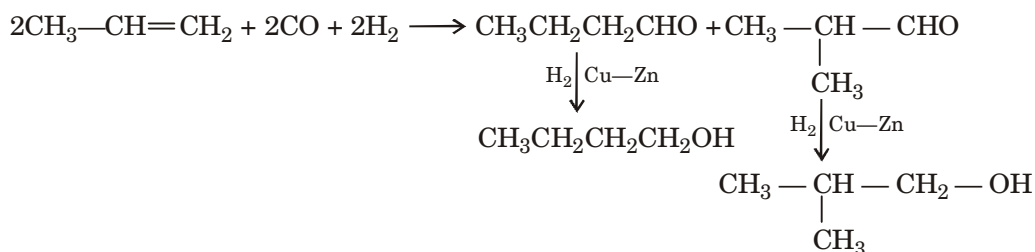
(ii) Action of Grignard reagent

Grignard reagent reacts with ethylene oxide to yield primary alcohols containing two more carbon atoms than the alkyl group of Grignard reagent.



9. Oxo Process

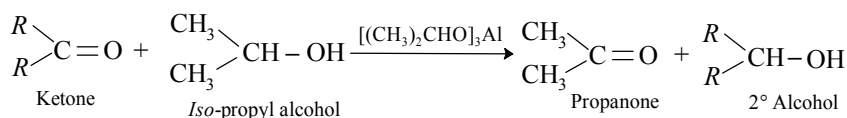
In this process, a mixture of alkene, carbon monoxide and hydrogen under pressure and elevated temperature in the presence of catalyst cobalt carbonyl hydride $[\text{CoH}(\text{CO})_4]$, forms aldehyde. This reaction is also known as **carbonylation** or **hydroformylation** reaction.



It is an industrial method of preparation of alcohols.

10. Meerwein-Ponndorf-Verley reduction

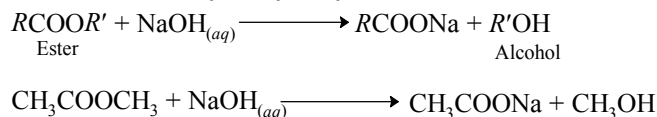
This is a method of reducing ketones to secondary alcohols by refluxing with aluminum isopropoxide in excess of *iso*-propyl alcohol solution.



Reaction just reverse to it is called **Oppenauer oxidation**, in which secondary alcohol is oxidised to ketone by refluxing with excess of acetone in presence of aluminium isopropoxide or tertiary butoxide.

11. Hydrolysis of esters

Esters on alkaline hydrolysis yield alcohols and salt of carboxylic acids.

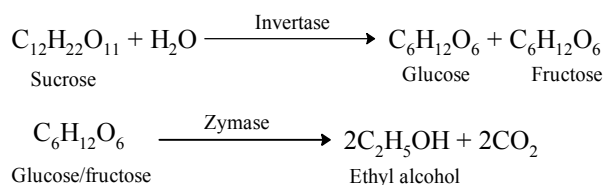


12. Fermentation of carbohydrates

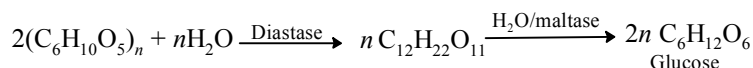
It is an industrial method for preparation of ethyl alcohol.

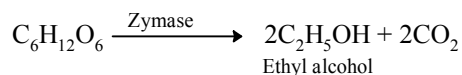
(i) From molasses

Molasses is the mother liquor left after crystallization of sugar from sugar solution.



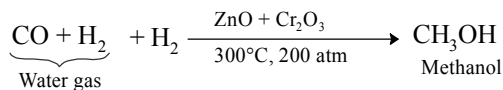
(ii) From starch





13. Reduction of water gas

It is an industrial method for preparation of methanol.



PHYSICAL PROPERTIES

- **Physical state :** Lower members are colourless liquids having a characteristic smell and burning taste, whereas the higher members are colourless, odourless, wax like solids.
- **Boiling points :** Lower members have low boiling points. With increase in molecular mass, boiling points increase. This is because of increase in van der Waal's forces. For isomeric alcohols boiling point decreases because with branching, the surface area decreases and therefore, the van der Waal's force also decreases.
- **Solubility :** Lower members of alcohols are highly soluble in water but solubility decreases with increase in molecular weight. In isomeric alcohols, the solubility increases with branching due to decrease in polar character.
- **Density :** Alcohols are lighter than water although the density increases with increase in molecular mass.
- **Intoxicating effects :** Methanol is poisonous. It is not good for drinking purposes. It may cause blindness and even death. Ethanol has been used for drinking purposes.

Note

We call the hydroxyl group *hydrophilic* (meaning water loving) because of its affinity for water and other polar substances. The alkyl group (of alcohol) is called *hydrophobic* (meaning water hating) and makes the alcohols less hydrophilic.

ILLUSTRATION

① Explain the following :

- Alcohols with three or fewer C atoms are water soluble; those with five or more C atoms are insoluble, and those with four C atoms are marginally soluble.
- When equal volumes of ethanol and water are mixed, the total volume is less than the sum of the two individual volumes.
- Propanol (M.Wt. = 60) has a higher boiling point than butane (M.Wt. = 58).

Soln : (a) The water solubility of alcohols is attributed to intermolecular H-bonding with H_2O . As the molecular weights of the alcohols increase, their solubility in water decreases, because greater carbon content makes the alcohols less hydrophilic. Conversely, their solubility in hydrocarbon solvents increases.

- H-bonding between ethanol and water molecules.
- Alcohol molecules attract each other by relatively strong H-bonds and somewhat weaker dipole-dipole interactions, resulting in a higher b.pt. In alkanes only weaker van der Waals' attractive forces must be overcome to vaporize the hydrocarbon.

CHEMICAL PROPERTIES

Chemical reactions of alcohols can be classified into following categories:

- Reactions due to O - H bond breaking.
- Reactions due to C - OH bond breaking.
- Reactions of alcohol molecule as a whole.

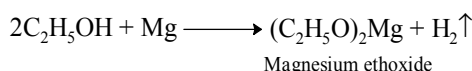
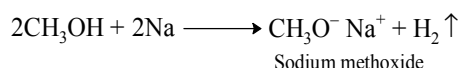
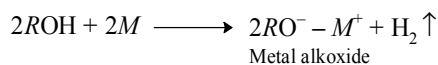
(A) Reactions due to O – H bond breaking

Order of ease of cleavage of O – H bond and thus order of reactivity is:

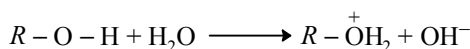
CH₃OH > primary > secondary > tertiary.

1. Reaction with active metals (acidic nature)

Active metals like Na, K, Mg, Al, Zn, etc. are strongly electropositive in nature. These react with alcohols to form metal alkoxide with evolution of hydrogen gas.



Above reactions confirm the acidic nature of alcohols. Alcohols act as Bronsted acids which lose a proton to strong base. Acidic character of alcohols can be explained by highly electronegative nature of oxygen atom which withdraws the electrons of O – H bond towards itself so that O – H bond becomes weak and proton is easily liberated. However alcohols are weak acids, even weaker than water.



Electron releasing inductive effect of alkyl group in alcohols increases the electron density around O – H bond which makes the alcohols weaker acid ($K_a \approx 10^{-17}$) than water ($K_w = 10^{-14}$). Amongst isomeric alcohols acidic strength follows the order:

CH₃OH > primary > secondary > tertiary

Above order of acidic strength can be explained by +I effect. Smaller the electron releasing inductive effect, higher is the acidic strength. Order of +I effect in various isomeric alcohols is:

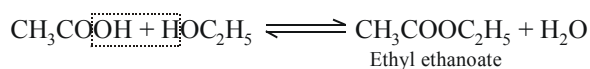
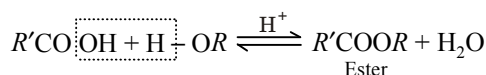
CH₃OH < primary < secondary < tertiary

On the basis of K_a values, relative acidic strength of some compounds can be given as

H₂O > ROH > CH≡CH > NH₃ > RH

2. Esterification

Alcohols on reaction with carboxylic acids in presence of acid catalyst yield esters. The reaction is known as esterification.



– If the above reaction is carried out with dry HCl gas as catalyst, the reaction is known as **Fischer-Speier esterification**.

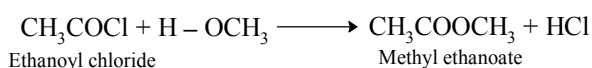
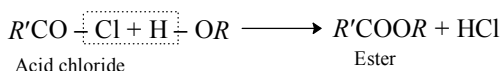
– Order of reactivity of different alcohols towards esterification is

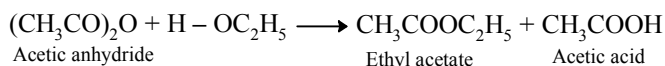
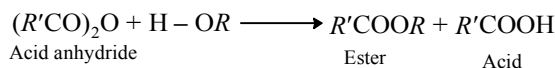
CH₃OH > RCH₂OH > R₂CHOH > R₃COH

As the size of hydrocarbon part (R) around –OH increases, rate of reaction decreases due to steric hindrance.

3. Reaction with acid chlorides and acid anhydrides

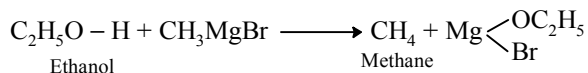
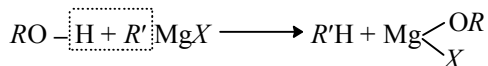
Alcohols form esters on treatment with acid chlorides and anhydrides.



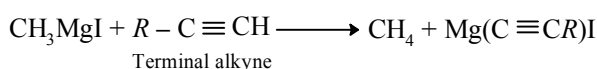
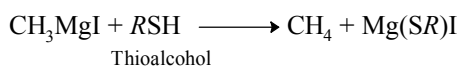
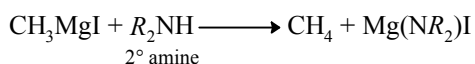
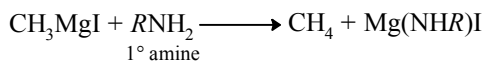
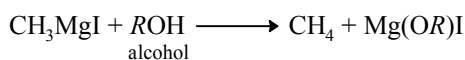


4. Reaction with Grignard reagent

Alcohols react with Grignard reagent to form alkanes corresponding to alkyl group of Grignard reagent.



H atom attached to highly electronegative atoms like O, N and S are called active hydrogens. Compounds containing active hydrogens like alcohols, phenols, amines, thioalcohols, terminal alkynes, etc. on reaction with Grignard reagent yield hydrocarbon corresponding to alkyl group of Grignard reagent.



Note **Relative acidities of H₂O, ROH, CH≡CH, NH₃, RH will be in order: H₂O > ROH > CH≡CH > NH₃ > RH**

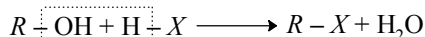
If the Grignard reagent used is CH₃MgX, the reaction is known as **Zerewitinoff active hydrogen determination**. In this reaction, by knowing the volume of CH₄ evolved at NTP, number of active hydrogens present in a compound can be calculated.

B. Reactions due to C—O bond breaking

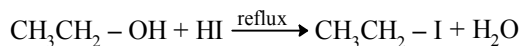
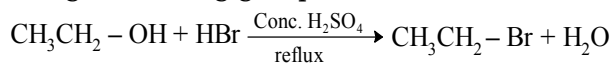
Order of ease of cleavage of C—OH bond and thus reactivity of different alcohols is :
Tertiary > Secondary > Primary > CH₃OH

1. Reaction with halogen acids

Alcohols react with halogen acids to form alkyl halides.

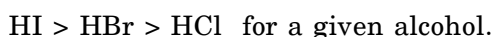


Alcohols require some catalyst like ZnCl₂ or acidic conditions to undergo nucleophilic substitution, since -OH is a poor leaving group. In acidic solution hydroxyl group gets protonated and thus becomes good leaving group.



However, for highly reactive tertiary alcohols no such conditions are necessary.

Order of reactivity of HX is



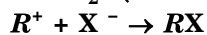
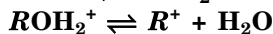
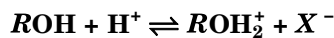
For a given hydrogen halide order of reactivity of different alcohols is

allyl > benzyl > 3° > 2° > 1°

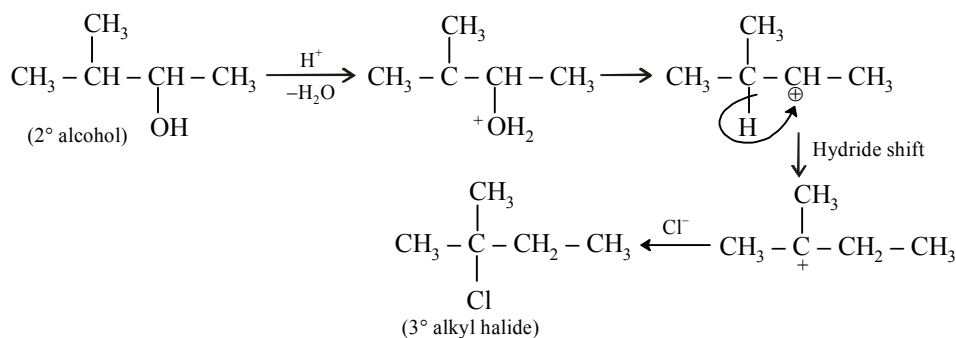
- Primary alcohols give substitution reaction by S_N2 mechanism, tertiary alcohols by S_N1 mechanism and secondary alcohols by either S_N1 or S_N2.
- Since S_N1 reaction involves formation of carbocation, rearrangements may take place.

Note

Protonation converts the hydroxyl group to a good leaving group.

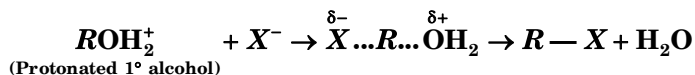


e.g.,



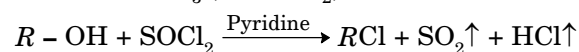
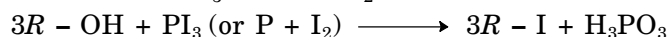
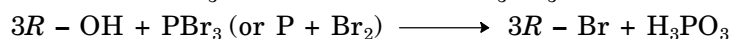
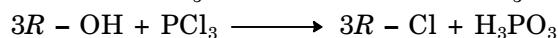
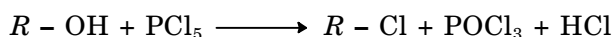
Note

In 1° alcohol, rearrangement does not take place because they follow S_N2 mechanism.



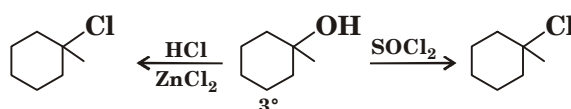
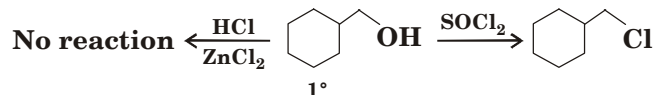
2. Reaction with phosphorus halides and thionyl chloride

Alcohols react with phosphorus halides and thionyl chloride to yield corresponding alkyl halides.



Note

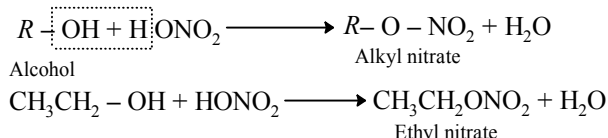
Reaction with PBr₃, P + I₂, and SOCl₂ provides a path of preparing 1° alkyl halides which are otherwise not possible with Lucas reagent.



SOCl₂ is often the best reagents for converting an alcohol to an alkyl chloride. The gaseous SO₂ and HCl by-products leave the reaction mixture and thus reverse reaction does not occur.

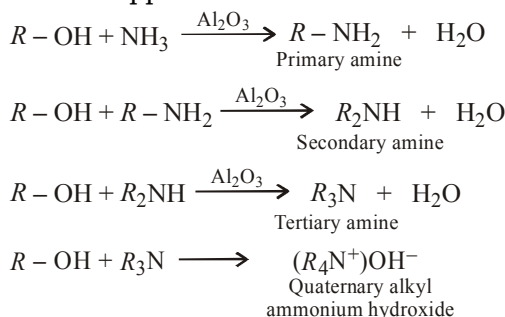
3. Reaction with nitric acid

Alcohols react with nitric acid to form alkyl nitrates.



4. Reaction with ammonia

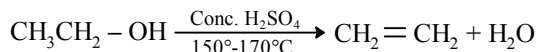
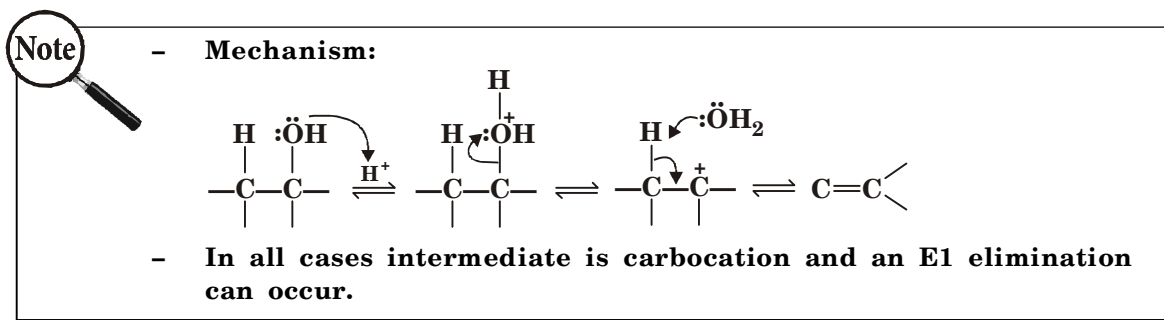
Alcohols give a mixture of amines on reaction with ammonia in presence of catalyst like alumina or copper chromite.



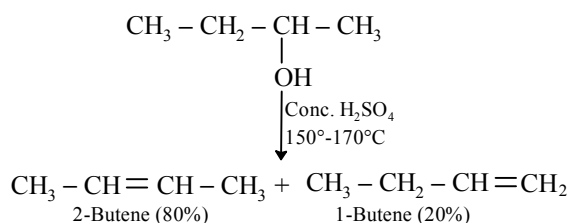
C. Reactions involving alcohol molecule as a whole

1. Dehydration of alcohols

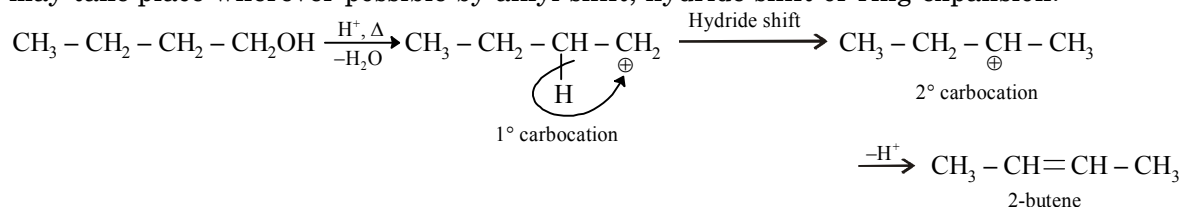
Dehydration of alcohols is a β -elimination reaction in which C-O bond is cleaved along with loss of proton from β -position. Reaction takes place by heating alcohol with protonic acid such as H_2SO_4 or H_3PO_4 or catalysts such as alumina or zinc chloride.

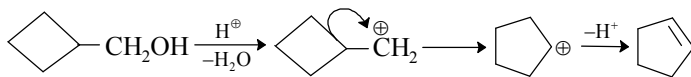


Alkene formation takes place according to **Saytzeff's rule**.



Reaction mechanism involves the formation of carbocation intermediate thus rearrangements may take place wherever possible by alkyl shift, hydride shift or ring expansion.





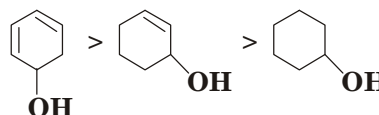
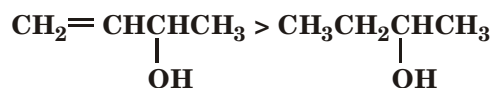
- Order of ease of dehydration of alcohols follows the order:
 3° alcohol $>$ 2° alcohol $>$ 1° alcohol
 Since the rate determining step is formation of carbocation.

2. Oxidation

Oxidation of alcohols gives different product according to nature of alcohol *i.e.* whether the alcohol is primary, secondary or tertiary. A variety of oxidants can be used for oxidation of alcohols like acidic or alkaline potassium permanganate (KMnO_4), acidified potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), nitric acid (HNO_3), chromic acid or chromium trioxide (CrO_3) complex with pyridine, etc.

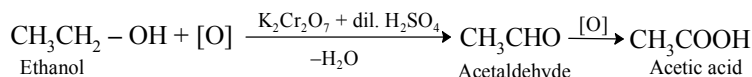
Note

Alcohols leading to conjugated alkenes are dehydrated to a greater extent than those of alcohols leading to non-conjugated alkenes. Thus dehydration is in order:



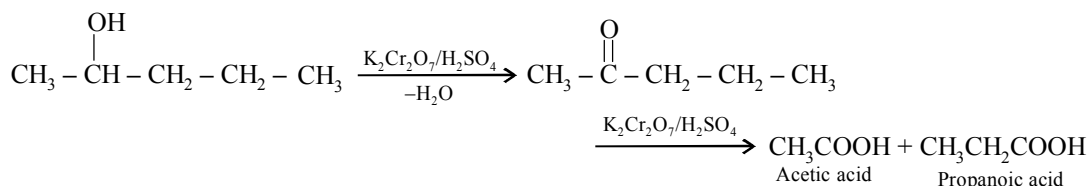
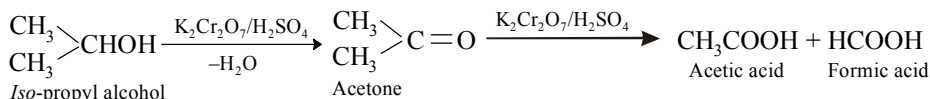
(i) Action of acidified $\text{K}_2\text{Cr}_2\text{O}_7$

- Primary alcohols on oxidation give aldehydes which further get oxidized to carboxylic acid with same number of carbon atoms.



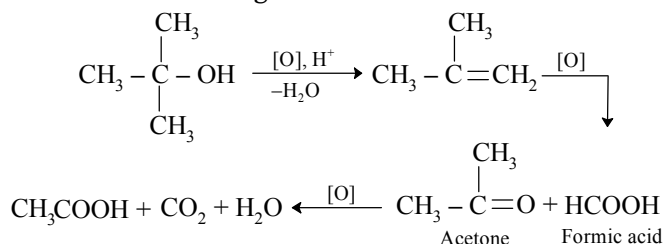
Oxidation can be stopped at aldehyde stage by using **Collin's reagent** ($\text{CrO}_3 \cdot 2\text{C}_5\text{H}_5\text{N}$, chromium trioxide - pyridine complex) or pyridinium chloro chromate, PCC ($\text{CrO}_3 \cdot \text{C}_5\text{H}_5\text{N} \cdot \text{HCl}$).

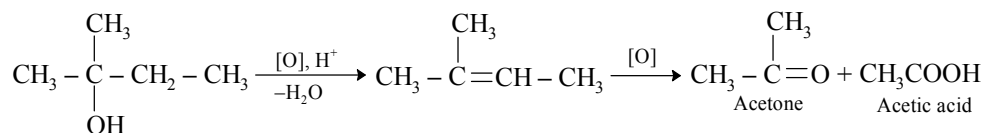
- Secondary alcohols on oxidation give ketones. Ketones can be further oxidized only under drastic conditions to give a mixture of carboxylic acids with lesser number of carbon atoms than the original alcohol.



Oxidation can be stopped at ketone stage by using chromic anhydride (CrO_3).

- Tertiary alcohols are not oxidized in alkaline or neutral conditions. Acidic oxidizing agents ($\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$, $\text{KMnO}_4/\text{H}_2\text{SO}_4$), first dehydrate the alcohol to an alkene which is then oxidized to ketone and carboxylic acid, each having lesser number of carbon atoms than that in original alcohol.

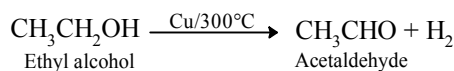




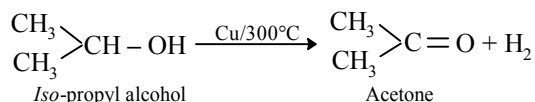
(ii) Action of copper

Alcohols can also be oxidised by catalytic dehydrogenation by passing their vapours over heated copper at 300°C.

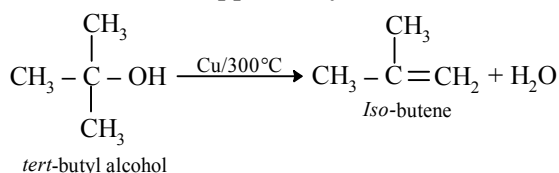
- Primary alcohols are oxidised to aldehydes.



- Secondary alcohols undergo oxidation to yield ketones.



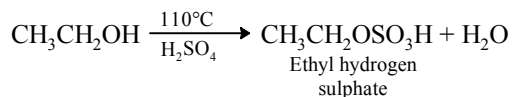
- Tertiary alcohols are resistant to oxidation. They undergo dehydration when their vapours are passed over heated copper to yield alkenes.



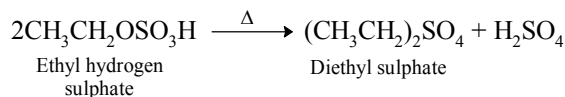
(iii) Action of concentrated sulphuric acid

On heating alcohols with concentrated H₂SO₄, different products are obtained under different conditions of temperature and pressure.

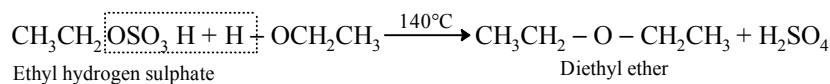
- If reaction is carried out at 110°C, alkyl hydrogen sulphate is formed.



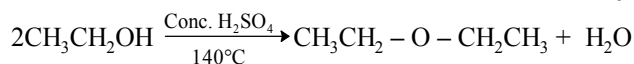
- Alkyl hydrogen sulphate on further heating under reduced pressure gives dialkyl sulphate.



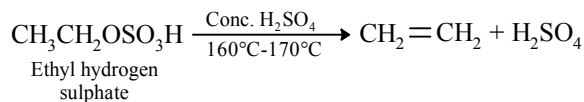
- Alkyl hydrogen sulphate on heating with excess of alcohol at 140°C form dialkyl ethers.



Formation of ethers from alcohols can be directly written as



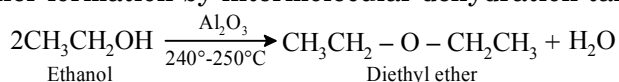
- Alkyl hydrogen sulphate on heating with excess of conc. H₂SO₄ at 160°-170°C yield alkene.



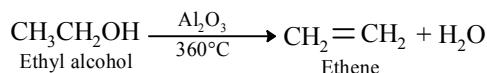
(iv) Action of heated alumina

On passing the vapours of alcohol over heated alumina (Al₂O₃), different products are obtained under different conditions of temperature.

- At 240°-250°C, ether formation by intermolecular dehydration takes place.



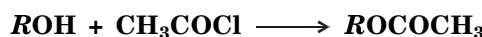
- At 360°C, alkene formation takes place by intramolecular dehydration.



Note

Number of —OH groups present in a compound can be predicted by knowing acylated product. For example if it is asked that how many —OH groups are present in a compound (A) which on acylation gives (B) having molecular formula $\text{C}_9\text{H}_{14}\text{O}_6$? It can be predicted as follows:

Acylation of one —OH group will increase in molecular formula by $\text{C}_2\text{H}_2\text{O}$ unit.



Since alcoholic group is acylated and total number of O-atom in product is 6, thus we can say that 3-OH groups are present in a compound which on acylation gives product having six 'O' atoms. The molecular formula for reactant will be $\text{C}_9\text{H}_{14}\text{O} - \text{C}_6\text{H}_6\text{O}_3 = \text{C}_3\text{H}_8\text{O}_3$

ILLUSTRATION

- ② *t*-butyl alcohol reacts less rapidly with metallic sodium than *n*-butyl alcohol. Explain.

Soln.: The +I effect of three methyl groups on central carbon atom of *t*-butyl alcohol makes it partially negative as a result it pushes the electron pair of O – H bonds towards H-atoms and thus H atom is not replaced easily.

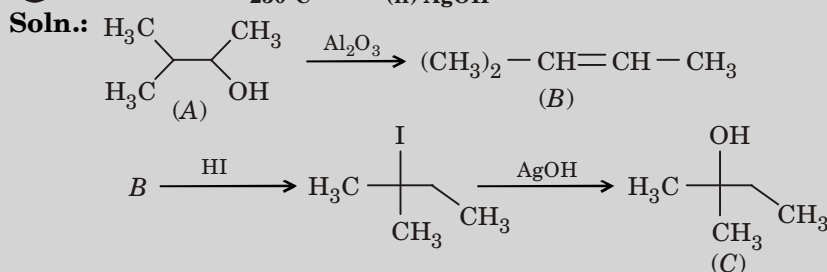
- ③ An organic compound of formula $\text{C}_3\text{H}_8\text{O}_3$ yields on acetylation with acetic anhydride a derivative of the formula $\text{C}_9\text{H}_{14}\text{O}_6$. How many hydroxyl groups are present in the compound?

Soln.: General reaction: $\text{R}-\text{OH} \xrightarrow{(\text{CH}_3\text{CO})_2\text{O}} \text{ROCOCH}_3$

According to reaction, total increase = $\text{C}_9\text{H}_{14}\text{O}_6 - \text{C}_3\text{H}_8\text{O}_3 = \text{C}_6\text{H}_6\text{O}_3$ or $3(\text{C}_2\text{H}_2\text{O})$

Hence, the increase is equivalent to three —OH groups.

- ④ $\text{C}_5\text{H}_{11}\text{OH}(\text{A}) \xrightarrow[250^\circ\text{C}]{\text{Al}_2\text{O}_3} (\text{B}) \xrightarrow[(\text{ii}) \text{AgOH}]{(\text{i}) \text{HI}} \text{C}_5\text{H}_{11}\text{OH}(\text{C})$ (An isomer of A). Identify A, B and C?



Methods of distinction between primary, secondary and tertiary alcohols

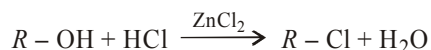
- Oxidation
- Lucas test
- Victor Meyer's test (best method)
- Catalytic hydrogenation by Cu at 300°C

(a) Oxidation

Primary alcohol	Secondary alcohol	Tertiary alcohol
Easily oxidised to aldehydes which further get oxidised to carboxylic acids. $\text{CH}_3\text{CH}_2-\text{OH} + [\text{O}] \xrightarrow[\text{-H}_2\text{O}]{\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4} \text{CH}_3\text{CHO}$ $\xrightarrow{[\text{O}]} \text{CH}_3\text{COOH}$	Oxidised to ketones which can be further oxidised under drastic conditions to yield a mixture of carboxylic acids. $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CH}_3-\text{CHOH} \\ \diagup \\ \text{CH}_3 \end{array} \xrightarrow[\text{-H}_2\text{O}]{\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4} \begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{CH}_3 \end{array}$ $\xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4} \begin{array}{c} \text{CH}_3\text{COOH} \\ + \\ \text{HCOOH} \end{array}$	Oxidised to ketones under drastic conditions which further get oxidised to carboxylic acids. $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{OH} \\ \\ \text{CH}_3 \end{array} \xrightarrow[\text{-H}_2\text{O}]{[\text{O}], \text{H}^+} \begin{array}{c} \text{CH}_3 \\ \\ \text{C}=\text{O} \\ \\ \text{CH}_3 \end{array}$ $\xrightarrow{[\text{O}]} \text{CH}_3\text{COOH} + \text{HCOOH}$

(b) Lucas test

Alcohols react with concentrated hydrochloric acid in presence of anhydrous zinc chloride to form alkyl halides.



Three types of alcohols undergo this reaction at different rates. The rates of reaction with Lucas reagent [conc. HCl + ZnCl₂ (anhydrous)] follow the given order :

Tertiary alcohol > Secondary alcohol > Primary alcohol

The following observations are made

- If cloudiness appears immediately, the alcohol is **tertiary**.
- If cloudiness appears within 5-10 minutes, the alcohol is **secondary**.
- If the solution remains clear, *i.e.*, no cloudiness is formed, the alcohol is **primary**.

*Primary alcohols do not react with Lucas reagent at room temperature. It requires high temperature.

(c) Victor Meyer's test

In this test, the following steps are involved

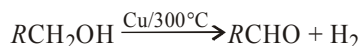
- Alcohol is first reacted with conc. HI or red phosphorus and iodine to form the corresponding alkyl iodide.
- Alkyl iodide is then treated with silver nitrite and the corresponding nitroalkane is formed.
- Nitroalkane is then treated with nitrous acid (NaNO₂ + HCl) and the solution is made alkaline by addition of excess of caustic soda.

Primary alcohol	Secondary alcohol	Tertiary alcohol
RCH_2OH	R_2CHOH	$\text{R}_3\text{C}-\text{OH}$
$\downarrow \text{HI}$	$\downarrow \text{HI}$	$\downarrow \text{HI}$
RCH_2I	R_2CHI	$\text{R}_3\text{C}-\text{I}$
$\downarrow \text{AgNO}_2$	$\downarrow \text{AgNO}_2$	$\downarrow \text{AgNO}_2$
RCH_2NO_2	R_2CHNO_2	$\text{R}_3\text{C}-\text{NO}_2$
$\downarrow \text{HONO}$	$\downarrow \text{HONO}$	$\downarrow \text{HONO}$
$\text{R}-\text{C}-\text{NO}_2$	$\text{R}_2\text{C}-\text{NO}_2$	No reaction
\parallel	\mid	$\downarrow \text{NaOH}$
NOH	NO	Colourless
Nitric acid	Pseudonitrol	
$\downarrow \text{NaOH}$	$\downarrow \text{NaOH}$	
Blood red colour	Blue colour	

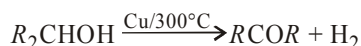
(d) Catalytic dehydrogenation

It involves the passing of vapours of alcohol over reduced copper at 300°C and the product thus formed is identified.

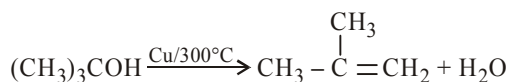
(i) Primary alcohols give aldehydes (dehydrogenation).



(ii) Secondary alcohols give ketones (dehydrogenation).



(iii) Tertiary alcohols form olefins (alkenes) by dehydration.



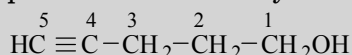
ILLUSTRATION

- 5 Compound X (C₅H₈O) does not react appreciably with Lucas reagent at room temperature but gives a white precipitate with ammoniacal silver nitrate solution. With excess of MeMgBr, 0.42 g of X gives 224 mL of CH₄ at STP. Treatment of X with H₂ in presence of Pt catalyst followed by boiling with HI, gives *n*-pentane. Suggest structure for X and write equations involved.

Soln.: As compound does not react with Lucas reagent it should be a primary alcohol, *i.e.* -CH₂OH group.

Compound gives a precipitate with silver nitrate hence it should have -C≡CH group.

The possible structure may be:



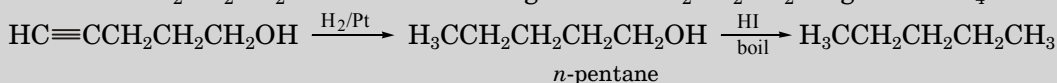
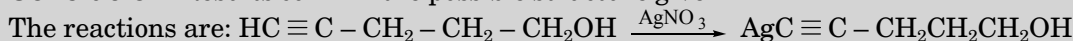
To determine molar ratio of CH₄ and compound:

Given: Molecular mass of X = 84

$$0.42 \text{ g of compound} = \frac{0.42}{84} = 0.005 \text{ mol} \qquad 224 \text{ mL of CH}_4 = \frac{224}{22400} = 0.01 \text{ mol}$$

0.005 mol of compound produces 0.01 mol of CH₄ indicating two active hydrogen atoms, one due to -C≡CH and the other due to -OH.

Conclusion: Results confirm the possible structure given

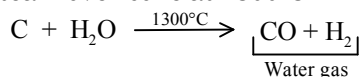


SOME COMMERCIALY IMPORTANT ALCOHOLS

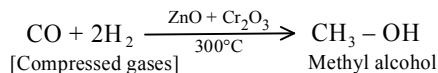
Preparation of Methyl Alcohol

(a) From water gas

Methyl alcohol obtained by this method is about 99% pure. The yield is also quantitative. Water gas is first formed by passing steam over coke at 1300°C.

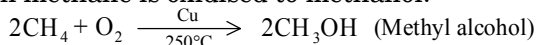


Water gas is mixed with half of its volume of hydrogen and the mixture is compressed to approximately 200-300 atmosphere. It is then passed over a catalyst (ZnO + Cr₂O₃) at 300°C, when methyl alcohol vapours are formed which can be condensed by means of a condenser.



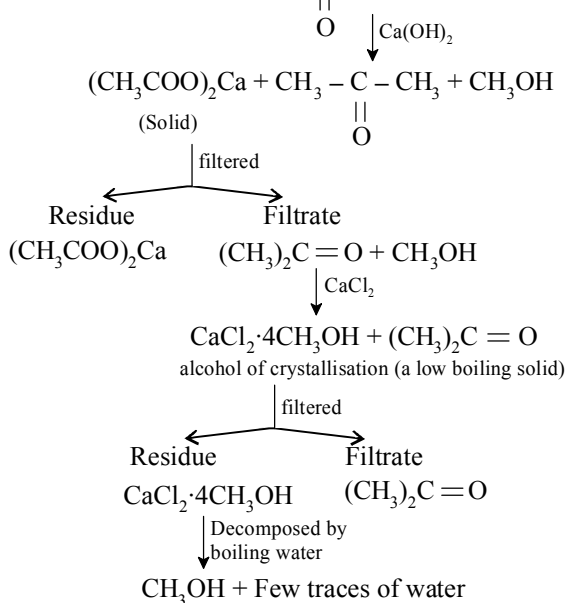
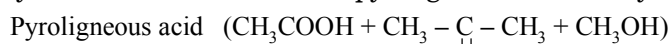
(b) From natural gas

A mixture of methane and oxygen (9:1 by volume) is passed over copper catalyst at 250°C under pressure (100 atm) when methane is oxidised to methanol.



(c) Commercial method

Methyl alcohol is obtained by destructive distillation of wood in absence of air. Distillate containing methyl alcohol is known as **pyroligneous acid** which is a mixture of acetic acid (7-10%), acetone (0.5%) and methyl alcohol (2.4 - 4.0%). From pyroligneous acid methyl alcohol can be separated as

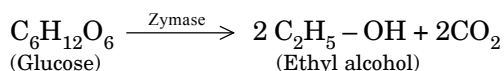
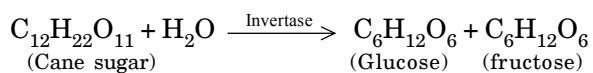


It can be distinguished by using anhydrous CuSO_4 which turns blue because of formation of blue vitriol ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$).

Preparation of Ethyl Alcohol

(a) From molasses

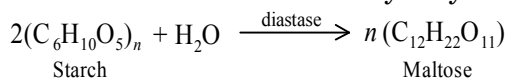
It is a dark brown coloured viscous liquid which contains mostly 50% sugar like sucrose, glucose and fructose. It is first diluted with water to get 8-10% of sugar solution. To this solution small quantity of dilute H_2SO_4 and some $(\text{NH}_4)_2\text{SO}_4$ is added to maintain the pH between 4 to 4.5. The solution is taken in a big tank and yeast is added, then the temperature is maintained at 30-40°C and left for few days. The yeast contains enzymes invertase and zymase, which bring about the conversion of sugar into ethyl alcohol.



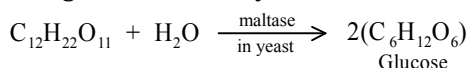
After completion of the process the resulting solution is filtered and from the filtrate ethyl alcohol is obtained by the process of distillation.

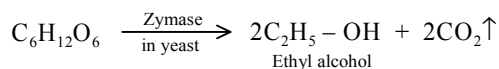
(b) From starch

Starch is obtained by boiling potatoes, rice, wheat, etc. When starch is mixed with barley (contains diastase an enzyme), it is converted to sugar known as maltose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$). Here, in presence of diastase starch is hydrolysed to maltose.



To the solution of maltose so obtained, now yeast is added at 30°C which furnishes enzymes maltase and zymase, maltase converts maltose into glucose, while the latter enzyme zymase converts glucose into ethyl alcohol.

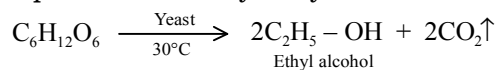




The ethyl alcohol so obtained is purified by fractional distillation.

(c) From glucose

Glucose solution is decomposed into ethyl alcohol and carbon dioxide under the influence of yeast which produces the enzyme zymase.



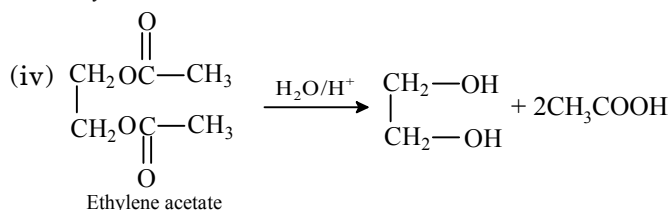
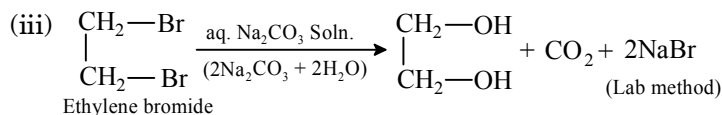
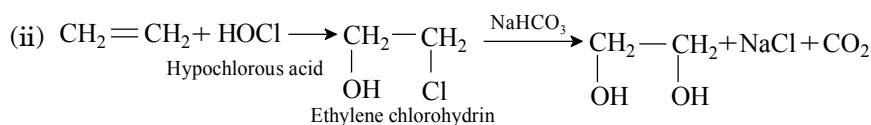
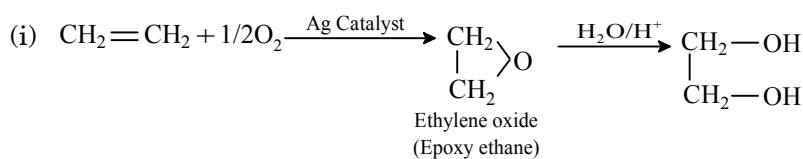
This conversion of glucose to ethyl alcohol in presence of zymase is known as **fermentation**.

POLYHYDROXY COMPOUNDS

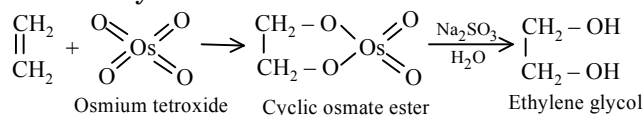
ETHYLENE GLYCOL

Preparation

It is simplest and most important dihydric alcohol. It is prepared by the following methods:



(v) Hydroxylation of a double bond can also be achieved by the action of osmium tetroxide (OsO_4) and the cyclic osmate ester thus formed on decomposition with ethanolic Na_2SO_3 solution gives glycol in quantitative yield.



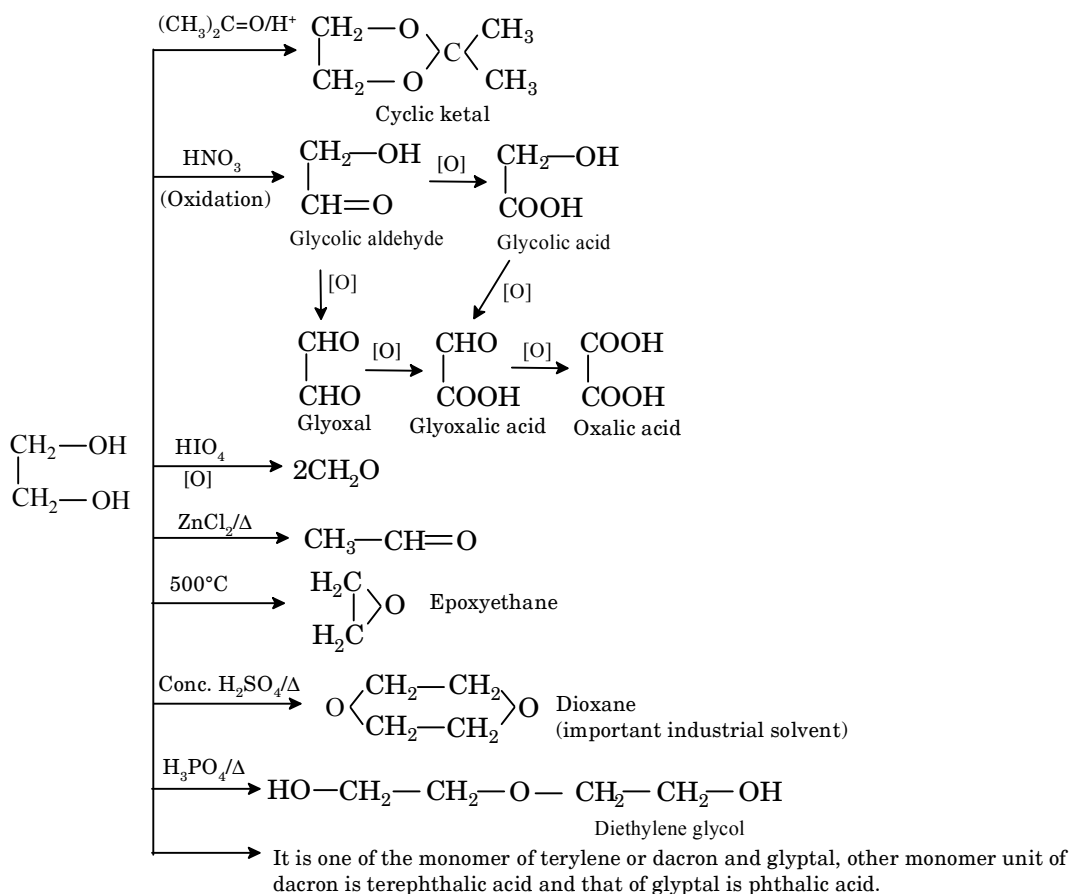
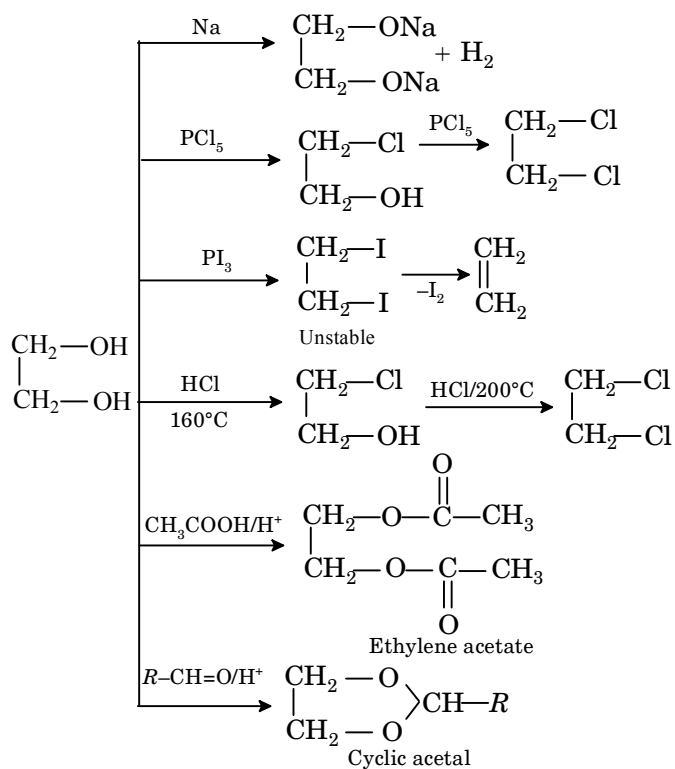
This reagent being very expensive and toxic is not used in routine laboratory preparation but is widely used in multistep organic synthesis where yields of the reactions are very important.

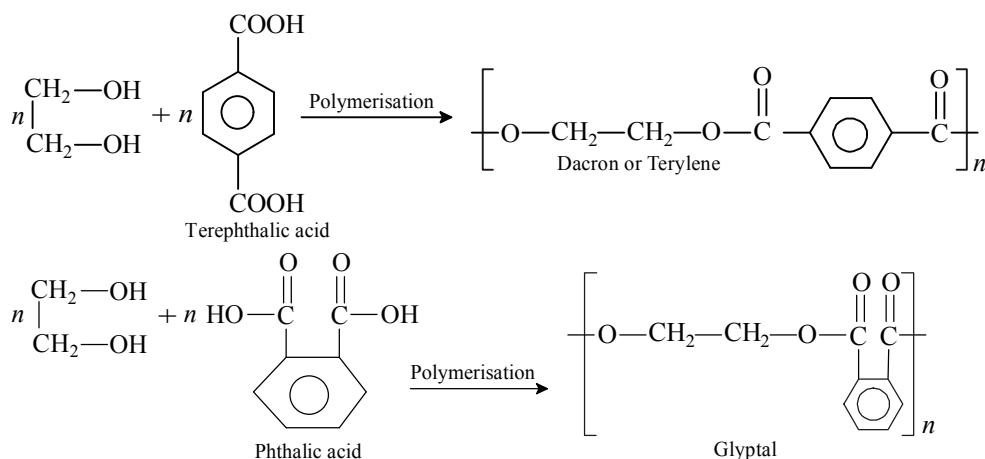
Physical Properties

- Ethylene glycol is colourless, viscous liquid with sweet taste hygroscopic nature.
- It is as toxic as methyl alcohol when taken orally.
- It has boiling point 197°C because of intramolecular H-bonding.

Chemical Properties

Ethylene glycol has two primary alcohol groups. The two $-\text{OH}$ groups however, are not equally reactive. Once one group is reacted then only reaction of the other $-\text{OH}$ group takes place. Reactions can be represented as

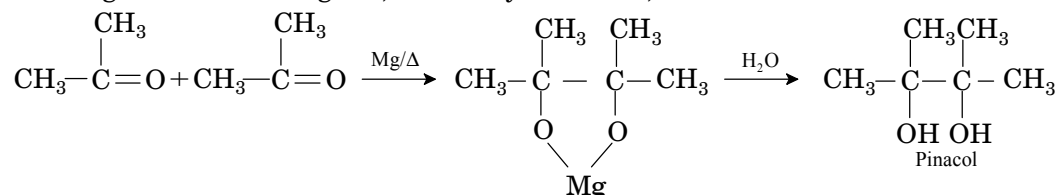




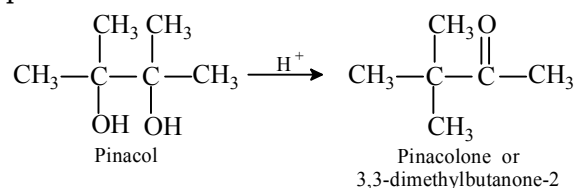
Note Ethylene glycol is used as anti-freeze for car radiators. An aqueous mixture containing 50% ethylene glycol freezes at 34°C and also used as de-icing fluid for aeroplane wings.

Pinacol-Pinacolone Rearrangement

- When two moles of acetone is heated with divalent active metal like magnesium followed by treating with water we get 2,3-dimethylbutane-2,3-diol (Pinacol) as—



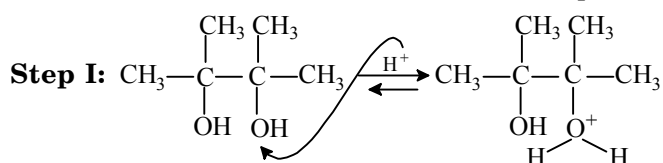
Completely substituted 1,2-diols produce aldehydes or ketones by rearrangement on treatment with mineral acids. During the reaction, there is first dehydration and then rearrangement to form carbonyl compounds. This reaction is called Pinacol-Pinacolone rearrangement.



The mechanism of above reactions involves following four steps:

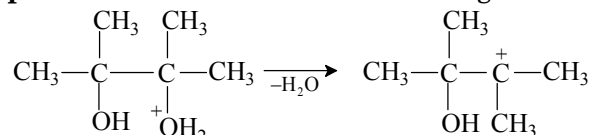
- Protonation of one of —OH, which in IInd step gives stable intermediate.
- Loss of water to give corresponding stable intermediate.
- 1, 2-shifting (migration) of H:, :R or :Ar to form a more stable cation or protonated ketone.
- Loss of proton to give product

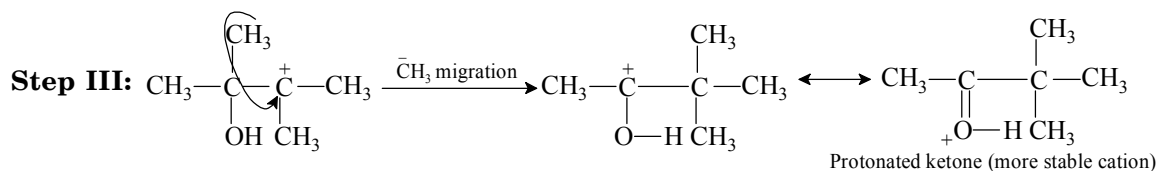
The mechanism of above reaction can be represented as -



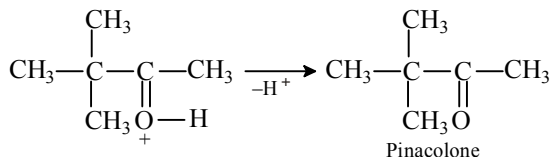
H⁺ will go to either of —OH group as given glycol is symmetrical one.

Step II: Removal of water molecule to get a carbocation.





Step IV: Loss of proton from protonated ketone to give pinacolone.

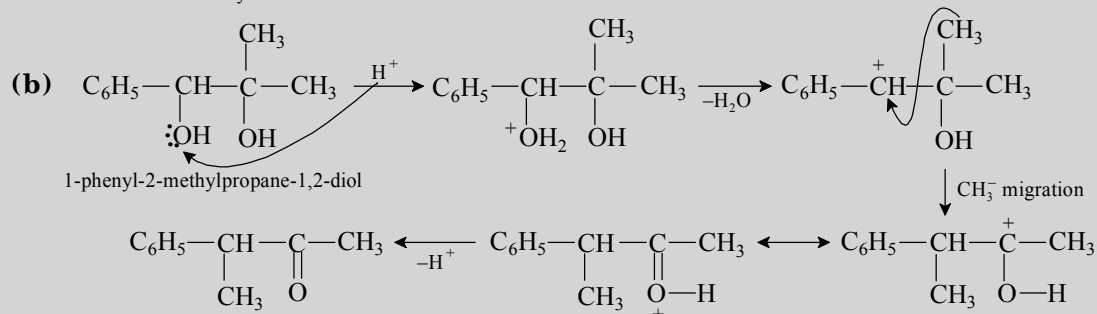
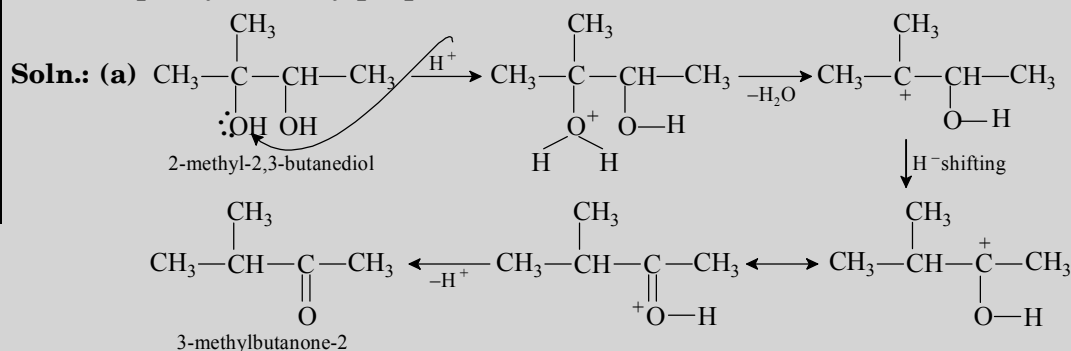


Note

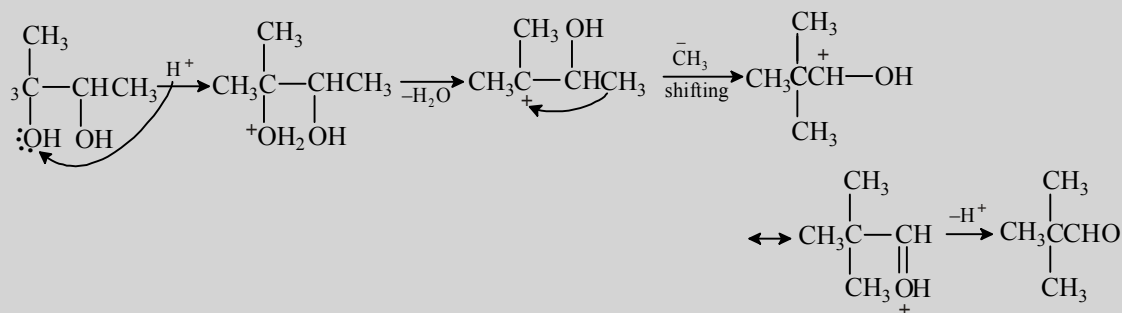
With unsymmetrical glycols, the product obtained is determined by removal of that -OH as water which gives more stable carbocation (Step II) and thereafter by which group migrates. It is observed that rearrangement aptitude follows: $\text{Ar} > \text{H} \text{ or } \text{R}$

ILLUSTRATION

- 6 Explain pinacol rearrangement in (a) 2-methyl-2,3-butanediol and (b) 1-phenyl-2-methylpropane-1,2-diol.



In case of (a) there may be $\bar{\text{C}}\text{H}_3$ shifting also as migratory tendency of H^- and $\bar{\text{C}}\text{H}_3$ are almost same hence we can get corresponding aldehyde too.

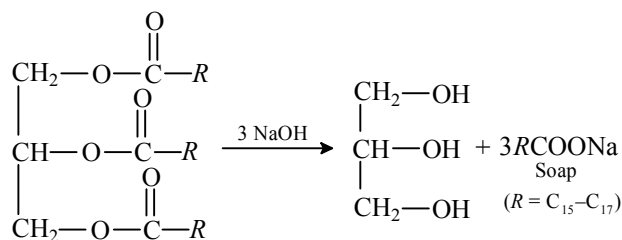


GLYCEROL OR GLYCERINE

It is a trihydric alcohol having one 2° alcohol and two 1° alcohols. Its IUPAC name is 1,2,3-propanetriol or propane-1,2,3-triol. It occurs in combined state as esters of fatty acids in almost all vegetables and animal oils.

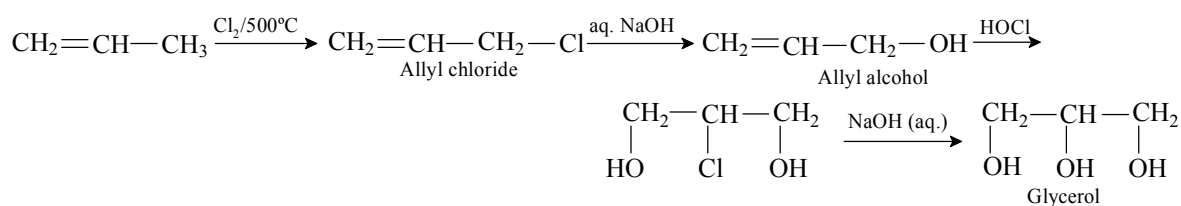
Preparation

- **By alkali hydrolysis of fats and oils** which are esters of fatty acid and glycerol. It is also said to be saponification which is irreversible in nature. Here alkyl part varies from C_{15} to C_{17} .

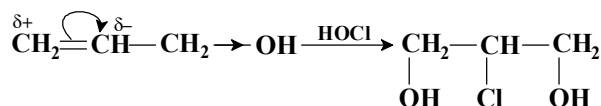


Generally this reaction is used for the manufacture of soap therefore glycerol is obtained as a byproduct from soap industry.

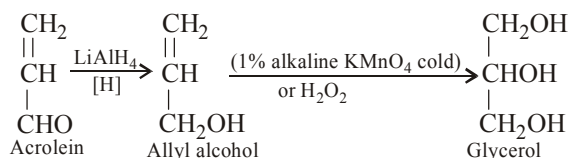
- **From propylene** ($\text{CH}_2 = \text{CH} - \text{CH}_3$): Propylene used for the manufacture of glycerol is obtained by the cracking of petroleum. Following steps are used :



Note At high temperature there is free radical substitution and allyl free radical formed is more stable and hence product is allyl chloride. Over allyl alcohol there is addition of HOCl which is like anti-Markownikoff's rule *i.e.* -ve part will go to that carbon of carbon-carbon double bond which has more number of hydrogen atoms. This is because of inductive effect by -OH group attached to sp^3 hybridized C-atom.



- Acrolein on reduction with LiAlH_4 gives allyl alcohol, which on treatment with Bayer's reagent gives glycerol.

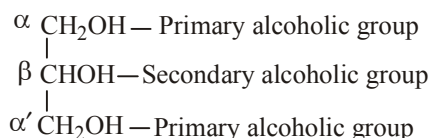


Physical Properties

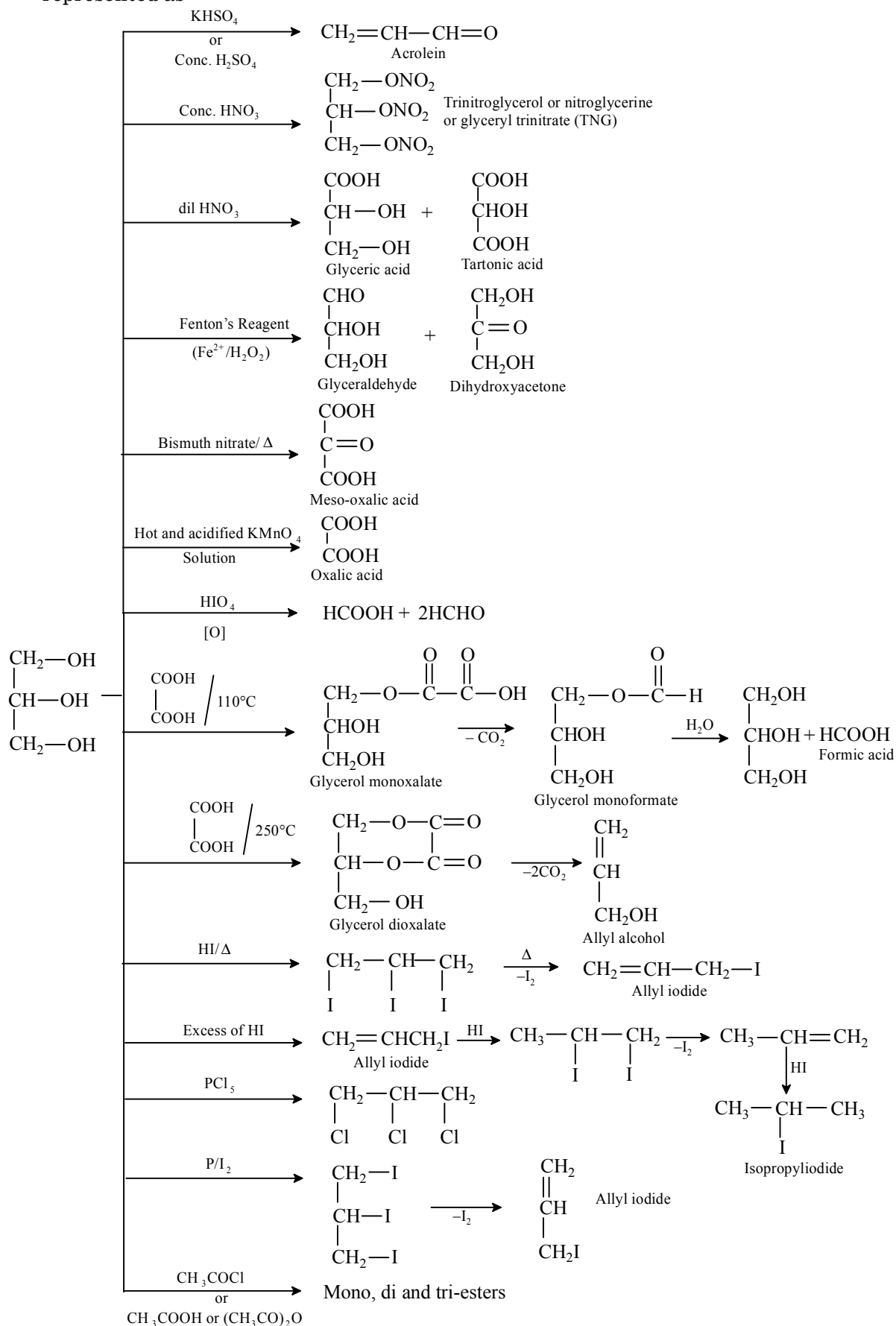
- Glycerol is colourless, odourless, viscous and hygroscopic liquid having sweet taste.
- It is non-toxic having boiling point 290°C .
- Viscous nature is because of association through hydrogen bonding.

Chemical Properties

- It contains primary and secondary alcoholic groups. In general primary alcohol is more reactive than the secondary alcohol.



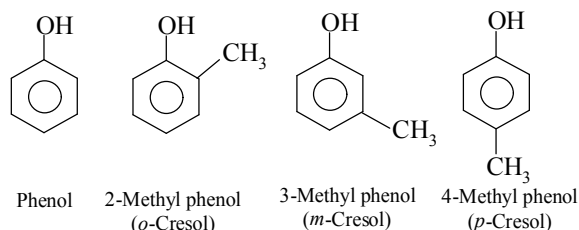
Thus, it shows characteristics of both primary and secondary alcohols. Reactions can be represented as



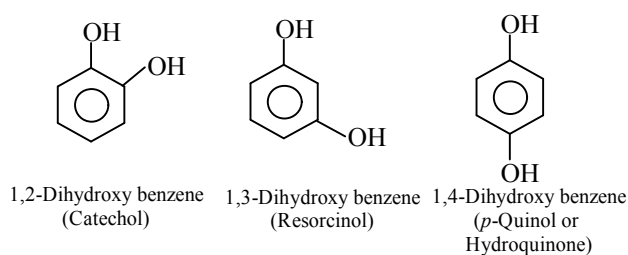
PHENOLS

Phenols are the aromatic compounds having hydroxyl group ($-\text{OH}$) directly attached to the benzene ring. Phenols are classified as mono, di and trihydric phenols according to the number of hydroxyl groups attached to the aromatic ring.

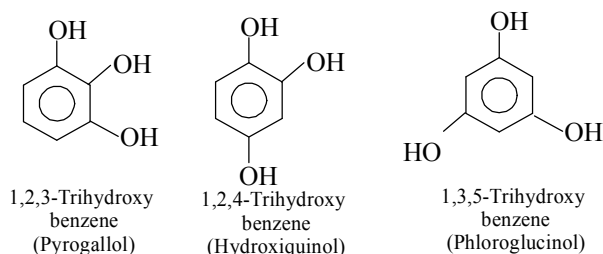
Monohydric phenols



Dihydric phenols



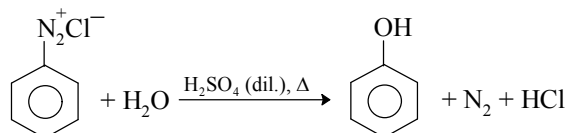
Trihydric phenols



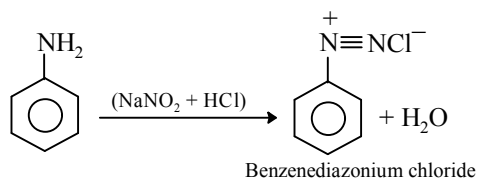
GENERAL METHODS OF PREPARATION

1. Hydrolysis of diazonium salts

Aqueous solution of diazonium salts on heating yield phenol.

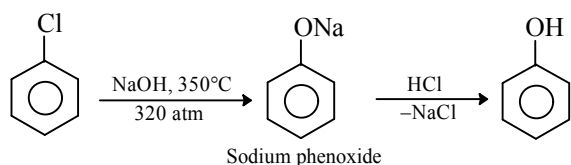


Diazonium salt itself is prepared by treating a primary amine with nitrous acid. The process is called **diazotization**.

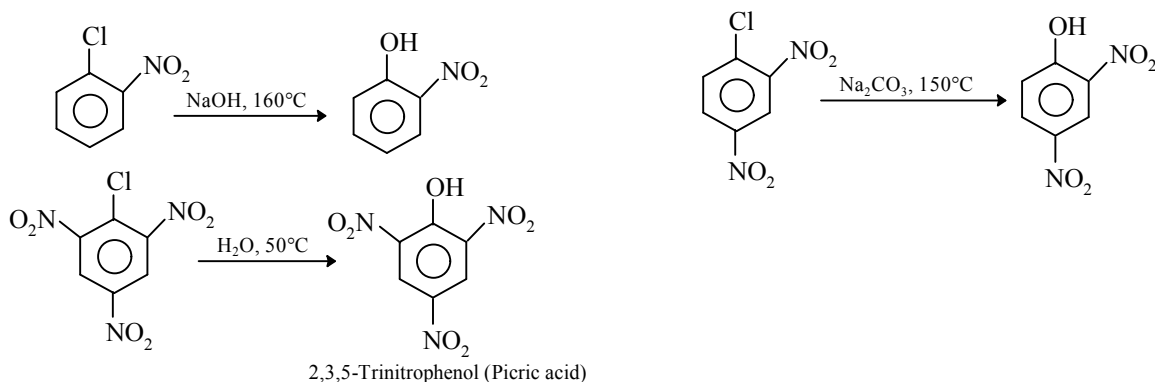


2. Hydrolysis of aryl halides (Dow's process)

Aryl halides on hydrolysis yield phenol but the process is not so simple because halogen atom attached to benzene ring does not undergo $\text{S}_{\text{N}}2$ reaction since $\text{C}-\text{X}$ bond is resonance stabilized. Hence reaction takes place at high pressure and elevated temperature.

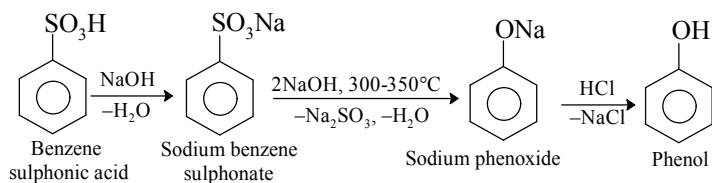


However if some electron withdrawing group is attached to benzene ring, then reaction conditions get relaxed.



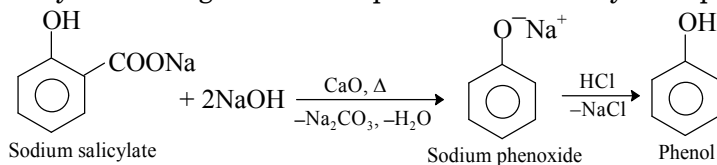
3. Alkali fusion of sulphonates

Sodium salt of aryl sulphonic acids on fusion with sodium hydroxide at 300-350°C yield phenol.



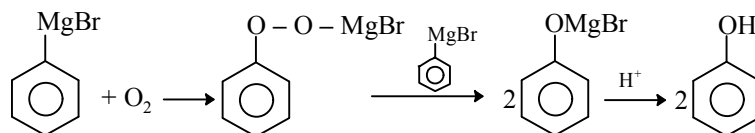
4. Decarboxylation of salicylic acid

Sodium salt of salicylic acid on distillation with sodalime (NaOH + CaO) undergoes decarboxylation to give sodium phenoxide which yields phenol on acidification.



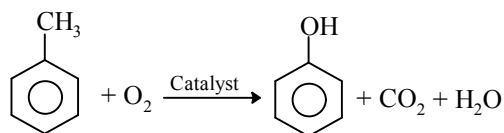
5. Oxidation of Grignard reagent

Etheral solution of phenyl magnesium bromide adds up molecular oxygen when bubbled through it to give an addition product which on treatment with acid gives phenol.



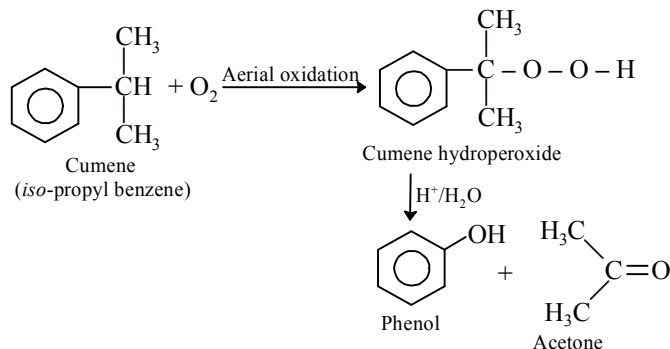
6. Oxidation of aromatic hydrocarbons

Catalytic oxidation of toluene by air in presence of cupric salt yields phenol on large scale.

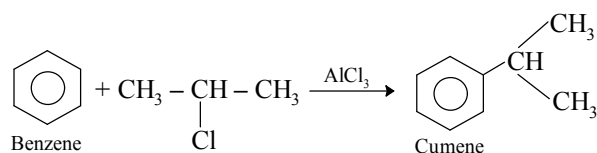


7. From cumene (*iso*-propyl benzene)

This is the widely used commercial method for preparation of phenol. Cumene on aerial oxidation forms cumene hydroperoxide which upon hydrolysis gives phenol and acetone.



Cumene itself is prepared by Friedel Crafts alkylation of benzene with 2-chloropropane.



8. From natural sources

Phenol is prepared commercially from middle fraction of coal-tar distillation also. We can obtain considerable amount of phenols, cresols, dihydroxy and trihydroxyphenols, etc.

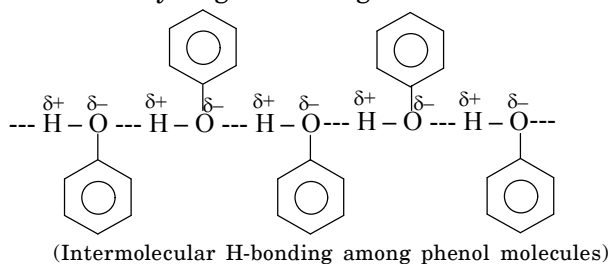
PHYSICAL PROPERTIES

(i) Physical state

Phenols are colourless liquids or low melting solids. But they turn reddish brown due to auto-oxidation on exposure to air and light.

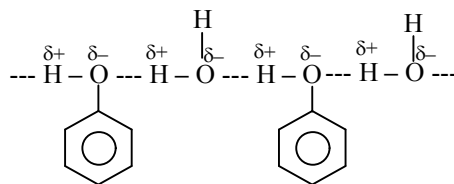
(ii) Boiling point

Phenols have much higher boiling points than the corresponding hydrocarbons due to intermolecular hydrogen bonding.



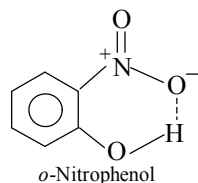
(iii) Solubility

Phenols form H-bonds with water molecules and hence soluble in water. But their solubility is lower than that of alcohols because of large hydrocarbon part.



(iv) Melting point

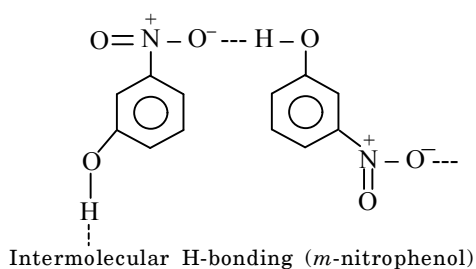
Amongst the isomeric nitrophenols, *o*-nitrophenol has much lower melting point and solubility than *meta* and *para*-isomers of nitrophenol because of intramolecular hydrogen bonding. Thus it does not undergo association with other molecules or molecule of water which results in low melting point and solubility. In fact, *ortho*-nitrophenol is steam volatile.



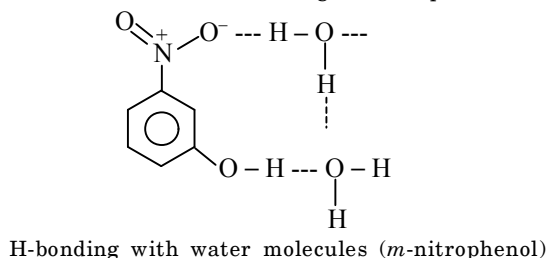
o-Nitrophenol

(Intramolecular H-bonding)

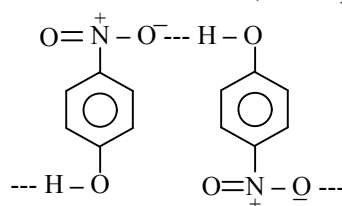
On the other hand, *meta* and *para*-nitrophenols exhibit intermolecular H-bonding with their own molecules as well as with water molecules and hence show comparatively higher melting point and solubility.



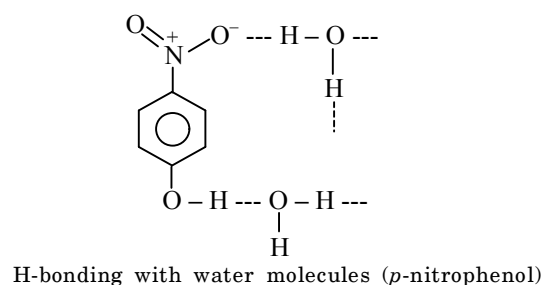
Intermolecular H-bonding (*m*-nitrophenol)



H-bonding with water molecules (*m*-nitrophenol)



Intermolecular H-bonding (*p*-nitrophenol)



H-bonding with water molecules (*p*-nitrophenol)

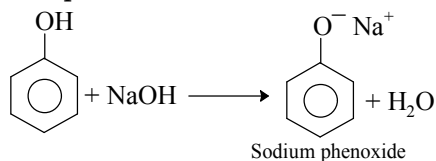
CHEMICAL PROPERTIES

Phenols generally do not give the reactions involving cleavage of C – OH bond since C – O bond acquires double bond character due to resonance. But they readily undergo the reactions involving cleavage of O – H bond reflecting their acidic nature and also undergo electrophilic substitution reaction of benzene ring.

(A) Reactions involving cleavage of O – H bond

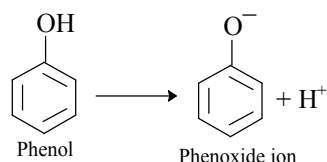
1. Acidic character of phenols

Phenols possess some acidic character and form salt with aqueous hydroxide.

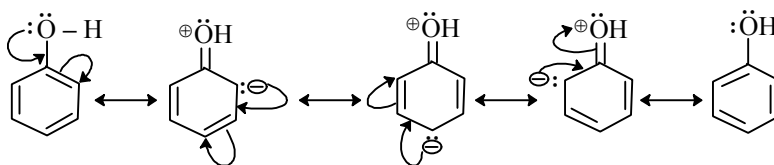


Thus phenols are stronger acids, ($K_a = 10^{-8}$ to 10^{-10}) than water. ($K_w = 10^{-14}$). But phenols are weaker acids than carboxylic acids ($K_a = 10^{-5}$) or even carbonic acid ($K_a = 10^{-7}$). Since they do not decompose carbonates and bicarbonates.

Phenols are stronger acids than alcohols ($K_a = 10^{-16}$ to 10^{-18}).

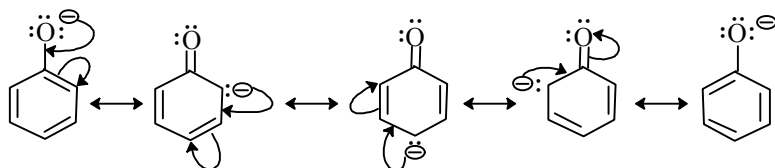


Phenol is resonance stabilised.

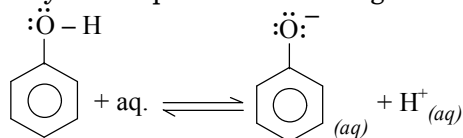


As we can see that by virtue of resonance oxygen atom acquires partial positive charge which weakens the O – H bond and thus facilitates the release of a proton.

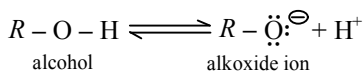
Phenoxide ion is also stabilised by resonance through following structures.



Thus in case of phenols, both phenol and phenoxide ion are resonance stabilised. Phenoxide ion is more stable than phenol, since it comprises only dispersal of negative charge whereas in phenol, separation of both positive and negative charge takes place. In addition to it, in phenol, highly electronegative oxygen atom carries positive charge which also affects the stability. Thus phenol has strong tendency to get converted to more stable phenoxide ion.



On the other hand neither alcohol nor alkoxide ion is resonance stabilised. Even alkoxide ion is less stable than alcohols due to presence of formal negative charge.

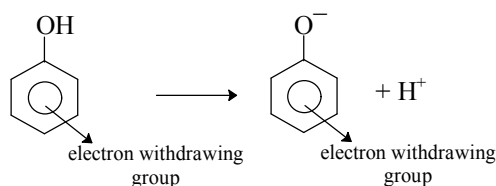


Thus, alcohols have less tendency to get converted to alkoxide ions by release of proton. Therefore, phenols are stronger acids than alcohols since they have greater tendency to lose protons to form more stable phenoxide ion.

Effect of substituents on acidic strength of phenols

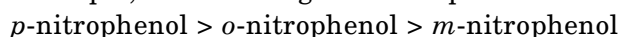
Acidic strength of phenols is explained by higher stability of phenoxide ion than phenol. Thus any group or substituent which increases the stability of phenoxide ion will increase the acidic strength.

- (i) An electron withdrawing group like $-\text{NO}_2$, $-\text{CN}$, $-\text{COOH}$, $-\text{X}$ (halogens), etc. stabilises the phenoxide ion by dispersing the negative charge. Thus it increases the acidic strength of phenols.



- The effect is however more pronounced at *ortho* and *para*-position. Higher the number of electron withdrawing groups at *o/p* positions, higher is the acidic strength.

For example, acidic strength of nitrophenol is in the order



Due to intramolecular hydrogen bonding *ortho*-nitrophenol is slightly less acidic than *para*-isomer.

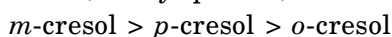
Further, 2,4,6-trinitrophenol > 2,4-dinitrophenol > 4-nitrophenol

> 2-nitrophenol > phenol

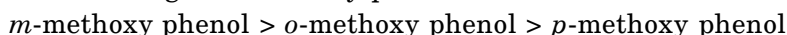
- Similarly for chlorophenol order of acidic strength is given as: *o*-chlorophenol > *m*-chlorophenol > *p*-chlorophenol.

Acidic strength of chlorophenol decreases with the increasing distance of $-\text{Cl}$ from $-\text{OH}$ group.

- (ii) Electron donating groups like $-\text{R}$, $-\text{OR}$, $-\text{NH}_2$, etc. destabilise the phenoxide ion by intensifying the negative charge of phenoxide. Thus it decreases the acidic strength of phenols. Effect of electron donating group is more pronounced at *ortho* and *para*-position, e.g., acidic strength of cresols (methyl phenol) is in the order



Acidic strength of methoxy phenol is in the order



- 7 Arrange the following groups of compounds according to their relative acid strengths:

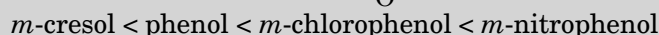
(a) phenol, *m*-chlorophenol, *m*-nitrophenol, *m*-cresol

(b) phenol, *p*-chlorophenol, *p*-nitrophenol, *p*-cresol

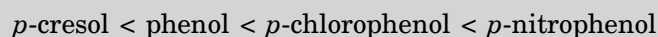
(c) phenol, *o*-nitrophenol, *m*-nitrophenol, *p*-nitrophenol

(d) phenol, *p*-chlorophenol, 2, 4, 6-trichlorophenol, 2, 4-dichlorophenol.

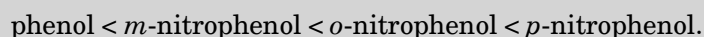
Soln.: (a) The electron withdrawing effect of $-\text{NO}_2$ is greater than $-\text{Cl}$ as it has +ve charge on N-atom.



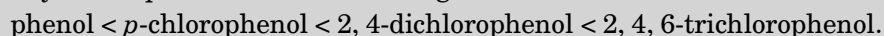
(b) *p*- NO_2 shows greater resonance effect as compared to *p*-Cl. The *p*- CH_3 is an electron releasing group.



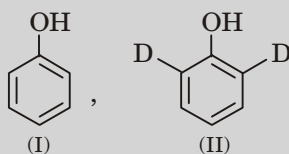
(c) The *ortho*-isomer shows intramolecular hydrogen bonding and is therefore weaker than the *para*-isomer.



(d) Acidity will depend on number of halogen atoms



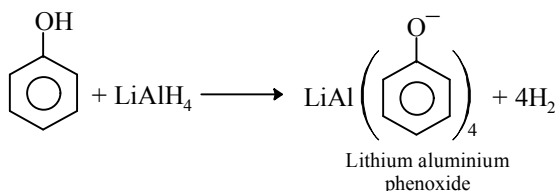
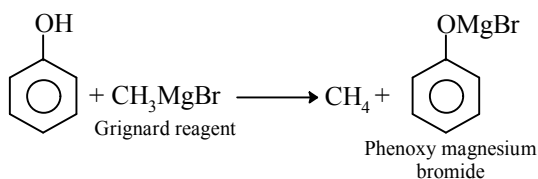
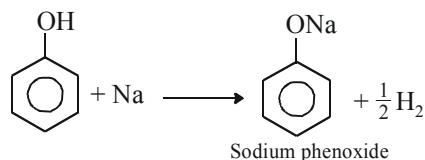
8 Which has higher value of K_a ?



Soln.: (II) < (I), because more +I effect of D than H.

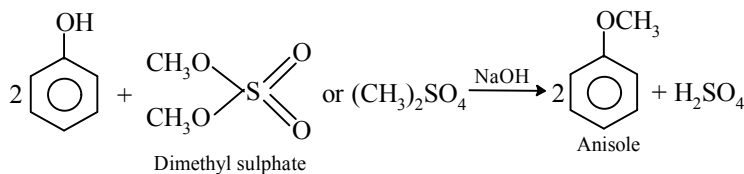
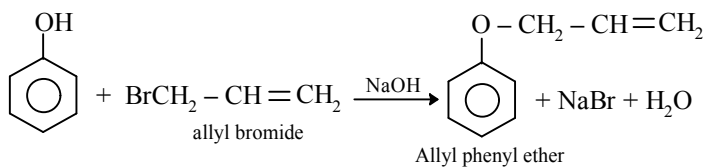
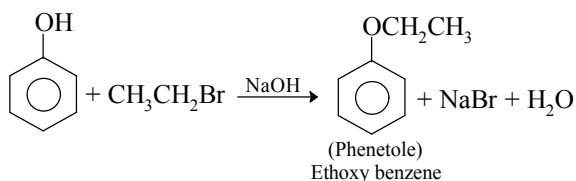
2. Salt formation

Phenols react with alkali metals, Grignard reagent and lithium aluminium hydride to form metal phenoxide.



3. Ether formation

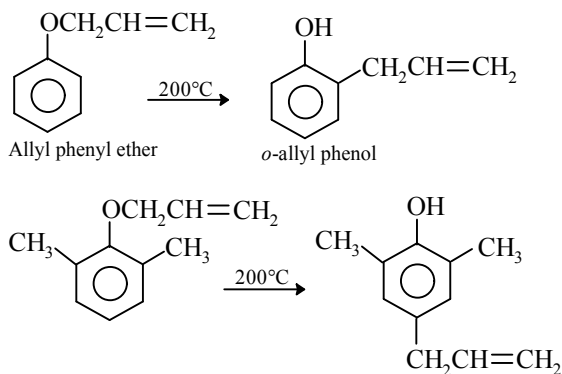
Phenols result in ether formation either on reaction with alkyl halides or with dialkyl sulphate in alkaline solution.



Formation of ether by phenoxide ion on reaction with alkyl halide is known as **Williamson's Synthesis**.

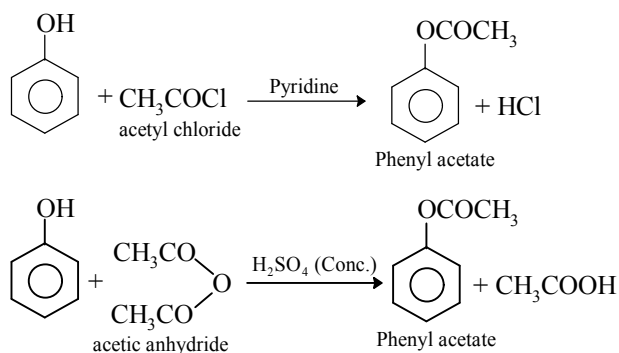
Claisen Rearrangement

Allyl aryl ethers on heating rearrange to allyl phenols. Allyl group migrates to *ortho*-position. If *ortho*-position is already occupied, then *para*-isomer is obtained.

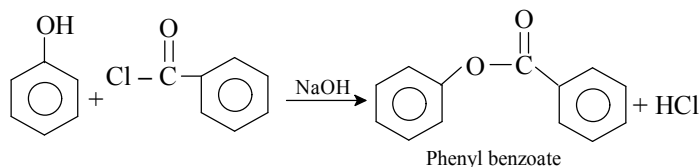


4. Ester formation

Phenols being weakly nucleophilic in nature do not form esters directly on reaction with carboxylic acids. But they can undergo ester formation with acid chlorides and acid anhydrides to give better yield. Reaction with acetyl chloride or acetic anhydride is known as **acylation**.



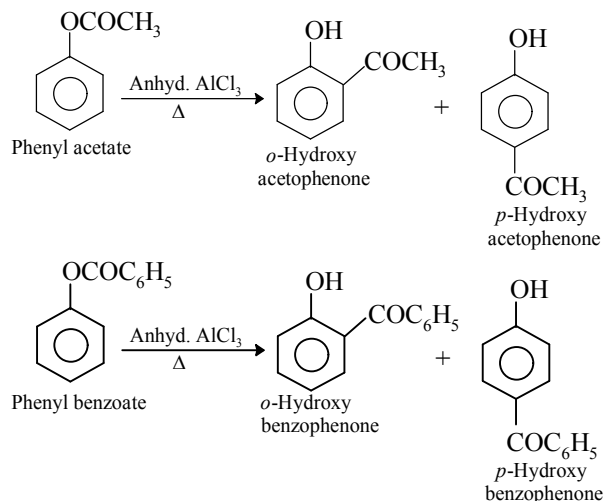
Reaction with benzoyl chloride is known as **benzoylation**.



Benzoylation of alcohols or phenols in presence of NaOH is called **Schotten-Baumann reaction**.

Fries rearrangement

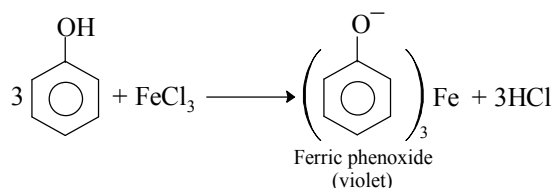
Phenyl esters on heating with anhydrous AlCl_3 undergo Fries rearrangement in which acyl group (acetyl, benzoyl, etc.) migrates from phenolic oxygen to *ortho* or *para*-position of benzene ring resulting in the formation of mixture of *o*- and *p*-hydroxyketone.



This reaction actually involves generation of acylium ion RCO^+ , which then attacks the ring as in ordinary **Friedel Crafts acylation**.

5. Reaction with ferric chloride

Phenol reacts with ferric chloride to give ferric phenoxide having characteristic violet colour.



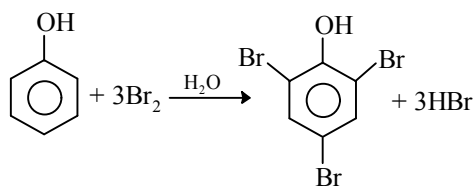
In fact compounds whether aliphatic or aromatic containing the enol group. *i.e.* $=\text{C}-\text{OH}$ gives characteristic colours with neutral FeCl_3 .

(B) Electrophilic aromatic substitution reactions

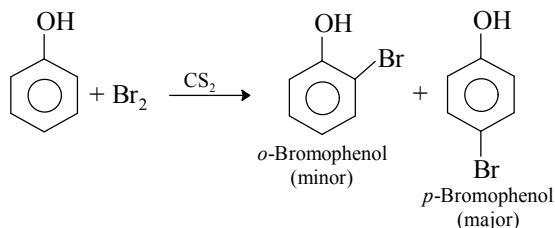
Phenols readily undergo electrophilic aromatic substitution reactions at *ortho* and *para*-positions due to activating effect of $-\text{OH}$ group.

1. Halogenation

With aqueous solution of chlorine or bromine phenol results in trihalogen derivatives.



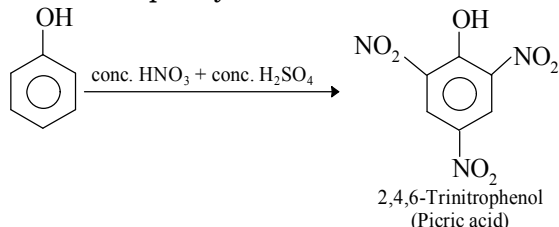
However if the solvent of low polarity like chloroform or carbon disulphide is used, then reaction can be limited to monosubstitution.



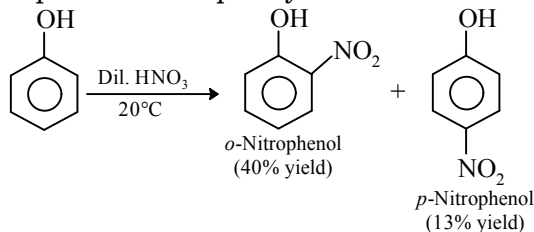
Due to steric hindrance at *ortho*-position, *para*-product predominates.

2. Nitration

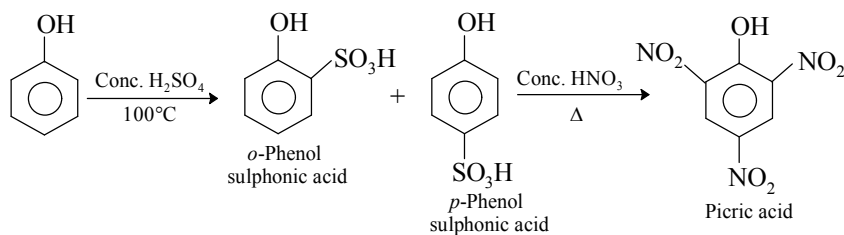
Phenol on reaction with conc. HNO_3 in presence of conc. H_2SO_4 yields 2,4,6-trinitrophenol (picric acid) in poor yield since the reaction is associated with considerable oxidation.



However, if reaction is carried out with dil. HNO_3 at low temperature, then mononitration takes place with a poor yield due to considerable oxidation of ring by acid.

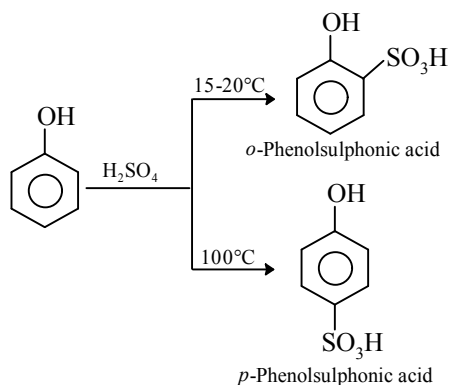


Picric acid with good yield can be produced by following scheme of reactions.



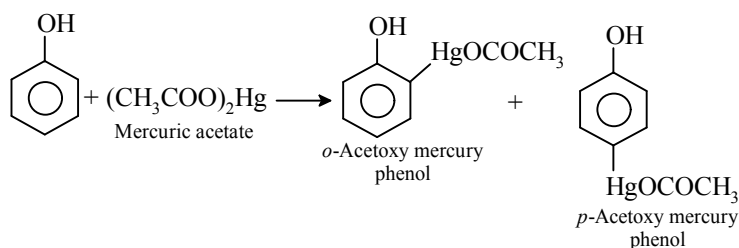
3. Sulphonation

On treatment with concentrated sulphuric acid, phenol yields phenolsulphonic acid. At low temperature, *ortho*-product predominates whereas at high temperature *para*-product predominates.



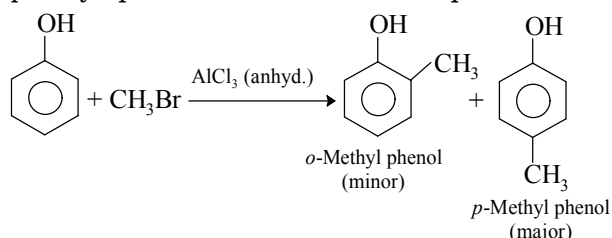
4. Mercuration

When refluxed with mercuric acetate, phenol undergoes mercuration.

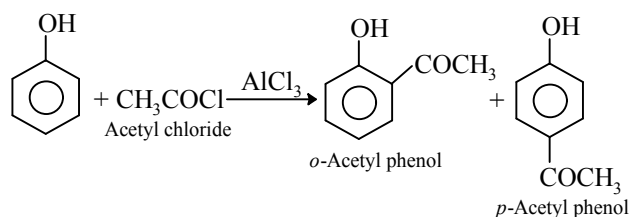


5. Friedel Crafts alkylation and acylation

Phenols on treatment with alkyl halides in presence of Lewis acid result in formation of *o*- and *p*-alkyl phenols which can be separated through steam distillation.

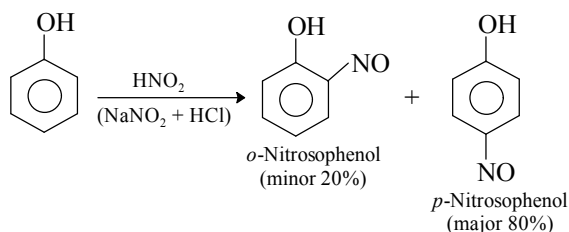


– Whereas on reaction with acyl halides in presence of Lewis acid, *o*- and *p*-acyl phenols are formed.



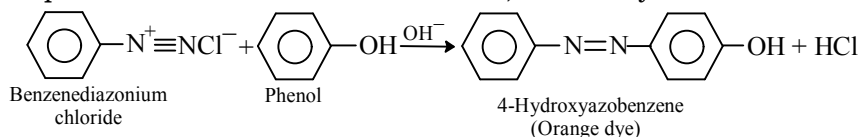
6. Nitrosation

o- and *p*-nitrosophenols are produced by the action of nitrous acid on phenol.



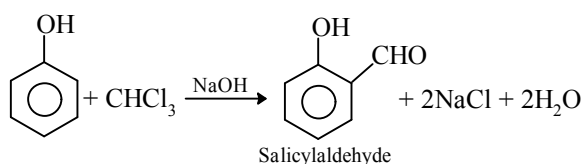
7. Coupling with diazonium salts

Phenols couple with benzenediazonium salts in weakly alkaline solution to form *p*-hydroxy azo compounds with a characteristic colour, commonly known as azo dyes.



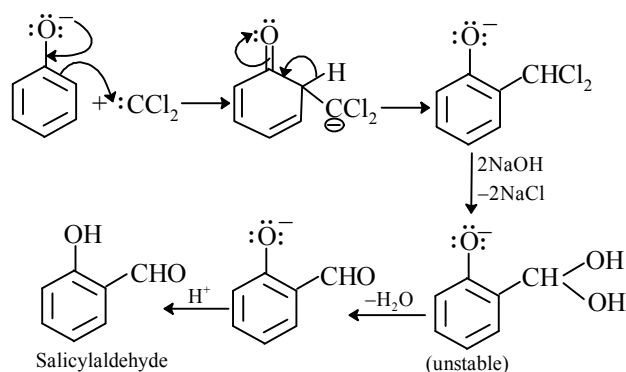
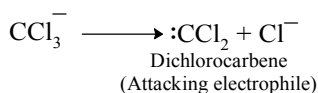
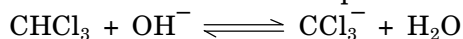
8. Reimer-Tiemann reaction

Phenols on reaction with chloroform in presence of aqueous sodium or potassium hydroxide solution followed by acidification yield 2-hydroxybenzaldehyde *i.e.* salicylaldehyde.

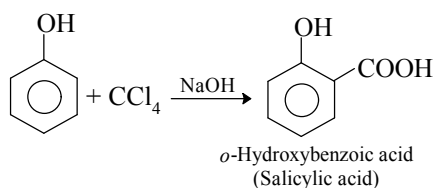


Mechanism

Reaction mechanism involves the electrophilic attack by dichlorocarbene generated from chloroform.

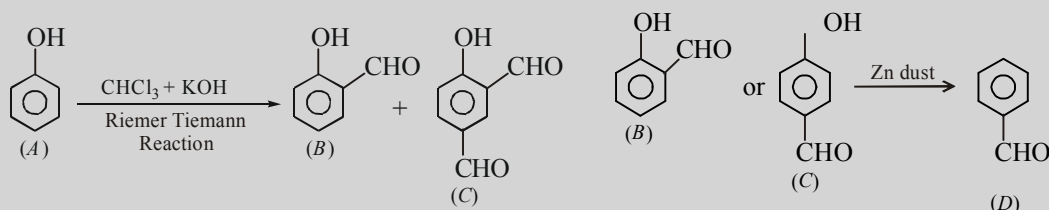


If the reaction is carried out with carbon tetrachloride (CCl_4) instead of chloroform, *o*-hydroxybenzoic acid (salicylic acid) is formed.



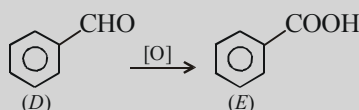
- 9 An organic aromatic compound (A) on treatment with CHCl_3 and KOH gives (B) and (C), both of which on distillation with Zn dust give the same compound (D). Oxidation of D yields (E) with formula $\text{C}_7\text{H}_6\text{O}_2$. The sodium salt of (E) on heating with sodalime gives (F) which is also obtained by distilling (A) with Zn dust. Identify (A) to (F).

Soln: Reactions suggest that (A) could be phenol, the reactants CHCl_3 and KOH are used for Reimer Tiemann reaction:

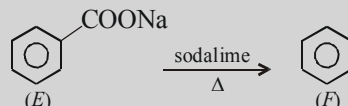


Zn dust distillation of (B) and (C) yields (D).

(D) is an aldehyde which on oxidation will yield (E) an acid.

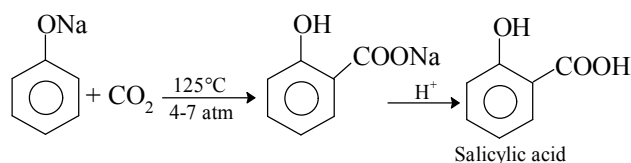


Heating of sodium salt of an acid with sodalime yields a hydrocarbon, the reaction is

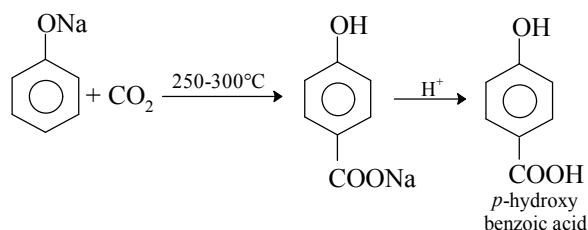


9. Kolbe's reaction

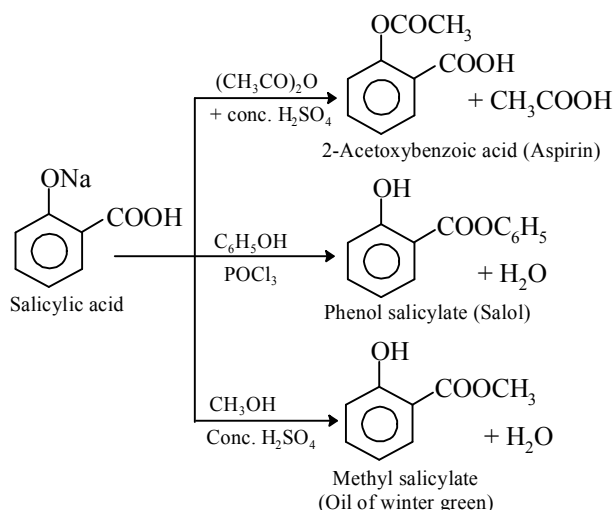
Sodium phenoxide on heating with carbon dioxide at 125°C and 4-7 atm pressure followed by acidification yields *o*-hydroxy benzoic acid (Salicylic acid) predominantly.



If the reaction is carried out at high temperature ($250\text{-}300^\circ\text{C}$), *p*-hydroxybenzoic acid is produced.

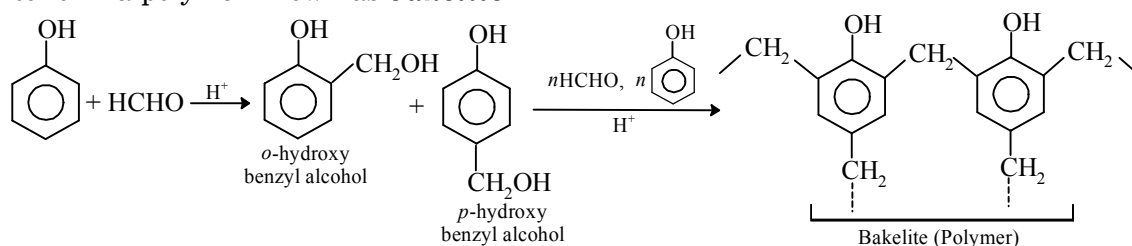


Salicylic acid is a starting material for number of useful chemicals such as **aspirin** (2-acetoxybenzoic acid) which is widely used as **analgesic** (pain reliever) and antipyretic (to lower body temperature during fever), **salol** (phenol salicylate) used as an intestinal antiseptic and oil of winter green (methyl salicylate), flavouring agent in food, drinks, etc.



10. Condensation with formaldehyde

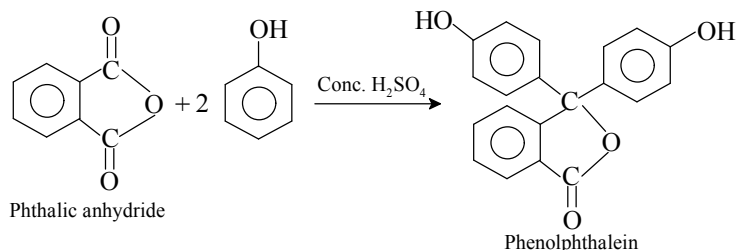
Phenol condenses with formaldehyde at *ortho* and *para*-positions in presence of acid or base to form a polymer known as **bakelite**.



(C) Other reactions of phenol

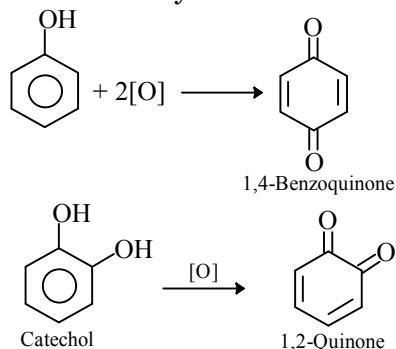
1. Phthalein reaction

Phenols or substituted phenols condense with phthalic anhydride in presence of conc. H_2SO_4 or ZnCl_2 to form **phthaleins** or **fluoresceins**.

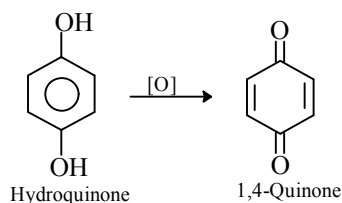


2. Oxidation

Phenols are easily oxidised with mild oxidising agents or even with air (auto-oxidation).

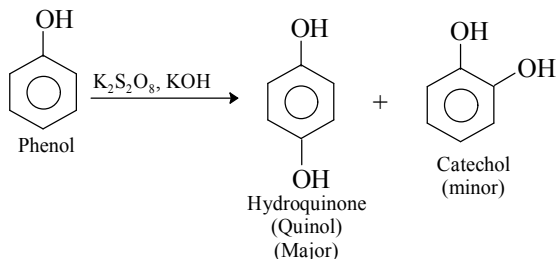


Because of this property phenols are used as anti-oxidants in gasoline, rubber, etc. Phenols readily react with oxygen shielding other organic compounds from oxidation and thus act as anti-oxidants.



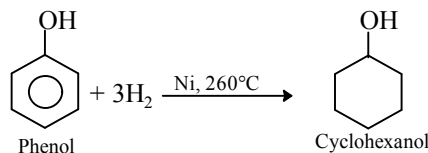
Elbs persulphate oxidation

Monohydric phenols are oxidised to dihydric phenols by the action of alkaline potassium persulphate. Next -OH group gets introduced generally at *para*-position, but if *para*-position is blocked then *o*-dihydric phenols are produced.

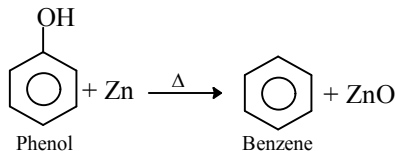


3. Reduction

Phenols undergo reduction with hydrogen in presence of finely divided nickel at 260°C.

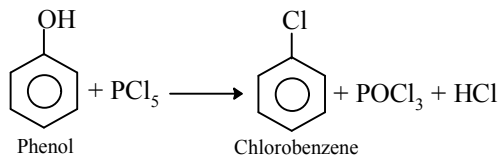


With zinc powder, phenol is reduced to benzene.



4. Reaction with phosphorus halides

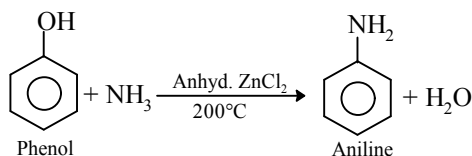
-OH group of phenols can be replaced by highly reactive PCl₅ to form chlorobenzene. The reaction is not possible with HX or PCl₃.



However the yield is poor due to formation of by-products like triaryl phosphate.

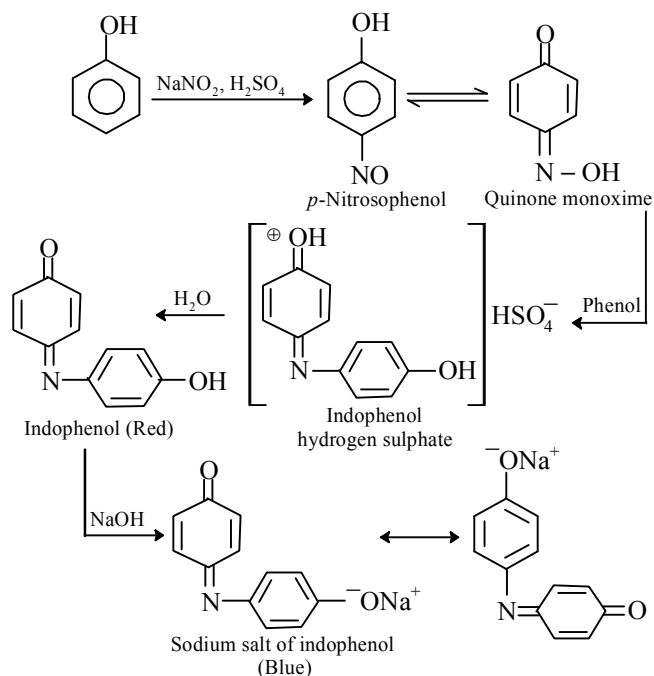
5. Reaction with ammonia

When phenol is heated with ammonia under pressure in presence of anhydrous ZnCl₂, -OH group is replaced by -NH₂ to form aniline.



6. Liebermann's nitroso reaction

Phenols on reaction with sodium nitrite and concentrated sulphuric acid give blue colouration which changes to red on dilution. However in alkaline solution blue colour is restored by following sequence of reactions.



This reaction is used as test for identification of phenols.

Tests to distinguish between alcohols and phenols

1. Litmus test

Phenol turns blue litmus red being acidic in nature but alcohols do not.

2. Ferric chloride test

Phenols react with neutral ferric chloride solution to form violet or green coloured solution whereas alcohols do not undergo such reactions.

3. Bromine water test

Aqueous solution of phenol forms white precipitate of 2,4,6-tribromophenol, when treated with bromine water. However alcohols do not give such precipitation.

4. Coupling test

Phenols couple with diazonium salts in slightly basic solution to form coloured azo dyes whereas alcohols do not undergo coupling reaction.

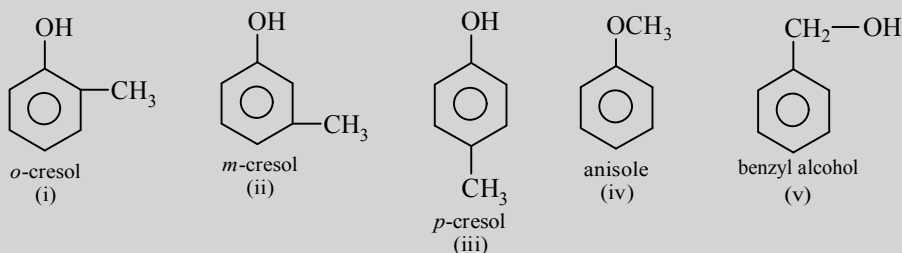
5. Liebermann's nitroso test

Phenols on reaction with sodium nitrite and sulphuric acid form a green or blue coloured solution which changes to red on dilution and back to blue if the solution is made alkaline. Alcohols do not undergo Liebermann's test.

ILLUSTRATION

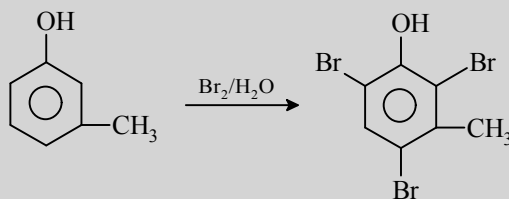
- 10 How many isomeric forms are possible for $\text{C}_7\text{H}_8\text{O}$? Which structure among the isomeric forms in spite of giving characteristic colour with FeCl_3 reacts with $\text{Br}_2/\text{H}_2\text{O}$ to give a precipitate of $\text{C}_7\text{H}_5\text{OBr}_3$?

Soln.: It is represented by following five isomeric forms:



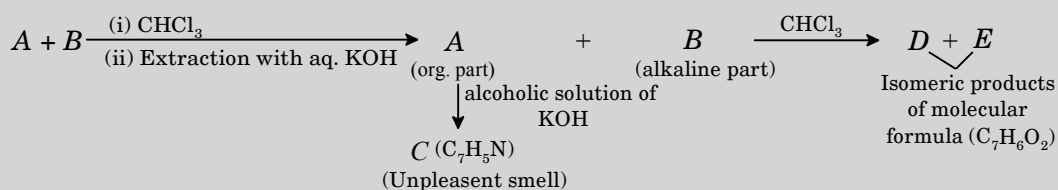
(i), (ii) and (iii) all these give characteristic colour with FeCl_3 , react with NaOH but do not react with NaHCO_3 solution.

Because of strong activation if a group is already present at *ortho*- and *para*-position to phenol, it is replaced by incoming electrophile when treated with $\text{Br}_2/\text{H}_2\text{O}$. Thus according to question $\text{C}_7\text{H}_8\text{O}$ will be *m*-cresol which when treated with $\text{Br}_2/\text{H}_2\text{O}$ gives $\text{C}_7\text{H}_5\text{OBr}_3$ as



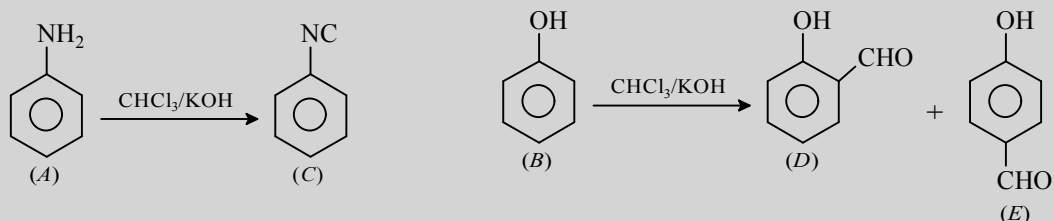
- 11 A mixture of two aromatic compounds (A) and (B) is separated by dissolving chloroform followed by extraction with aqueous KOH . Organic part containing (A) when heated with alcoholic solution of KOH produced a compound (C) ($\text{C}_7\text{H}_5\text{N}$) of unpleasant smell. The alkaline aqueous layer on the other hand, when heated with chloroform and then acidified gives a mixture of two isomeric products D and E of molecular formula $\text{C}_7\text{H}_6\text{O}_2$. Identify A to E and write the structure.

Soln.: The question can be summarised as



It is known that if an organic compound when treated with chloroform in the presence of alkali gives unpleasant odour, compound will be either primary amine or aniline. This reaction is known as carbylamine reaction.

Also it is known that an organic compound when treated with chloroform and alkali gives isomeric product which will be phenol. This reaction is known as Reimer-Tiemann reaction. Thus (A) will be aniline as given compound is aromatic compound and (B) will be phenol.



ETHERS

Ethers have a general formula $R - O - R'$ where R and R' may be same or different and regarded as alkyl oxide or anhydrides of alcohol. Ethers are isomeric with monohydric alcohols. For example, $\text{C}_2\text{H}_6\text{O}$ has two functional isomers.



Ethers may be classified as aliphatic and aromatic ethers. If both R and R' groups are alkyl groups, then ether is **aliphatic ether**. For example,

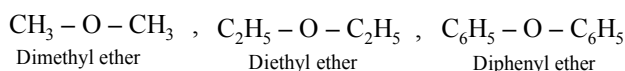


If both R and R' or any of them is aryl group, then ether is **aromatic ether**. For example,

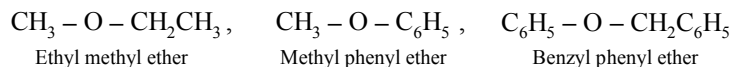


Ethers may also be classified as symmetrical and unsymmetrical ethers. If the two groups

R and R' present in ether are same then ether is known as **simple** or **symmetrical ether**. For example,



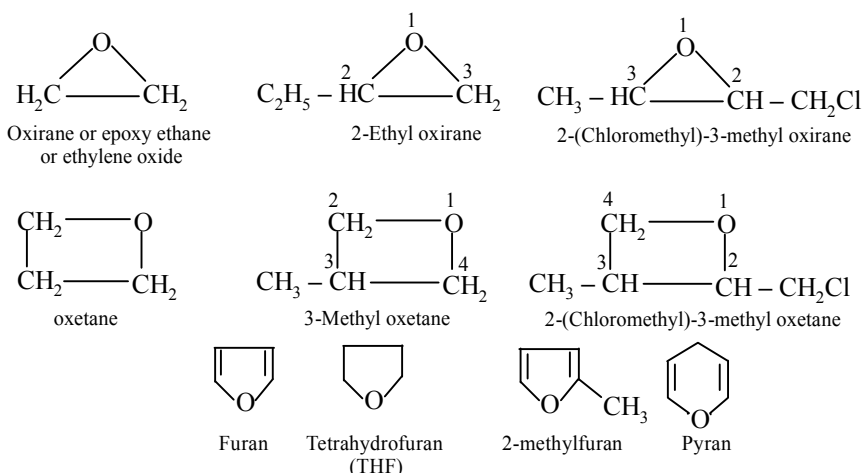
If ether molecule has two different groups in the molecule, the ether is known as **mixed** or **unsymmetrical ethers**. For example,



Cyclic ethers containing three and four-membered rings are called oxiranes and oxetanes respectively.

Epoxides are more reactive than large ring cyclic ethers because of the Baeyer strain (angle strain) associated with small rings.

Ethers may be open chain compounds or cyclic ring compounds. Three membered cyclic ethers are also known as epoxy alkanes. All cyclic ethers are considered as heterocyclic compound.

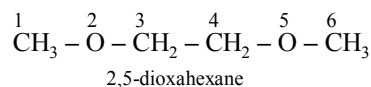
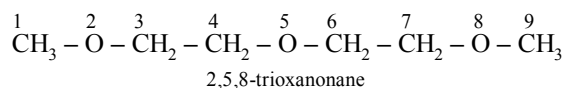


POLYETHERS

Polyethers may also be acyclic or cyclic.

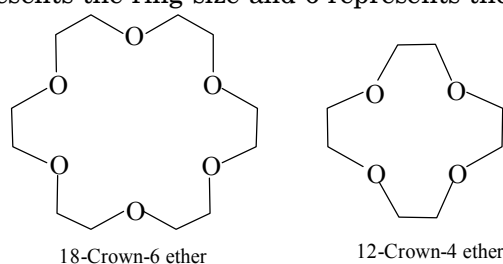
Acyclic polyethers

Acyclic polyethers are named as oxyderivatives of alkane. For example,



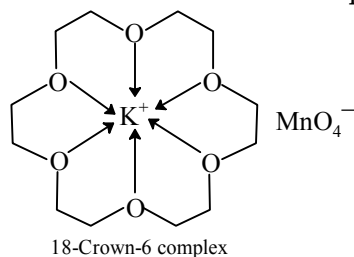
Cyclic Polyethers or Crown Ethers

These are the large ring ethers with at least four $-\text{OCH}_2\text{CH}_2-$ repeating units. These are named crown ethers since they have crown like shape. 18-Crown-6 ether is the commonest example of crown ethers in which 18 represents the ring size and 6 represents the number of oxygen atoms.



Crown ethers can chelate with metal ions and give metal complexes, which are soluble in

non-polar organic solvents. For example, 18-crown-6 ether forms a complex with potassium permanganate which is soluble in benzene and is called purple benzene.

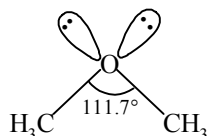


Structure

Ethers may be considered as dialkyl derivative of water and their structure can be explained in a similar way.



Oxygen atom in ethers is sp^3 -hybridised and forms two sigma bonds with two sp^3 -hybridised alkyl groups. Oxygen atom has two lone-pairs of electrons in remaining two sp^3 -hybridised orbitals. C - O - C bond angle in ethers is slightly greater than tetrahedral bond angle due to repulsion between two bulky alkyl groups. In dimethyl ether, C - O - C bond angle is 111.7° .

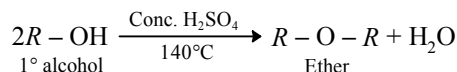


Note As the size of R (alkyl group) in ethers increases, van der Waals repulsion increases and hence bond angle also increases.

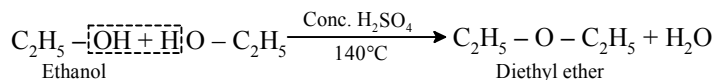
GENERAL METHODS OF PREPARATION

1. Acidic dehydration of alcohols

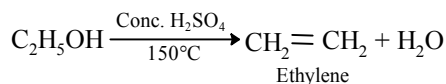
Primary alcohols on heating with conc. H_2SO_4 at 140°C undergo dehydration to yield ethers.



This method is used to prepare simple or symmetrical ethers.



In this reaction, reaction conditions have to be carefully controlled to get the maximum yield of ether. At a slightly higher temperature (150°C) alkene is obtained instead of ether.

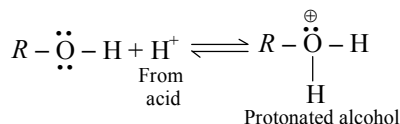


Note This method is suitable for preparation of ethers from primary alcohols only since secondary and tertiary alcohols yield alkenes with conc. H_2SO_4 . Secondary alcohols give a very low yield of ether in addition to alkene.

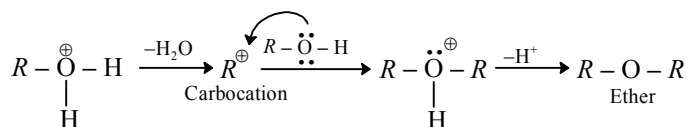
Mechanism

Thus order of ease of dehydration of alcohols to form ethers is primary alcohol > secondary alcohol > tertiary alcohol

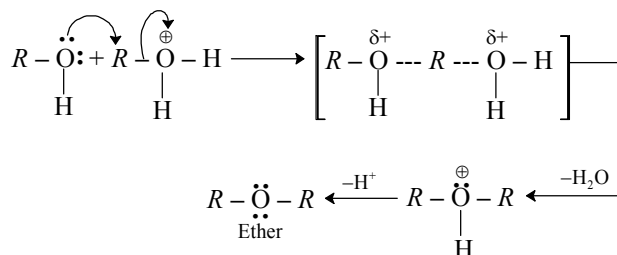
Ether formation by dehydration is an example of nucleophilic substitution reaction ($\text{S}_{\text{N}}1$ reaction) in which protonated alcohol acts as substrate and second molecule of alcohol acts as nucleophile.



$\text{S}_{\text{N}}1$ mechanism :



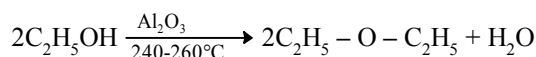
S_N2 mechanism :



- Primary alcohols react by generally S_N2 mechanism whereas secondary and tertiary alcohols undergo the reaction by S_N1 mechanism.

2. Catalytic dehydration of alcohols

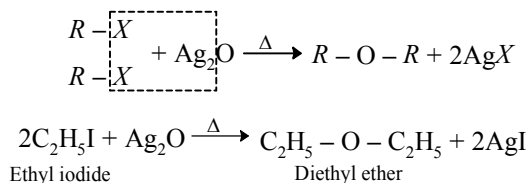
Lower alcohols can be catalytically dehydrated by passing their vapours over heated alumina at 240-260°C.



This method is applicable for primary alcohols only, since secondary and tertiary alcohols yield alkenes at these conditions.

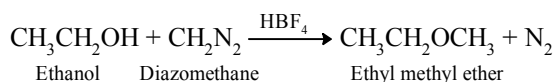
3. Action of silver oxide on alkyl halides

Alkyl halides on heating with silver oxide yield symmetrical or simple ethers.



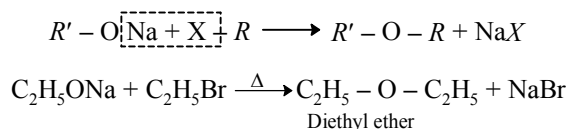
4. Action of diazomethane on alcohols

Alcohols react with diazomethane (CH_2N_2) in presence of tetrafluoroboric acid to yield methyl ethers.



5. Williamson synthesis

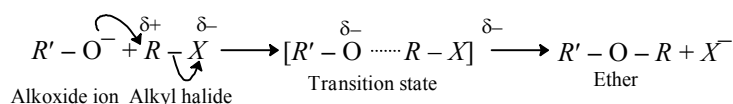
Alkyl halides on reaction with sodium or potassium alkoxide yield ethers.



Both symmetrical and unsymmetrical ethers can be prepared by this method. Generally mixed ethers are obtained in this method.

Mechanism

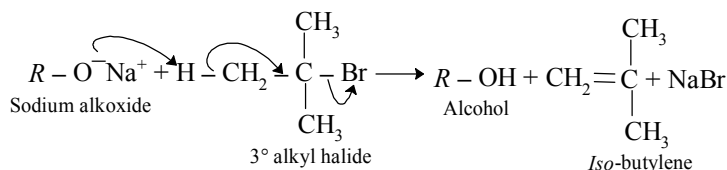
This reaction takes place by S_N2 mechanism involving nucleophilic attack of alkoxide ion on alkyl halide.



Order of reactivity of alkyl halides towards this reaction is

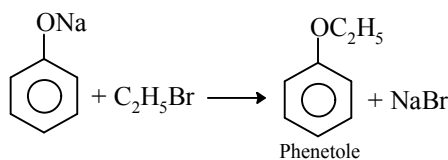
Primary > Secondary > Tertiary

- Secondary and tertiary alkyl halides readily undergo E2 elimination reaction in presence of base such as alkoxide ions to form alkene.

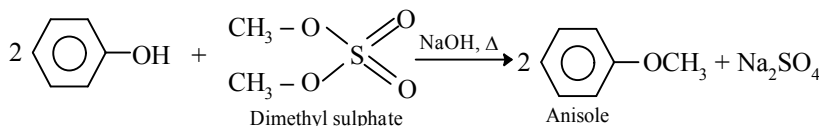
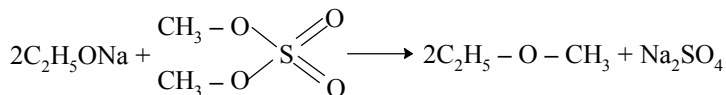


Note

Diaryl ethers can't be produced by this method since aryl halides do not undergo nucleophilic substitution reaction readily. Infact alkyl aryl ethers (phenolic ethers) can be produced by reacting sodium phenoxide with alkyl halide and not by reacting aryl halide with sodium alkoxide.



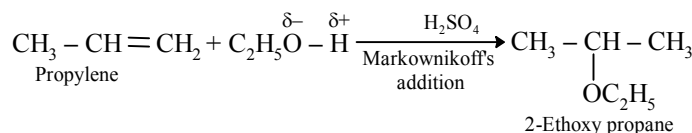
Dimethyl or diethyl sulphates can also be used in place of alkyl halides to form methyl or ethyl ethers respectively, since sulphate is also a good leaving group like halide ion.



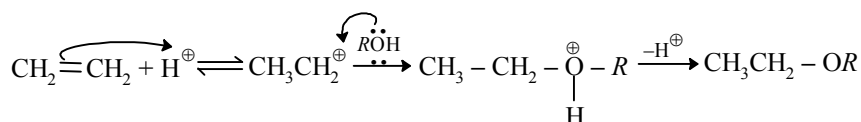
6. Addition of alcohols to alkenes

(i) Direct addition

Alcohols get added to alkenes in presence of mineral acid such as H_2SO_4 as catalyst according to Markownikoff's rule to yield mixed ethers.

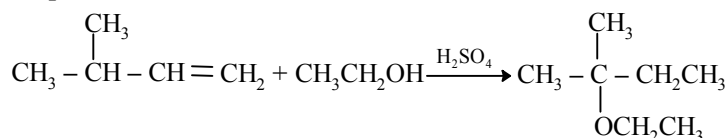


Mechanism



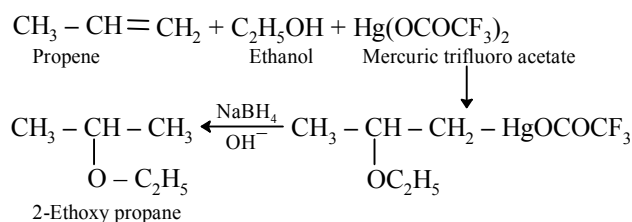
Since the mechanism involves formation of carbocation intermediate, rearranged products may be obtained by 1,2-hydride shift or 1,2-methyl shift.

For example,



(ii) **Alkoxymercuration-demercuration or alkoxy-mercuration - reduction**

Alkenes on reaction with mercuric trifluoroacetate in presence of an alcohol yield alkoxy mercurial compounds which upon reduction with NaBH_4 in basic medium yield ether in excellent yield.

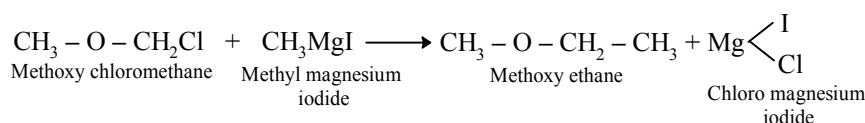


Note

This reaction does not involve formation of carbocation intermediate, so no rearranged products are formed. In addition, the reaction is free from competitive elimination reaction.

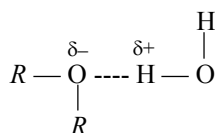
7. **From Grignard reagent**

Higher ethers can be produced by reacting α -haloethers with suitable Grignard reagent.



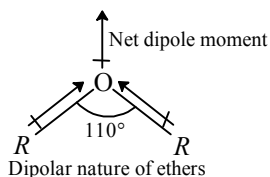
PHYSICAL PROPERTIES

- Dimethyl ether and ethyl methyl ether are exceptionally gases at room temperature whereas all other ethers are colourless liquids with characteristic **etheral smell**.
- Ethers have lower boiling points than isomeric alcohols due to their incapability to form hydrogen bonds and get associated. But lower ethers have slightly higher boiling point than n -alkanes of comparable molecular masses due to dipole-dipole interactions. However higher ethers (containing carbon atom more than four) have slightly lower boiling points than n -alkanes of comparable molecular masses due to weak van der Waals forces of attraction.
- Ethers are soluble in water to a certain extent due to hydrogen bonding. However solubility decreases with increase of molecular mass (*i.e.* increase in the hydrocarbon portion). Ethers are fairly soluble in all organic solvents such as alcohol, chloroform, benzene, etc.



H-bonding between ether and water molecule

- Ethers are polar in nature with a dipole moment varying from 1.15 D to 1.30 D. Since ethers have a bent structure, the polarities of two C - O bond do not cancel each other.



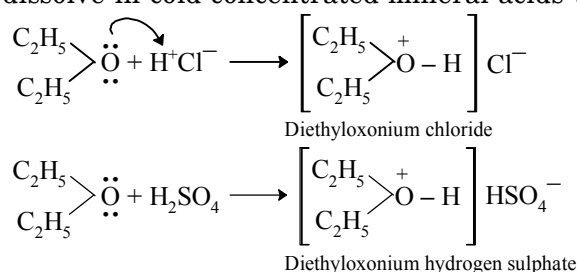
- Ethers have low density. All ethers are lighter than water.

CHEMICAL PROPERTIES

Ethers have very very low reactivity. They are as inert as alkanes. This is due to lack of any active site in the molecule. They are inert towards dilute acids, bases, oxidising and reducing agents. Ethers give only few reactions under specific conditions by virtue of lone pair of oxygen or cleavage of C – O bond.

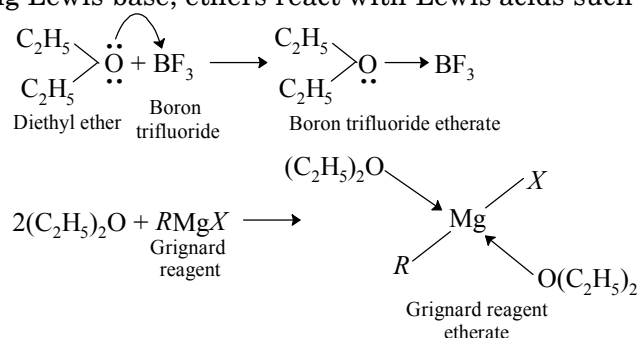
1. Action of acids/formation of oxonium salts

Due to the presence of lone pairs of electron on oxygen atom, ethers behave as Lewis bases and dissolve in cold concentrated mineral acids to form oxonium salts.



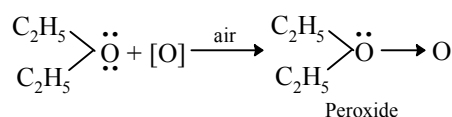
2. Formation of coordinate complexes

Being Lewis base, ethers react with Lewis acids such as BF_3 to form coordinate complexes.



3. Auto-oxidation (Formation of peroxides)

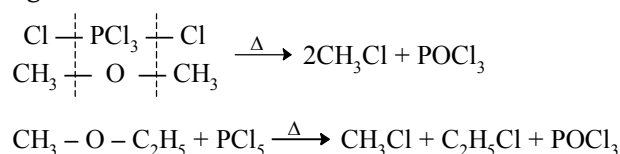
Most aliphatic ethers in presence of air get oxidised to peroxides.



Although peroxides are present in low concentration but these are very dangerous and may cause violent explosion during distillation. Hence care should be taken during use of an old ether solution.

4. Reaction with phosphorus pentachloride

Ethers on heating with phosphorus pentachloride give alkyl chloride by cleavage of C – O bond.



Note

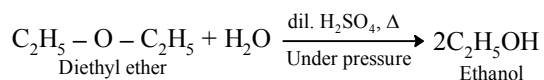
Presence of peroxide can be detected by appearance of red colour on shaking the ether with aqueous solution of ferrous ammonium sulphate and potassium thiocyanate.

Peroxide present can be removed either by washing ether with a solution of ferrous ions (which reduces the peroxide) or by distillation with concentrated sulphuric acid (which oxidises the peroxide).

Ether peroxide formation can also be checked by adding little Cu_2O to it.

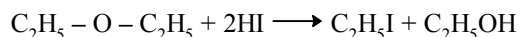
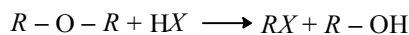
5. Hydrolysis

Ethers are hydrolysed to alcohols on heating with dilute sulphuric acid under pressure.

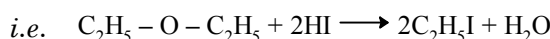
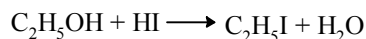


6. Reaction with halogen acids

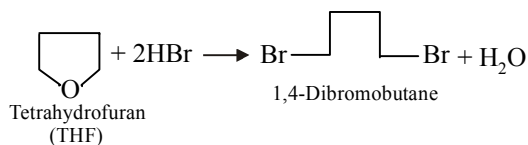
Ethers are readily cleaved by action of HI or HBr to form alcohol and alkyl halide.



If excess of halogen acid is used, then alcohol formed reacts further with halogen acid to produce alkyl halide.



Cyclic ethers are cleaved to dihaloalkanes.

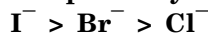


Note

Reactivity of halogen acids towards the given reaction follows the order

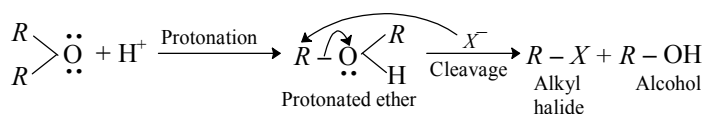


Above order of reactivity can be explained on the basis of order of nucleophilicity which is



Stronger the nucleophile *i.e.* greater the nucleophilicity, more is the reactivity.

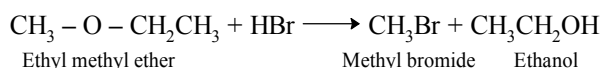
Mechanism



Cleavage involves nucleophilic attack of halide ion on protonated ether with displacement of the weakly basic alcohol molecule.

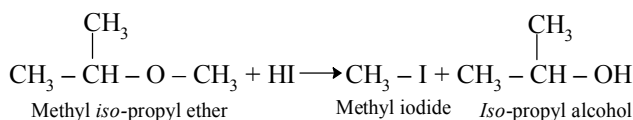
Cleavage of unsymmetrical ethers

During the cleavage of unsymmetrical ethers, smaller alkyl group produces alkyl halide. For example,

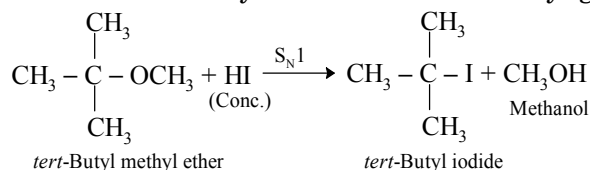


Cleavage of unsymmetrical ethers may take place either by $\text{S}_{\text{N}}1$ mechanism or $\text{S}_{\text{N}}2$ mechanism depending upon the structure.

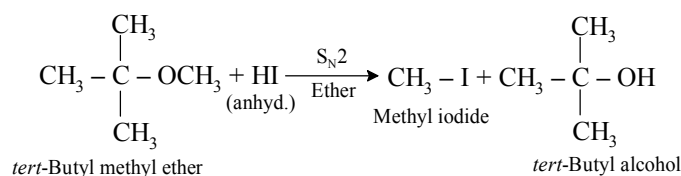
If ether consists of one methyl group and one 1° or 2° alkyl group, then $\text{S}_{\text{N}}2$ mechanism takes place. In such case methyl halide is obtained with alcohol of bulkier alkyl group. Because halide ion attacks least sterically hindered group.



- If ether consists of one methyl group and one 3° alkyl group, then reaction is completed by S_N1 mechanism. In such case, tertiary alkyl group yields alkyl halide because of the stability associated with tertiary carbocation and methyl group gives alcohol.

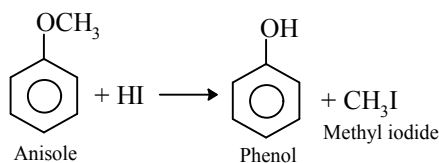


Note High polarity solvents like water favour S_N1 mechanism whereas low polarity solvents like ether favour S_N2 mechanism *i.e.* if the above reaction is carried out with anhydrous HI in ether, then iodide ion would attack less hindered methyl group.



Cleavage of alkyl aryl ethers

Alkyl aryl ethers always give phenol and alkyl halide on cleavage with HI. This can be explained by preferred attack of halide ion on less sterically hindered alkyl group rather than aryl group.



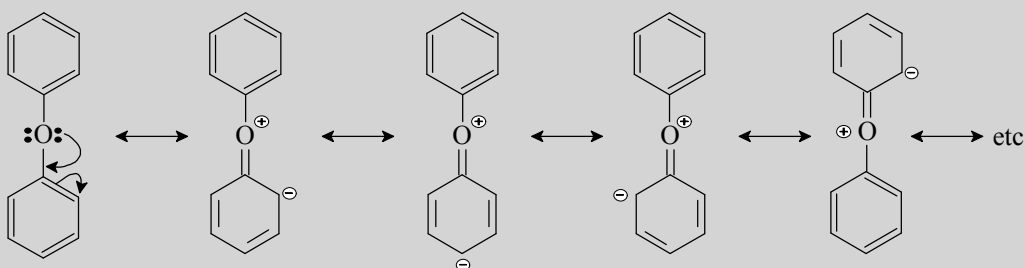
Note Zeisel method for alkoxy group estimation is based on cleavage of ether by HI. The alkyl iodide produced from alkoxy group by action of HI is absorbed in alcoholic silver nitrate solution and silver iodide thus formed is weighed.

- Diaryl ethers are not cleaved by HI.

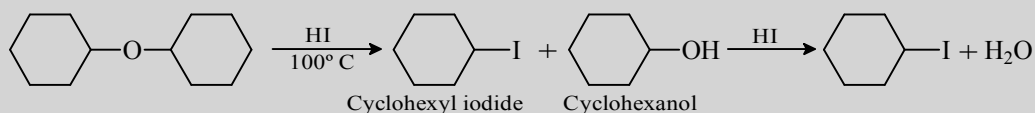
ILLUSTRATION

12 Dicycloalkyl ethers can be readily cleaved by HI whereas diarylethers are difficult to cleave. Why?

Soln.: In diarylethers, lone pair of electrons present at oxygen atom will conjugate with p-electron of benzene ring as a result, double bond is developed between the carbon and oxygen bond and hence this bond is not cleaved easily.

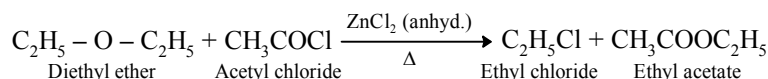


In contrast, there is no such type of hyperconjugation in case of dicyclohexyl ether hence O - C bond remains as single bond only that is why it is cleaved easily by HI.

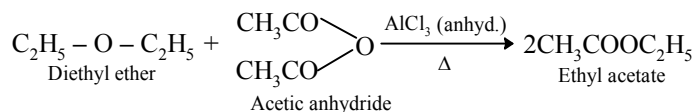


7. Reaction with acid chlorides and anhydrides

Ethers on heating with acid chlorides in presence of $ZnCl_2$ or $AlCl_3$ yields alkyl halides and esters.

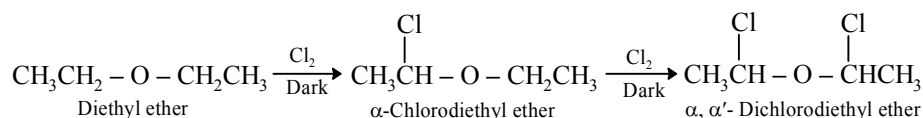


On the other hand on reaction with anhydrides only esters are produced.

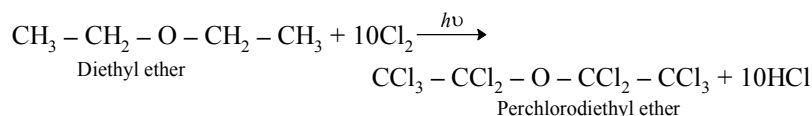


8. Substitution reaction (Halogenation)

On reaction with chlorine or bromine, ethers yield substitution products. Extent of substitution depends on reaction conditions. For example, in dark α, α' -disubstituted product is obtained.

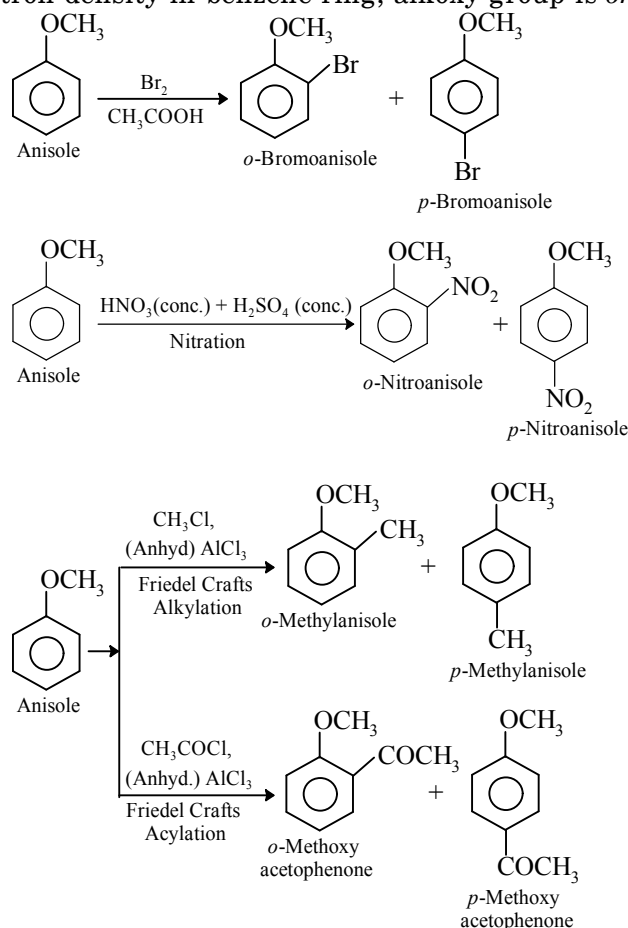


However in presence of light and excess of chlorine, complete substitution takes place.



9. Electrophilic aromatic substitutions

Alkyl aryl ethers readily undergo electrophilic substitution reaction. Since the +R effect of alkoxy group activates the benzene ring towards the above said reaction by increasing electron density in benzene ring, alkoxy group is *ortho*, *para*-directing. For example,



Xtra SUPPLEMENT for competitive exams

NATURE OF DIFFERENT TYPES OF ALCOHOLS

Types	Composition
Absolute alcohol	100% ethanol
Rectified spirit	95% alcohol + 5% water
Denatured spirit	95% ethanol + 5% methanol
Methylated spirit	90% ethanol + 9% methanol + 1% other poisonous substances
Power alcohol	80% petrol + 20% absolute alcohol

CHEMICAL TEST TO DISTINGUISH

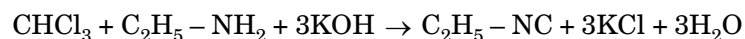
(a) **Methanol from ethanol:** Ethyl alcohol can be distinguished from methyl alcohol either by the iodoform test or by salicylic acid test.

Ethyl alcohol reacts with iodine in presence of caustic soda giving a yellow ppt. of iodoform, while no such precipitate is obtained by methyl alcohol.



Again methyl alcohol reacts with salicylic acid giving a characteristic smell of oil of winter green. No such smell is produced by ethyl alcohol.

(b) **Chloroform from methanol:** Chloroform reacts with ethyl amine in presence of caustic potash solution giving an unpleasant smelling compound ethyl isocyanide. This reaction is also known as carbylamine reaction, while methanol does not respond to the test.



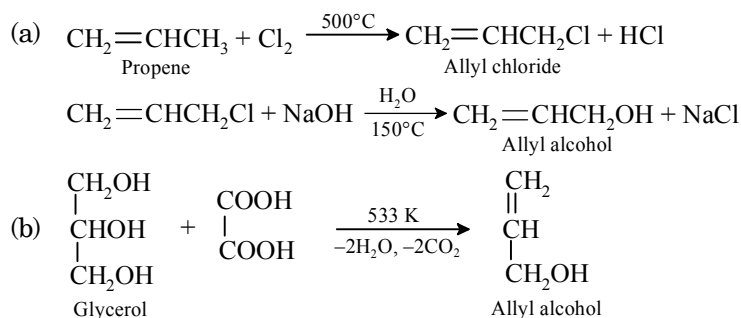
(c) **Chloroform from ethanol:** Chloroform can be distinguished from ethanol either by iodoform test or by carbylamine test. Ethyl alcohol responds to iodoform test only, while chloroform responds to carbylamine test only.

REDUCING NATURE OF DIFFERENT REAGENTS

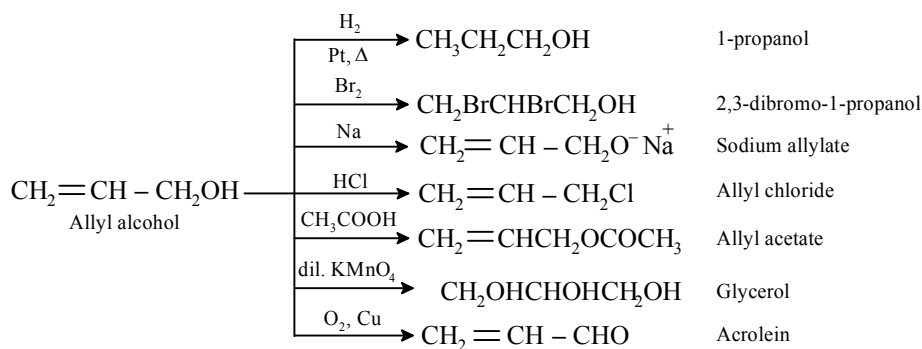
Conversions	LiAlH ₄ /ether	NaBH ₄ /C ₂ H ₅ OH	H ₂ /Metal	B ₂ H ₆ /THF
CHO → CH ₂ OH	✓	✓	✓	✓
>CO → >CHOH	✓	✓	✓	✓
COOH → CH ₂ OH	✓	✗	✗	✓
COCl → CH ₂ OH	✓	✓	✗	✓
(RCO) ₂ O → RCH ₂ OH	✓	✗	✓	✓
COOR → CH ₂ OH	✓	✗	✓	✓
>C=C< → >CH-CH<	✗	✗	✓	✓

ALLYL ALCOHOL

- Allyl alcohol is an important unsaturated alcohol.
- It is prepared by following methods.



Properties : Allyl alcohol is a colourless pungent smelling liquid. It shows the properties of an unsaturated compound as well as primary alcohol.



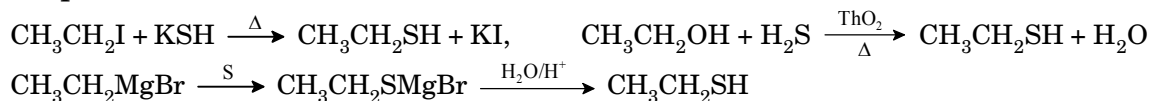
THIOLS

- In organic chemistry, a thiol is a compound that contains the functional group composed of a sulphur atom and a hydrogen atom ($-\text{SH}$). Being the sulphur analogue of an alcoholic group ($-\text{OH}$), this functional group is referred to either as a thiol group or a sulfhydryl group. More traditionally, thiols are often referred to as **mercaptans** (RSH).

Nomenclature:

Compound	Common name	IUPAC name
CH_3SH	Methyl mercaptan	Methanethiol
$\text{CH}_3\text{CH}_2\text{SH}$	Ethyl mercaptan	Ethanethiol

Preparation:

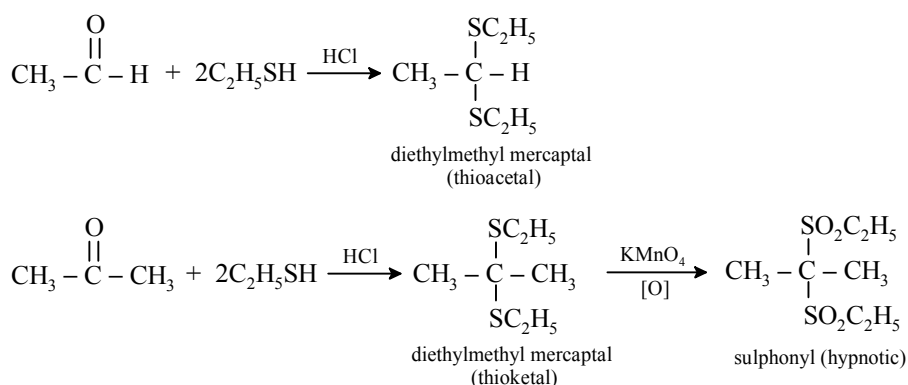


Properties :

Since sulphur and oxygen belong to the same group of periodic table, they share some similar chemical properties.

- (1) *Reaction with sodium* : $2\text{C}_2\text{H}_5\text{SH} + \text{Na} \longrightarrow \text{C}_2\text{H}_5\text{S}^-\text{Na}^+ + \text{H}_2\uparrow$
- (2) *Reaction with acid*: $\text{CH}_3\text{COOH} + \text{HSC}_2\text{H}_5 \longrightarrow \text{CH}_3\text{COSC}_2\text{H}_5 + \text{H}_2\text{O}$
ethyl thioacetate
- (3) *Oxidation*:
 - (a) With mild oxidising agents : $2\text{C}_2\text{H}_5\text{SH} + \text{H}_2\text{O}_2 \longrightarrow \text{C}_2\text{H}_5-\text{S}-\text{S}-\text{C}_2\text{H}_5 + 2\text{H}_2\text{O}$
diethyl disulphate
 - (b) With strong oxidising agents : $\text{C}_2\text{H}_5\text{SH} \xrightarrow[\text{or HNO}_3]{\text{KMnO}_4} \text{C}_2\text{H}_5\text{SO}_3\text{H}$
ethanesulphonic acid

(4) *Reaction with aldehydes and ketones:*



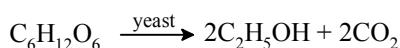
BIOLOGICAL IMPORTANCE

As the functional group of the amino acid cysteine, the thiol group plays an important role in biological systems. When the thiol groups of two cysteine residues (as in monomers or constituent units) are brought close to each other in the course of protein folding, an oxidation reaction can create cysteine unit with a disulphide bond (–S–S–). Disulphide bonds can contribute to a protein's tertiary structure if the cysteines are part of the same peptide chain, or contribute to the quaternary structure of multi-unit proteins by forming fairly strong covalent bonds between different peptide chains. The heavy and light chains of antibodies are held together by disulphide bridges. Also, the cases in curly hair are a product of cysteine formation. The chemicals used in hair straightening are reductants that reduce cysteine disulphide bridges to free cysteine sulphhydryl groups, while chemicals used in hair curling are oxidants that oxidize cysteine Sulphhydryl groups to form cystine disulphide bridges. Sulphhydryl groups in the active site of an enzyme can form noncovalent bonds with the enzyme's substrate as well, contributing to catalytic activity.

FERMENTATION

The process of fermentation is the slow decomposition of complex organic compounds into simpler substances through the agency of complex nitrogenous compounds called enzymes produced in living organisms.

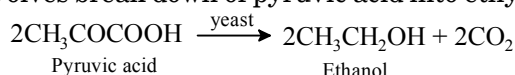
Fermentation is also defined as anaerobic breakdown of carbohydrates and other organic compounds to form alcohol and organic acids with the help of microorganisms or their enzymes. The science of fermentation is known as **zymology**.



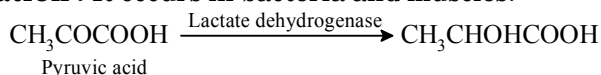
Fermentation usually implies that the action of the microorganisms is desirable, and the process is used to produce alcoholic beverages such as wine, beer and cider. Fermentation is also employed in preservation to create lactic acid in sour foods such as pickled cucumbers, kimchi and yogurt. Occasionally wines are enhanced through the process of fermentation. This term was first used by Pasteur (1857). The name fermentation has been derived from Latin word *fervere* meaning to boil, as during this process there is lot of frothing due to evolution of CO_2 and this gives the appearance of boiling liquid. Favourable conditions for fermentation are (a) optimum temperature (25-30°C), (b) low concentration of solution, (c) presence of certain inorganic compounds (like ammonium sulphate, phosphate, etc.) which act as food for the ferment cells.

Different types of fermentations are as follows:

- 1. Alcoholic fermentation :** Most common type. It occurs in some fungi (yeast) and higher plants during anaerobic conditions. It involves break down of pyruvic acid into ethyl alcohol and carbon dioxide.



- 2. Lactic acid fermentation :** It occurs in bacteria and muscles.



SOME INDUSTRIAL USES OF DIFFERENT TYPES OF FERMENTATION

Fermentation End-product(s)	Industrial or Commercial use	Starting material	Microorganism
Ethanol	Beer Wine Fuel	Malt extract Grape or other fruit Agricultural wastes	<i>Saccharomyces cerevisiae</i> (yeast, a fungus) <i>Saccharomyces cerevisiae</i> var. <i>ellipsoideus</i> <i>Saccharomyces cerevisiae</i>
Acetic acid	Vinegar	Ethanol	<i>Acetobacter</i> (bacterium)
Lactic acid	Cheese, yogurt	Milk	<i>Lactobacillus</i> , <i>Streptococcus</i> (bacteria)
Propionic acid (bacterium) and carbon dioxide	Rye bread Summer sausage Swiss cheese	Grain, sugar Meat Lactic acid	<i>Lactobacillus bulgaricus</i> (bacterium) <i>Pediococcus</i> (bacterium) <i>Propionibacterium freudenreichii</i>
Acetone and butanol	Pharmaceutical, industrial uses	Molasses	<i>Clostridium acetobutylicum</i> (bacterium)
Glycerol	Pharmaceutical, industrial uses	Molasses	<i>Saccharomyces cerevisiae</i>
Citric acid	Flavouring	Molasses	<i>Aspergillus</i> (fungus)
Methane	Fuel	Acetic acid	<i>Methanosarcina</i> (bacterium)
Sorbose	Vitamin C (ascorbic acid)	Sorbitol	<i>Acetobacter</i>

ALCOHOLIC BEVERAGES

An alcoholic beverage is a drink containing ethyl alcohol as the principal constituent. Besides alcohol, these contain large amount of water, colouring and flavouring materials.

Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), the active ingredient in alcoholic drinks, for consumption purposes is always produced by fermentation - the metabolism of carbohydrates by certain species of yeast in the absence of oxygen. The process of culturing yeast under alcohol-producing conditions is referred to as *brewing*. The same process produces carbon dioxide *in situ*, and may be used to carbonate the drink in home brewing.

Percentage of alcohol present in various products

	Products	Percentage of alcohol	Starting material
1.	Beer	3 - 8%	Grains
2.	Wine	7 - 18%	Fruit juices of grapes, cherries, raspberries
3.	Whisky	40 - 50%	Grains
4.	Gin	40 - 45%	Grains, juniper berries
5.	Brandy	60 - 70%	Grape juice
6.	Rum	40 - 75%	Fermented cane sugar product

Alcoholic beverages when taken in small quantity act as stimulants but when taken regularly in excess, may decrease the energy of the body, retard the mental powers and damage the liver causing cirrhosis of liver. The process of determining the percentage of alcohol in a given sample is known as alcoholometry. This is done by measuring the specific gravity of the sample with the help of hydrometer and then reading the percentage of alcohol against this value of specific gravity from a standard reference table. An alcohol-water mixture having specific gravity 0.91976 at 15°C and containing 57.1% of ethyl alcohol by volume or 49.3% by weight is called **proof-spirit**. A sample having higher percentage of ethyl alcohol in comparison to proof-spirit is referred to as **over proof** (O.P) and the one having lower alcohol content than proof-spirit is known as **under proof** (U.P.). Thus 15 U.P. means that 100 mL of the sample contains as much alcohol as 85 mL of proof-spirit. Similarly, 15 O.P. means that 100 mL of the sample contains as much of alcohol as 115 mL of proof spirit.

IMPORTANT CONVERSIONS

☞ Higher alcohol to lower alcohol and vice versa

- $$\text{C}_2\text{H}_5\text{OH} \xrightarrow[170^\circ\text{C}]{\text{conc. H}_2\text{SO}_4} \text{CH}_2=\text{CH}_2 \xrightarrow[\text{Zn/H}_2\text{O}]{\text{O}_3} \text{H}-\text{CHO} \xrightarrow[2\text{H}]{\text{LiAlH}_4} \text{CH}_3-\text{OH}$$

Ethyl alcohol Methyl alcohol
- $$\text{C}_2\text{H}_5\text{OH} \xrightarrow[\text{[O]}]{\text{K}_2\text{Cr}_2\text{O}_7} \text{CH}_3-\text{COOH} \xrightarrow{\text{NaOH}} \text{CH}_3-\text{COONa} \xrightarrow[\Delta]{\text{NaOH/CaO}} \text{CH}_4$$

$\xrightarrow[\text{U.V.}]{\text{Cl}_2} \text{CH}_3-\text{Cl} \xrightarrow{\text{aq. KOH}} \text{CH}_3-\text{OH}$

Methyl alcohol
- $$\text{CH}_3-\text{OH} \xrightarrow[\text{conc. H}_2\text{SO}_4]{\text{KBr}} \text{CH}_3-\text{Br} \xrightarrow[\text{dry ether}]{\text{Na}} \text{CH}_3-\text{CH}_3 \xrightarrow[\text{U.V.}]{\text{Cl}_2} \text{CH}_3-\text{CH}_2-\text{Cl} \xrightarrow{\text{aq. KOH}} \text{CH}_3-\text{CH}_2-\text{OH}$$

Methyl alcohol (Ethyl alcohol)
- $$\text{CH}_3-\text{OH} \xrightarrow{\text{HI}} \text{CH}_3-\text{I} \xrightarrow{\text{KCN}} \text{CH}_3-\text{CN} \xrightarrow{\text{LiAlH}_4} \text{CH}_3-\text{CH}_2-\text{NH}_2 \xrightarrow{\text{HNO}_2} \text{CH}_3-\text{CH}_2-\text{OH}$$

Ethyl alcohol

☞ 1°-alcohol to 2°-alcohol or 3°-alcohol and vice versa

- $$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{OH} \xrightarrow{\text{P/I}_2} \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{I} \xrightarrow[\Delta]{\text{KOH(alc.)}} \text{CH}_3-\text{CH}=\text{CH}_2 \xrightarrow{\text{HBr}} \text{CH}_3-\underset{\text{Br}}{\text{CH}}-\text{CH}_3$$

1° alcohol 2° alcohol

$\downarrow \text{KOH(aq.)}$

OH

$\text{CH}_3-\text{CH}-\text{CH}_3$
- $$\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{OH} \xrightarrow[170^\circ\text{C}]{\text{conc. H}_2\text{SO}_4} \text{CH}_3-\underset{\text{CH}_3}{\text{C}}=\text{CH}_2 \xrightarrow{\text{HBr}} \text{CH}_3-\underset{\text{CH}_3}{\overset{\text{Br}}{\text{C}}}-\text{CH}_3 \xrightarrow{\text{KOH(aq.)}} \text{CH}_3-\underset{\text{CH}_3}{\overset{\text{OH}}{\text{C}}}-\text{CH}_3$$

1° alcohol 3° alcohol
- $$\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\text{CH}_3 \xrightarrow{\text{HI}} \text{CH}_3-\underset{\text{I}}{\text{CH}}-\text{CH}_3 \xrightarrow{\text{KOH(alc.)}} \text{CH}_3-\text{CH}=\text{CH}_2 \xrightarrow[\text{H}_2\text{O}]{\text{HBr}} \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{Br}$$

2° alcohol 1° alcohol

$\downarrow \text{KOH(aq.)}$

$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{OH}$
- $$\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\text{CH}_3 \xrightarrow[\text{[O]}]{\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4} \text{CH}_3-\underset{\text{O}}{\text{C}}-\text{CH}_3 \xrightarrow{\text{CH}_3\text{MgBr}} \text{CH}_3-\underset{\text{OMgBr}}{\overset{\text{CH}_3}{\text{C}}}-\text{CH}_3 \xrightarrow[\text{H}^+]{\text{H}_2\text{O}} \text{CH}_3-\underset{\text{CH}_3}{\overset{\text{OH}}{\text{C}}}-\text{CH}_3$$

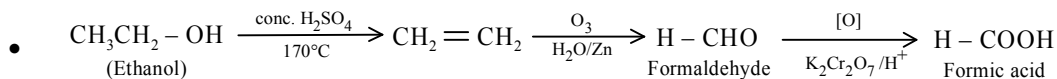
2° alcohol 3° alcohol
- $$\text{CH}_3-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}-\text{OH} \xrightarrow[300^\circ\text{C}]{\text{Cu}} \text{CH}_3-\underset{\text{CH}_3}{\text{C}}=\text{CH}_2 \xrightarrow[\text{H}_2\text{O}]{\text{HBr}} \text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{Br} \xrightarrow{\text{KOH(aq.)}} \text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{OH}$$

3° alcohol 1° alcohol

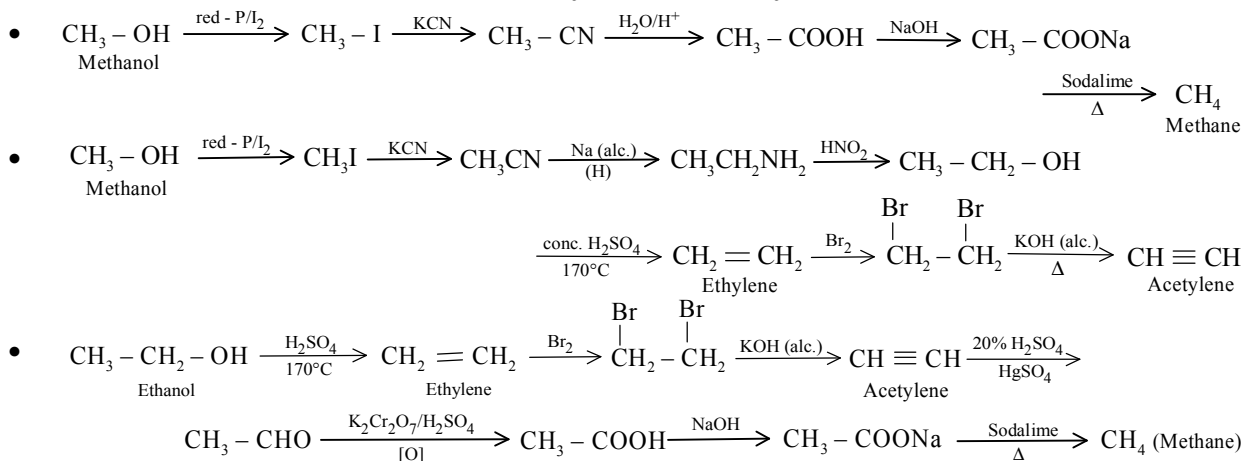
☞ Methanol and ethanol into formaldehyde and formic acid

- $$\text{CH}_3-\text{OH} \xrightarrow[\text{[O]}]{\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+} \text{H}-\text{CHO} \xrightarrow[\text{[O]}]{\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+} \text{H}-\text{COOH}$$

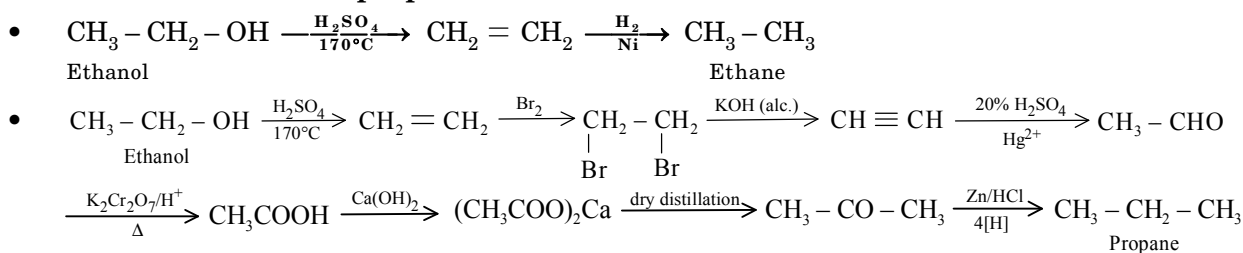
Methanol Formaldehyde Formic acid



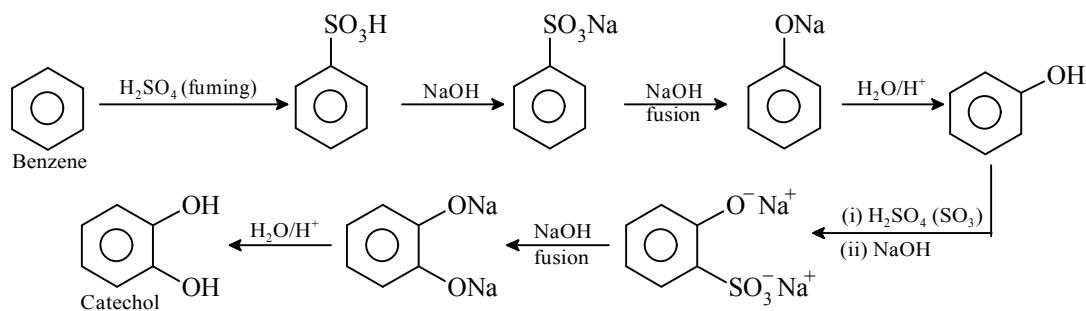
☞ Methanol and ethanol into methane, ethylene and acetylene



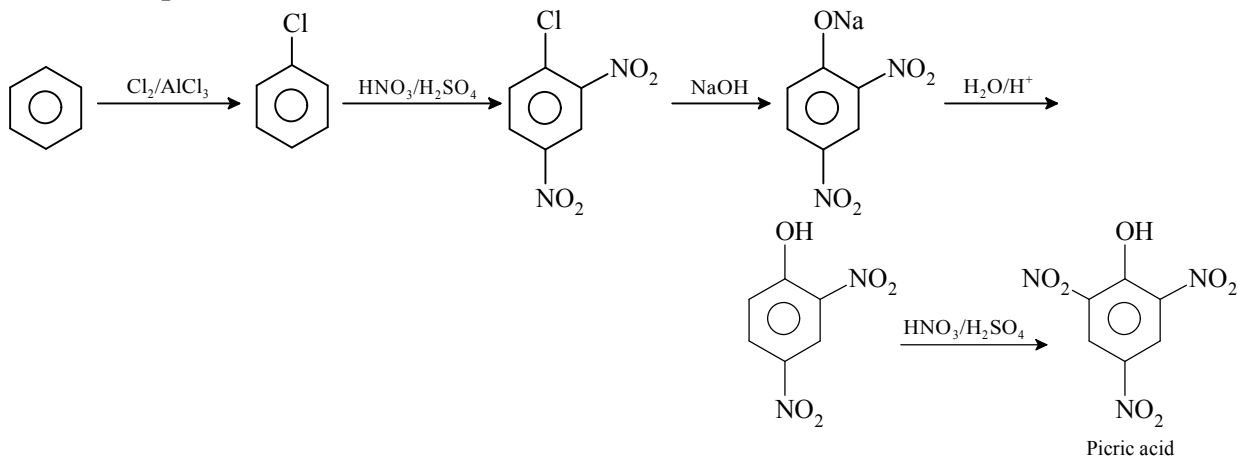
☞ Ethanol into ethane and propane



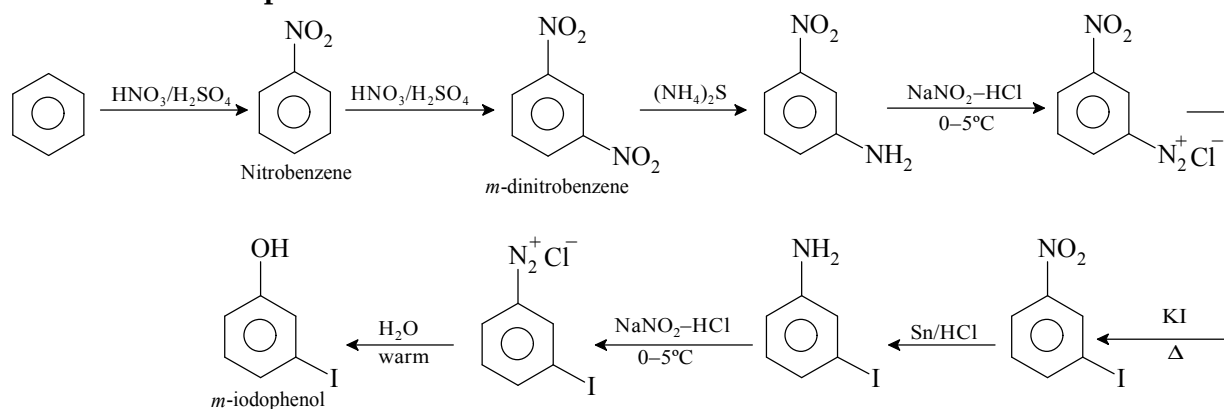
☞ Benzene to catechol



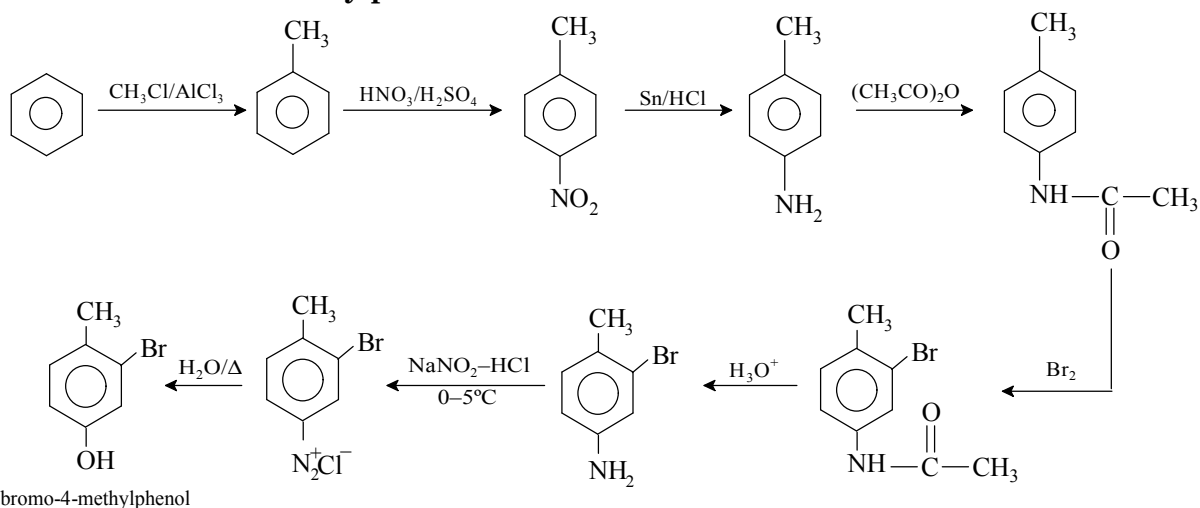
☞ Benzene to picric acid



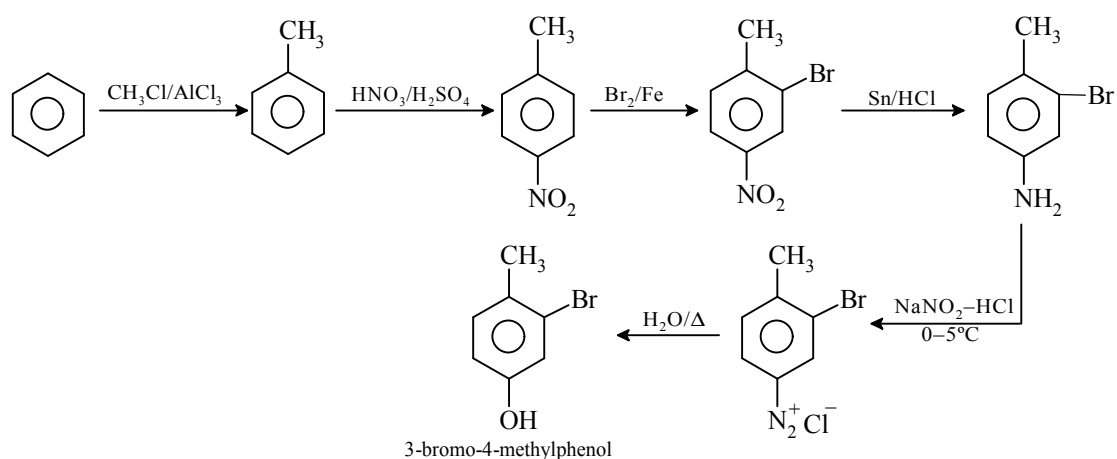
☞ **Benzene to *m*-iodophenol**



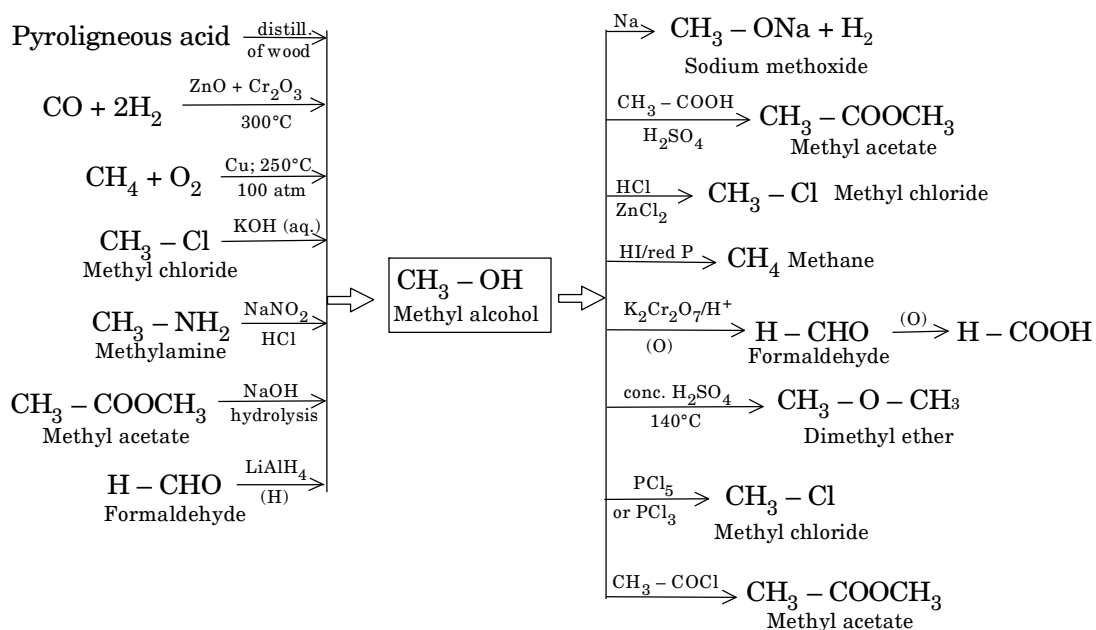
☞ **Benzene to 2-bromo-4-methylphenol**



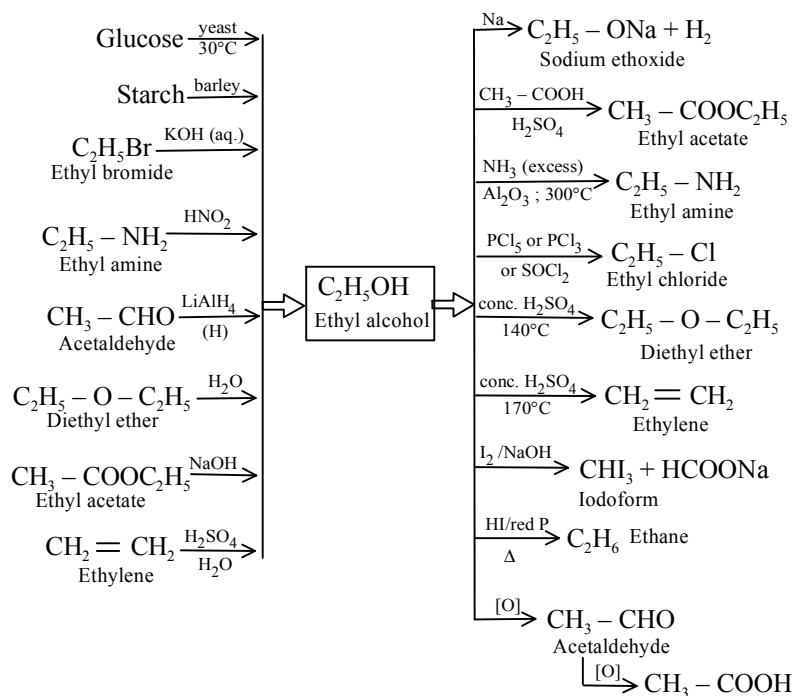
☞ **Benzene to 3-bromo-4-methylphenol**



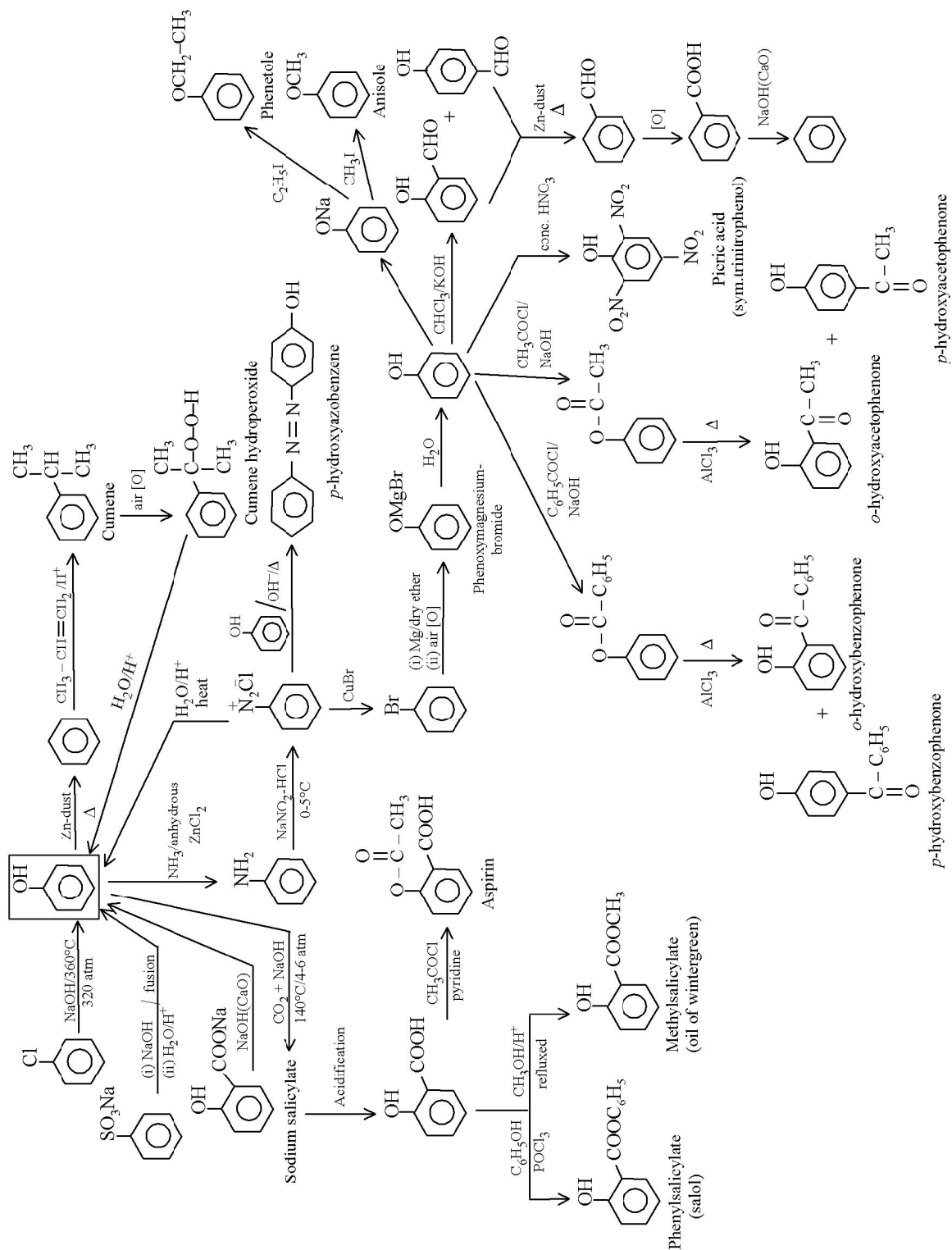
FLOW CHART OF METHYL ALCOHOL



FLOW CHART OF ETHYL ALCOHOL



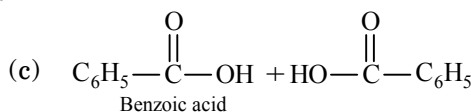
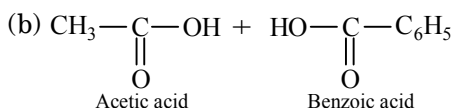
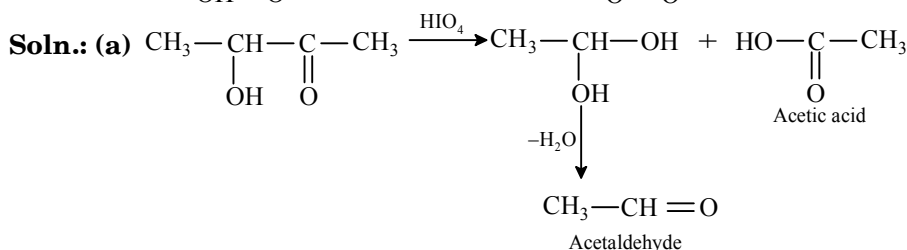
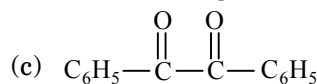
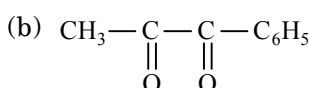
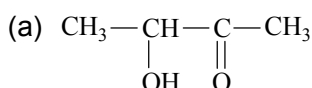
FLOW CHART OF PHENOL



Miscellaneous

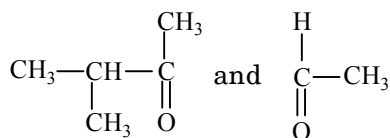
Examples

1. Periodate cleavage also occurs with α -hydroxyketone and α -diketones. Assuming this what will be periodic acid oxidation product for?



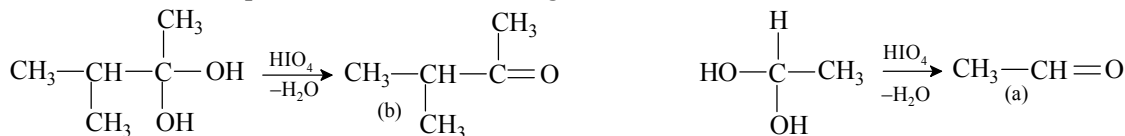
2. Which glycol is oxidised to (a) $\text{CH}_3-\text{CH}=\text{O}$ and (b) $\text{CH}_3-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}-\text{O}$ by HIO_4 ?

Soln.: Write the structures for the products with $\text{C}=\text{O}$ groups aligned vertically.



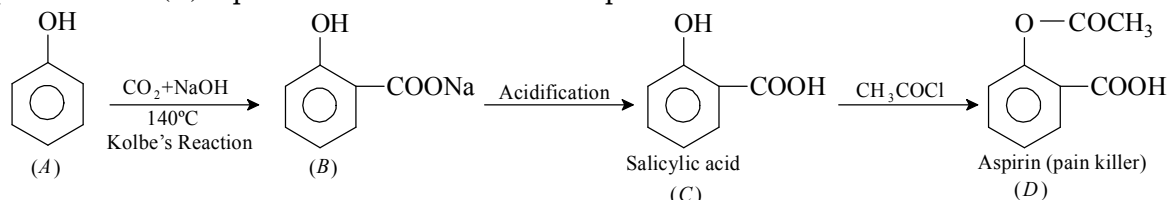
Join the structures through $\text{C}=\text{O}$ carbons and change the $=\text{O}$ to $-\text{OH}$ to give $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\overset{\text{CH}_3}{\overset{\text{OH}}{\text{C}}}-\overset{\text{H}}{\overset{\text{OH}}{\text{C}}}-\text{CH}_3$

This structure on periodic acid oxidation gives -

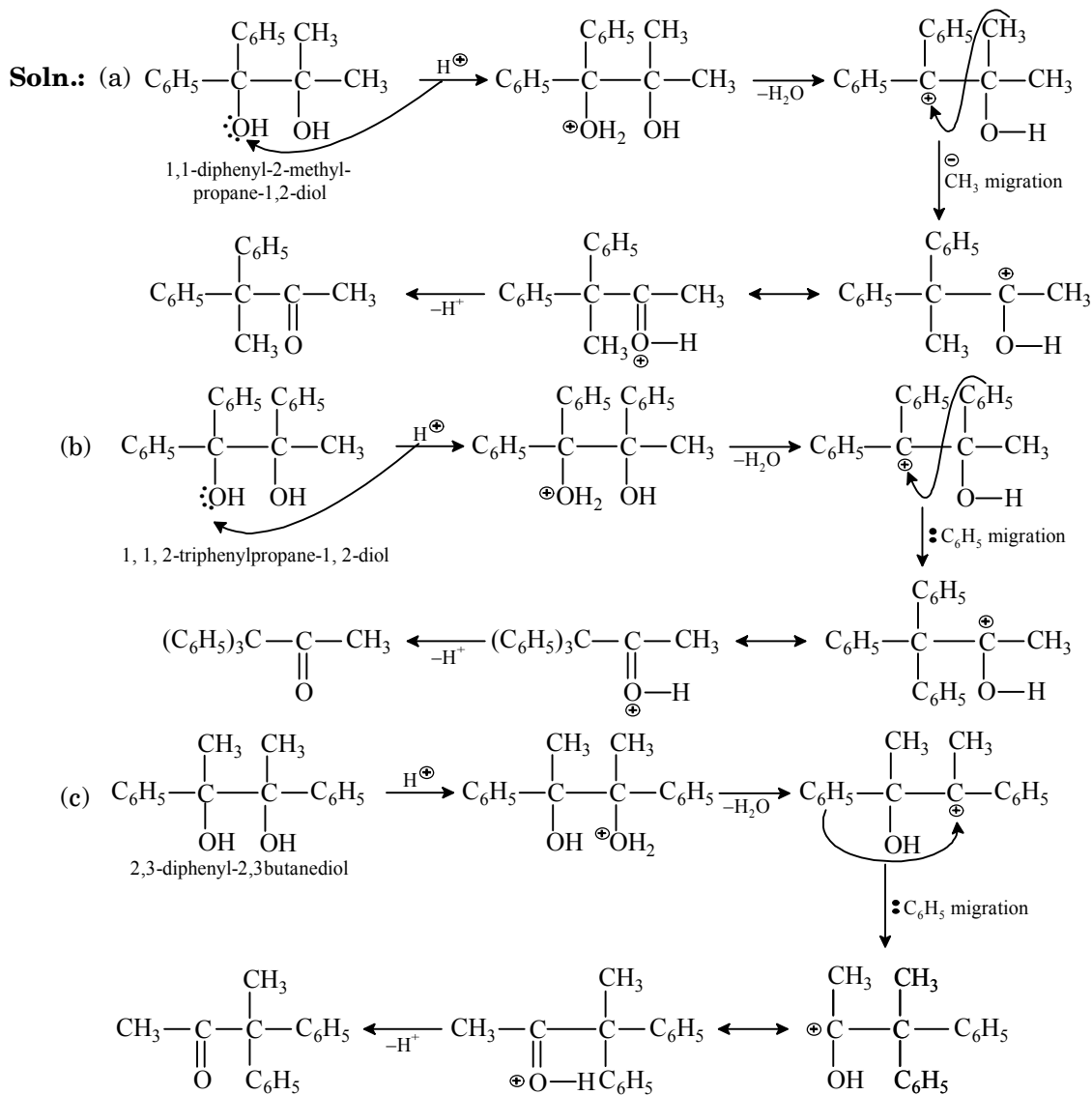


3. An organic compound (A) having vapour density 47, gives characteristic colour with FeCl_3 . (A) when treated with CO_2 and NaOH at 140°C under pressure gives (B) which on being acidified gives (C). It reacts with acetyl chloride to give (D), a pain killer write structures from A to D.

Soln.: As it gives characteristic colour with FeCl_3 hence it has $-\text{OH}$ group attached to sp^2 hybridized C-atom. Also it has vapour density 47 hence molecular mass will be 94 which is corresponded to mass of phenol. Thus (A) is phenol. Other reactions are represented as :

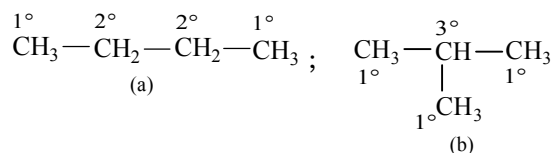


4. Give structural formula of the product formed from the pinacol rearrangement of
 (a) 1, 1-diphenyl-2-methylpropane-1, 2-diol (b) 1, 1, 2-triphenylpropane-1, 2-diol
 (c) 2, 3-diphenyl-2, 3-butanediol



5. How many etherial forms are possible for $C_4H_{10}O$?

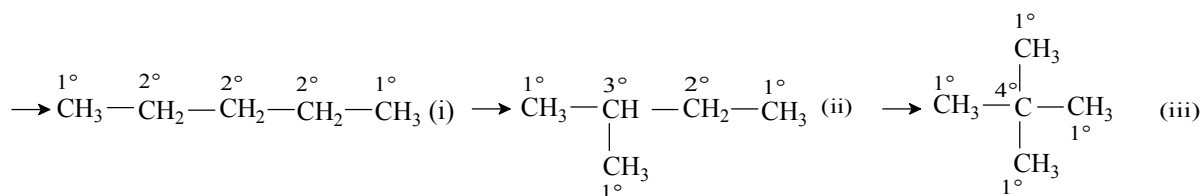
Soln.: We have to place O atom between the two carbon atoms of C_4H_{10} which are



Since (a) has two types of C—C bond ($1^\circ - 2^\circ$ and $2^\circ - 2^\circ$) hence it will give two forms of ether as $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{OCH}_3$ and $\text{CH}_3 - \text{CH}_2 - \text{O} - \text{CH}_2 - \text{CH}_3$ and (b) has only one of C—C bond ($1^\circ - 3^\circ$) hence it will give only one ether as $\text{CH}_3 - \text{OCH}(\text{CH}_3)_2$. Thus total etherial forms of $C_4H_{10}O$ will be three.

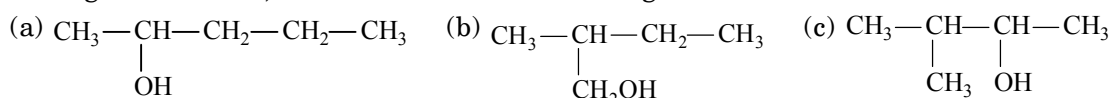
6. How many isomeric structures are possible for $C_5H_{12}O$?

Soln.: 14, C_5H_{12} can be represented as -

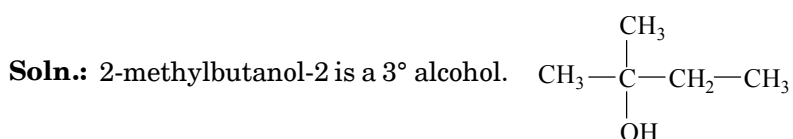


Structure (i) has three replaceable hydrogen atoms and two types of C—C bonds hence it will give three alcoholic forms and two ethereal forms. Structure (ii) has four replaceable hydrogen atoms and three types of C—C bonds hence it will give four alcohols and three ethereal forms. Structure (iii) has only one replaceable hydrogen atom and one type of C—C bonds hence it will give one alcoholic and one ethereal forms.

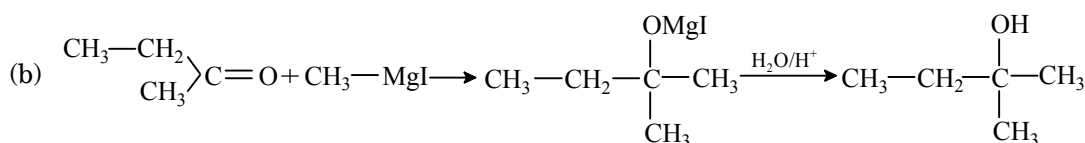
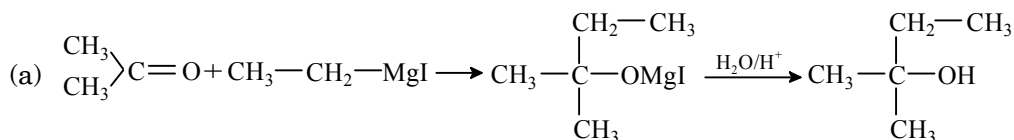
Thus total number of structural alcoholic forms of $\text{C}_5\text{H}_{12}\text{O}$ will be 8 and ethereal forms will be 6. Among the alcohols, structures of alcohols having chiral C-atoms are



7. Grignard reagent used to get 2-methyl-2-butanol is

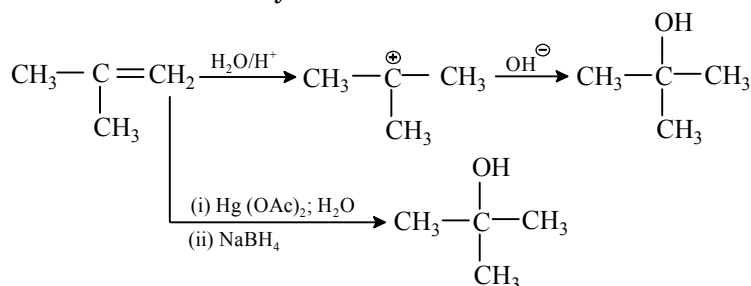


Here among the three alkyl groups attached to C-atom having —OH groups two are same and third one is different hence Grignard reagent will be of two types. The reactions may be either (a) or (b).

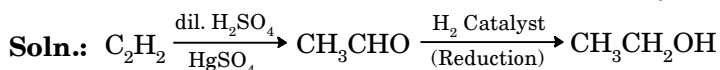


8. Hydration and oxymercuration product of isobutylene is

Soln.: In hydration we get product corresponding to most stable carbocation where as in mercuration there is simple water addition over alkene without rearrangement. Thus products corresponding to hydration and mercuration of isobutylene will be



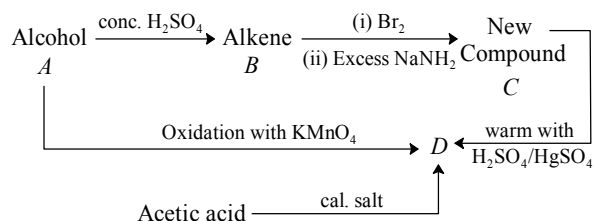
9. State the conditions under which the following preparation is carried out. Give the necessary equations which need not be balanced. Ethanol from acetylene.



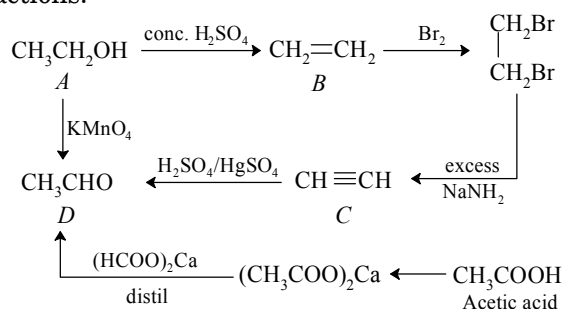
10. An alcohol A, when heated with concentrated H_2SO_4 gives an alkene B. When B is bubbled through bromine water and the product obtained is dehydrohalogenated with excess of sodamide, a new

compound *C* is obtained. The compound *C* gives *D* when treated with warm dilute H_2SO_4 in presence of HgSO_4 . *D* can also be obtained either by oxidising *A* with KMnO_4 or from acetic acid through its calcium salt. Identify *A*, *B*, *C* and *D*.

Soln.: The facts given in the problem can be summarised as follows:

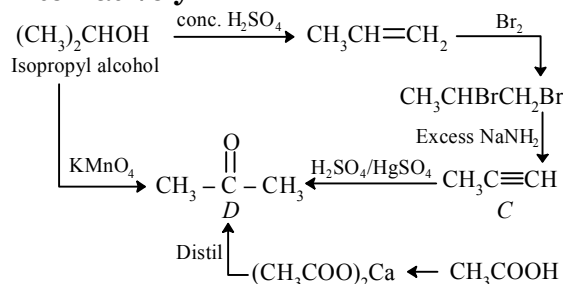


From the above reactions it appears that *C* is an alkyne and *D* is an aldehyde or ketone. Since *D* can be obtained from acetic acid through its calcium salt it must be either acetaldehyde or acetone. Hence proceeding backwards, *A* may be either ethyl alcohol or isopropyl alcohol. Both of these can explain various reactions.



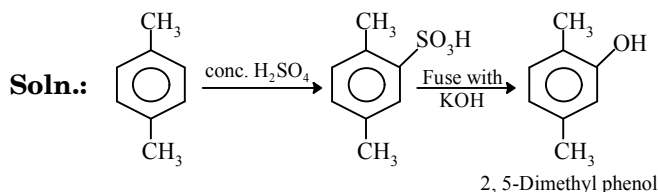
Hence *A* = Ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$)
B = Ethylene ($\text{CH}_2 = \text{CH}_2$)
C = Acetylene ($\text{CH} \equiv \text{CH}$)
D = Acetaldehyde (CH_3CHO)

Alternatively



Hence *A* = Isopropyl alcohol, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$
B = Propene ($\text{CH}_3\text{CH} = \text{CH}_2$)
C = Propyne ($\text{CH}_3\text{C} \equiv \text{CH}$)
D = Acetone (CH_3COCH_3)

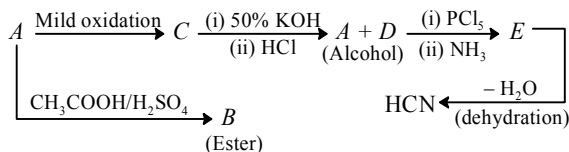
11. What happens when *p*-xylene is reacted with concentrated sulphuric acid and the resultant product is fused with KOH ?



12. An organic compound (*A*) on treatment with acetic acid in the presence of sulphuric acid produces an ester (*B*), (*A*) on mild oxidation gives (*C*), (*C*) with 50% potassium hydroxide followed by acidification with dilute hydrochloric acid generates (*A*) and (*D*), (*D*) with phosphorus pentachloride followed by

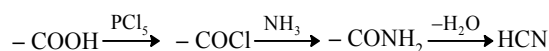
reaction with ammonia gives (*E*), (*E*) on dehydration produces hydrocyanic acid. Identify the compounds *A*, *B*, *C*, *D* and *E*.

Soln.: Various facts given in problem can be summarized as follows:



Taking into consideration the above facts following conclusions can be drawn:

- (i) Since *A* reacts with CH_3COOH in presence of H_2SO_4 to yield *B* which is an ester so we can conclude that *A* is an alcohol (alcohol + acid \rightarrow ester + water).
- (ii) *C* on reaction with 50% KOH followed by acidification gives alcohol *A* and another compound *D*. It appears to be Cannizzaro's reaction, hence *C* must be an aldehyde and *D* must be an acid. The conclusion that *C* is an aldehyde is further supported by another fact given in the problem, *i.e.*, *C* is obtained by mild oxidation of *A* (an alcohol).
(A primary alcohol on mild oxidation yields an aldehyde).
- (iii) The structure of *D* (may be an acid) is established as follows, from the various reactions given in problem.

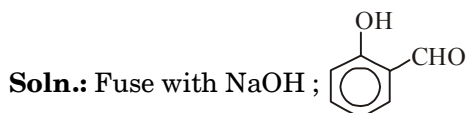
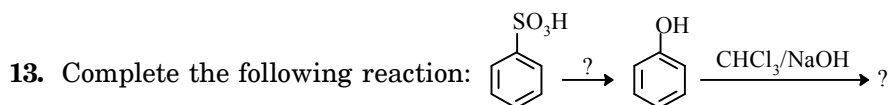


Formation of HCN by dehydration of *E* establishes that *E* is HCONH_2 and hence *D* is HCOOH .

- (iv) Therefore the alcohol *A* produced along with *D* (*i.e.* HCOOH) during Cannizzaro's reaction of *C* must be CH_3OH and so *C* must be HCHO (an aldehyde).

Thus the various compounds are:

- A* - CH_3OH (Alcohol, Methanol)
B - $\text{CH}_3\text{COOCH}_3$ (Ester, Methyl acetate)
C - HCHO (Aldehyde, Formaldehyde)
D - HCOOH (Acid, Formic acid)
E - HCONH_2 (Amide, Formamide).



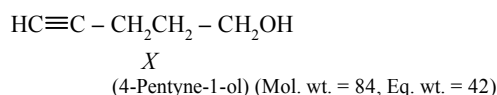
14. Compound *X* (molecular formula, $\text{C}_5\text{H}_8\text{O}$) does not react appreciably with Lucas reagent at room temperature but gives a precipitate with ammoniacal silver nitrate. With excess of MeMgBr , 0.42 g of *X* gives 224 ml of CH_4 at STP. Treatment of *X* with H_2 in presence of Pt catalyst followed by boiling with excess HI, gives *n*-pentane. Suggest structure for *X* and write the equation involved.

Soln.: (i) : There is no appreciable reaction of *X* ($\text{C}_5\text{H}_8\text{O}$) with Lucas reagent, it indicates that *X* is a primary alcohol.

(ii) The formation of a precipitate on reaction of *X* with ammoniacal silver nitrate indicates that *X* contains an acetylenic hydrogen atom (*i.e.* $\equiv \text{C}-\text{H}$ grouping is present in it).

(iii) Treatment of *X* with H_2/Pt followed by boiling with excess of HI yields *n*-pentane. This fact indicates that in *X* there is no side chain.

Keeping in mind the above facts, we can assign the following structure of *X* ($\text{C}_5\text{H}_8\text{O}$).



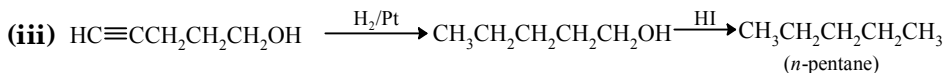
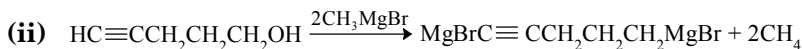
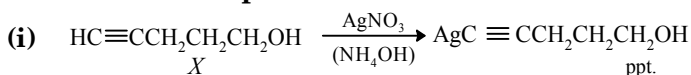
Calculations of Eq. Wt. of *X*

224 mL of CH_4 at STP is obtained from 0.42 g of *X*

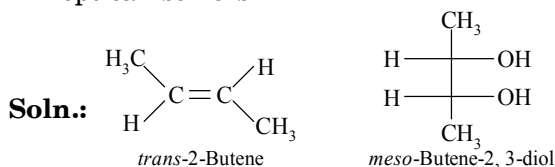
$$\therefore 22400 \text{ ml of } \text{CH}_4 \text{ at STP is obtained from } = \frac{0.42}{224} \times 22400 \text{ g} = 42 \text{ g of } X$$

$$\therefore \text{Eq. wt. of } X = 42$$

Reactions of compound X



15. Identify C (C₄H₈) which when treated with H₂O/H₂SO₄ gives C₄H₁₀O which cannot be resolved into optical isomers.



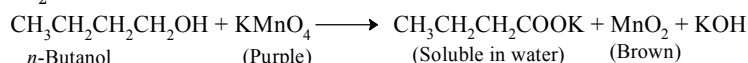
It should be a *trans*-isomer because on hydration (H₂O/H₂SO₄) it gives non-resolvable compounds (*i.e.* *meso*-isomer).

We know that electrophilic addition on alkene occurs in *trans* manner.

Thus *cis*-2-butene on hydration gives *dl*-butane-2,3-diol (resolvable in *d*- and *l*-isomers) while *trans*-2-butene produces *meso*-butane-2,3-diol (non-resolvable).

16. When *t*-butanol and *n*-butanol are separately treated with a few drops of dilute KMnO₄, in one case only the purple colour disappears and a brown precipitate is formed. Which of the two alcohols gives the above reaction and what is the brown precipitate?

Soln.: *n*-Butanol gives the following reaction in which the colour of KMnO₄ changes to brown. The brown colour is due to MnO₂.

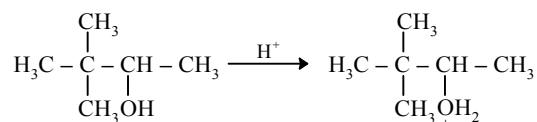


tert-alcohols are not oxidised easily and so there is no change in purple colour of KMnO₄.

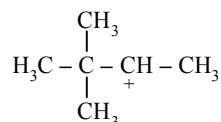
17. 3, 3-Dimethylbutan-2-ol loses a molecule of water in the presence of concentrated sulphuric acid to give tetramethylethylene as a major product. Suggest a suitable mechanism.

Soln.: Various steps involved in the suggested mechanism are:

- (a) Protonation of hydroxyl group

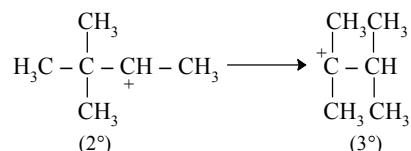


- (b) Removal of H₂O to form a secondary (2°) carbonium ion.

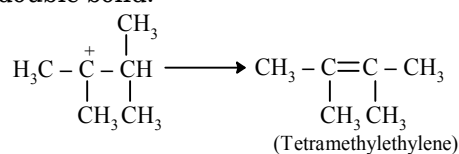


(2°) secondary carbonium ion.

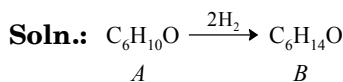
- (c) The conversion of secondary (2°) carbonium ion to stable tertiary (3°) carbonium ion by shift of -CH₃ group.



(d) The removal of H^+ to form a double bond.



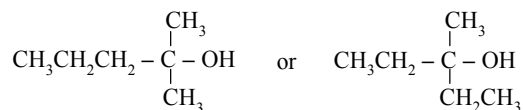
18. An optically active alcohol A ($C_6H_{10}O$) absorbs two moles of hydrogen per mole of A upon catalytic hydrogenation and gives a product B . The compound B is resistant to oxidation by CrO_3 and does not show any optical activity. Deduce the structures of A and B .



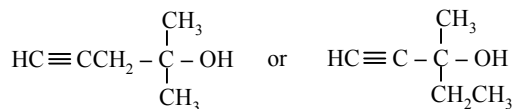
(i) Since B is resistant to oxidation, it must be *tert.* alcohol.

(ii) Since B is optically inactive, it must have at least two similar alkyl groups.

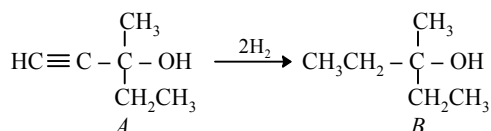
Thus the five carbon atoms can be adjusted into three alkyl groups (of which two are similar) either as $-\text{CH}_3$, $-\text{CH}_3$ and $-\text{C}_3\text{H}_7$ or as $-\text{C}_2\text{H}_5$, $-\text{C}_2\text{H}_5$ and $-\text{CH}_3$. Thus the possible structure of alcohol B is either



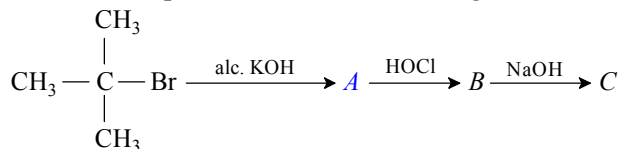
Hence the corresponding compound A is either



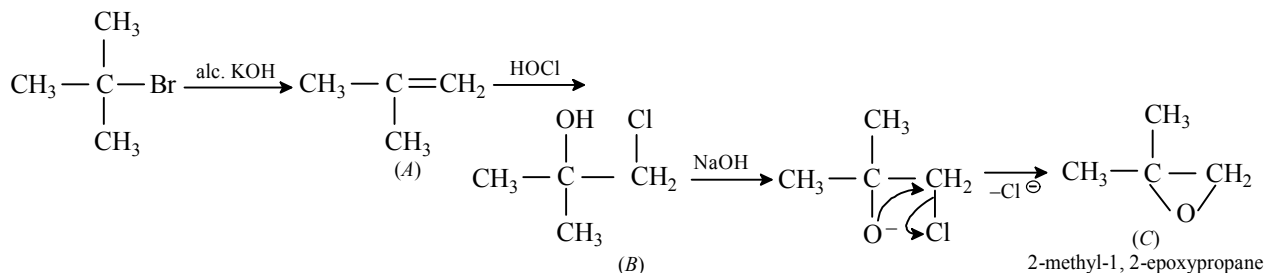
However compound A is optically active so its structure should be $\text{HC}\equiv\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_2\text{CH}_3}{\text{C}}}-\text{OH}$ which contains a chiral C-atom.



19. Predict the product for the following:



Soln.: Alcoholic KOH is dehydrohalogenating reagent hence (A) is alkene. Addition of HOCl according to Markownikoff's gives (B) which on treating with NaOH gives epoxy product (C) by S_Ni -path (Nucleophilic substitution internal)



EXERCISE

Multiple Choice Questions

- Ethyl alcohol can be used for preparation of which of the following?
 - Ethyl acetate
 - Ethylene
 - Acetic acid
 - All of these.
- Conversion of ethyl alcohol into acetaldehyde is an example of
 - reduction
 - molecular rearrangement
 - hydrolysis
 - oxidation.
- Which of the following reagents will convert propanoic acid to propan-1-ol?
 - KMnO₄
 - MnO₂
 - Cr₂O₃
 - LiAlH₄
- Ethylene reacts with 1% cold alkaline KMnO₄ to give
 - oxalic acid
 - acetone
 - ethylene glycol
 - formaldehyde.
- Glycerol, on heating with oxalic acid at 110°C gives
 - ethanol
 - methanoic acid
 - ether
 - acetone.
- Absolute ethyl alcohol can be converted to diethyl ether by heating it to 410 K in presence of
 - dil. H₂SO₄
 - dil. HCl
 - conc. H₂SO₄
 - conc. CH₃COOH.
- Propanone is the product obtained by dehydrogenation of
 - 2-propanol
 - 1-propanol
 - iso*-butyl alcohol
 - propanethiol.
- Which of the following combinations can be used to synthesize *iso*-propyl alcohol?
 - CH₃MgI and CH₃COCH₃
 - CH₃MgI and C₂H₅OH
 - CH₃MgI and CH₃COOC₂H₅
 - CH₃MgI and HCOOC₂H₅
- Which of the following is not formed when glycerol reacts with HI?
 - CH₂=CH-CH₂I
 - CH₂OH-CHI-CH₂OH
 - CH₃-CH=CH₂
 - CH₃-CHI-CH₃
- Identify the final product.

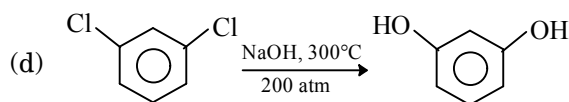
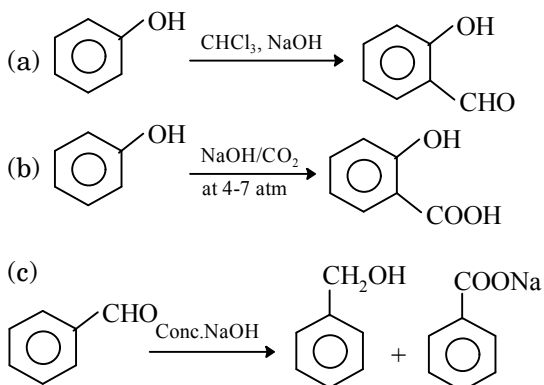
$$\text{CH}_2=\text{CH}_2 \xrightarrow{\text{O}_2, \text{Ag}} \text{X} \xrightarrow{473 \text{ K}} \text{Y}$$
 - Ethanol
 - Ethanal
 - Epoxy ethane
 - Ethylene glycol.
- $$\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\text{CH}_3 \xrightarrow{\text{PBr}_3} (\text{X}) \xrightarrow{\text{Mg/ether}} (\text{Y})$$

$$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2-\text{CH}_2 \end{array} \xrightarrow{\text{H}_2\text{O}} \xrightarrow{\Delta}$$

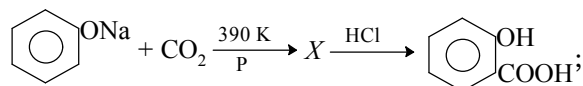
The final product is

 - $$\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2\text{CH}_2\text{OH}$$
 - $$\text{CH}_3-\text{O}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{CH}_3$$
 - $$\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{O}-\text{CH}_2-\text{CH}_3$$
 - none of the above.
- Dyes are formed when diazonium salts react with
 - phenols
 - aldehydes
 - ketones
 - alcohols.
- Bakelite is obtained from phenol by reacting with
 - Acetaldehyde
 - Formaldehyde
 - Baking soda
 - Formic acid.
- Which of the following alcohols is dehydrated most readily with conc. H₂SO₄?
 - p*-O₂NC₆H₄CH(OH)CH₃
 - p*-ClC₆H₄CH(OH)CH₃
 - p*-CH₃OC₆H₄CH(OH)CH₃
 - C₆H₅CH(OH)CH₃
- Rate of substitution in phenol is
 - slower than that in benzene
 - faster than that in benzene
 - equal to that in benzene
 - none of the above.
- The major product obtained when 3-phenyl-1,2-propanediol is heated with H₂SO₄ is
 - C₆H₅-CH₂-CO-CH₃
 - C₆H₅-CH₂-CH₂-CHO
 - C₆H₅-CH₂-CH=CH₂
 - $$\text{C}_6\text{H}_5-\text{CH}_2-\underset{\text{O}}{\text{CH}}-\text{CH}_2$$

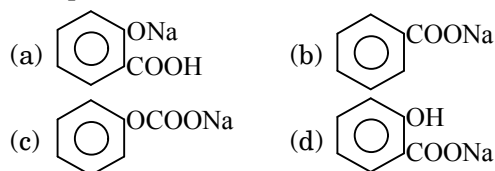
17. Phenol is
 (a) a base weaker than NH_3
 (b) an acid stronger than carbonic acid
 (c) an acid weaker than carbonic acid
 (d) neutral.
18. Which of the following is phenol?
 (a) Benzenol (b) Cresol
 (c) Catechol (d) All of these.
19. Carboic acid is the name used for
 (a) Opium (b) Phenol
 (c) Chloroform (d) H_2CO_3 .
20. In phenols,
 (a) —OH Group is attached to side chain
 (b) —OH Group is directly attached to benzene nucleus
 (c) Both (a) and (b)
 (d) None of the above.
21. Phenol with dilute HNO_3 gives
 (a) *meta*- and *para*-nitrophenol
 (b) *ortho*- and *para*-nitrophenol
 (c) trinitrophenol
 (d) *ortho*- and *meta*-nitrophenol.
22. Which of the following is an explosive?
 (a) PCl_5 (b) HNO_3
 (c) $\text{C}_6\text{H}_5\text{OH}$
 (d) 2,4,6-Trinitrophenol.
23. Which concept best explains that *o*-nitrophenol is more volatile than *p*-nitrophenol?
 (a) Resonance (b) Hydrogen bonding
 (c) Hyperconjugation (d) Steric hindrance.
24. Between *p*-nitrophenol and salicylaldehyde, solubility in base is
 (a) almost nil in both cases
 (b) higher in *p*-nitrophenol
 (c) higher for salicylaldehyde
 (d) equal in nature.
25. Which represents Reimer-Tiemann reaction?



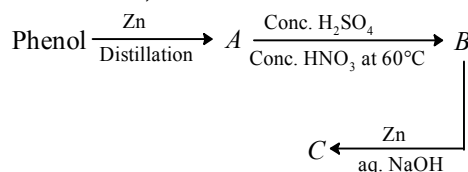
26. Phenol reacts with Br_2 in CCl_4 at low temperature to give
 (a) *m*-bromophenol
 (b) *o*- and *p*-bromophenol
 (c) *p*-bromophenol
 (d) 2,4,6-tribromophenol.
27. Among acetic acid, phenol and *n*-hexanol, which of the compound(s) will react with NaHCO_3 solution to give sodium salt and CO_2 ?
 (a) Acetic acid and phenol
 (b) Acetic acid
 (c) Phenol (d) *n*-Hexanol.
28. Phenol on oxidation gives chloranil. The oxidant used is
 (a) $\text{K}_2\text{S}_2\text{O}_8$ (b) KMnO_4
 (c) $\text{KClO}_3 + \text{HCl}$ (d) none of these.
- 29.



The product X in the reaction is

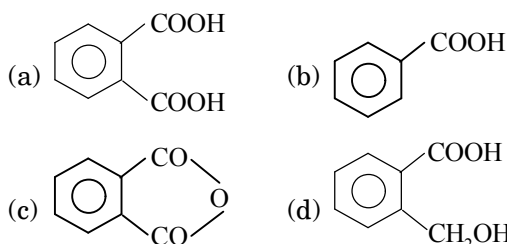
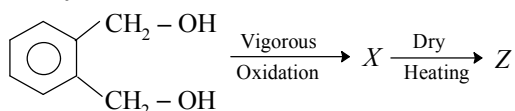


30. Which of the following statements regarding phenols is not correct?
 (a) Phenols are stronger acids than water and alcohols.
 (b) Phenols are weaker acids than carboxylic acids.
 (c) Phenols are soluble in both aqueous NaOH and aqueous NaHCO_3 .
 (d) Phenoxide ions are more stable than the corresponding phenols.
31. In the reaction,



- The compounds A, B and C are the following
 (a) benzene, nitrobenzene and aniline
 (b) benzene, dinitrobenzene and *m*-toluidine
 (c) toluene, nitrobenzene and *m*-toluidine
 (d) benzene, nitrobenzene and hydrazobenzene.

32. Identify Z in



33. A characteristic group test for phenolic group is

- (a) Liebermann's nitroso reaction
 (b) coupling with diazonium salt
 (c) aq. FeCl_3 (d) all of these.

34. Phenol is less acidic than

- (a) water (b) *p*-methoxyphenol
 (c) *p*-nitrophenol (d) ethanol.

35. Acidic character of phenol is due to

- (a) resonance of phenoxide ion
 (b) tautomerism occurring in phenol
 (c) the fact that the electronegativity of oxygen is more than that of hydrogen
 (d) none of the above.

36. Which compound is formed when sodium phenoxide is heated with ethyl iodide?

- (a) Phenetole (b) Ethyl phenyl alcohol
 (c) Phenol (d) None of these.

37. Salicylic acid as compared to benzoic acid

- (a) is more acidic (b) has same acidity
 (c) has less acidity (d) none of these.

38. Phenolphthalein is produced on heating phthalic anhydride and conc. sulphuric acid with

- (a) salicylic acid (b) phenol
 (c) phenacetin (d) phenanthrene.

39. Phenol on sulphonation gives

- (a) *o*-phenolsulphonic acid
 (b) *p*-phenolsulphonic acid
 (c) *m*-phenolsulphonic acid
 (d) mixture of *o*- and *p*-phenolsulphonic acids.

40. Dow's process is used for the conversion of chlorobenzene to

- (a) benzene (b) nitrobenzene
 (c) phenol (d) gammexane.

41. Which of the following has highest boiling point?

- (a) Benzene (b) Phenol
 (c) Toluene (d) Ethyl benzene.

42. When phenol is treated with PCl_5 , the yield of chlorobenzene is generally poor because of the formation of

- (a) benzoyl chloride (b) *p*-chlorophenol
 (c) *o*-chlorophenol (d) tertiary phosphate.

43. Salicylic acid when treated with zinc dust gives

- (a) phenol (b) salicylaldehyde
 (c) benzene (d) benzoic acid.

44. Phenol and benzoic acid can be distinguished by

- (a) aqueous NaHCO_3 (b) aqueous NaNO_3
 (c) aqueous NaOH (d) conc. H_2SO_4 .

45. *o*-Nitrophenol can form hydrogen bonds within the molecule. It thus has

- (a) very high melting point
 (b) very high viscosity
 (c) low melting point
 (d) none of the above.

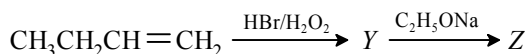
46. Cumene is

- (a) *o*-methyl phenol (b) *p*-cresol
 (c) *iso*-propyl benzene
 (d) phenyl *n*-propane.

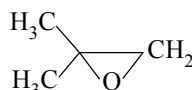
47. Increasing order of acidic strength among *p*-methoxyphenol, *p*-methylphenol and *p*-nitrophenol is

- (a) *p*-nitrophenol, *p*-methoxyphenol, *p*-methylphenol
 (b) *p*-methylphenol, *p*-methoxyphenol, *p*-nitrophenol
 (c) *p*-nitrophenol, *p*-methylphenol, *p*-methoxyphenol
 (d) *p*-methoxyphenol, *p*-methylphenol, *p*-nitrophenol

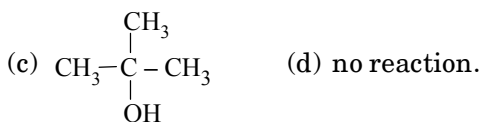
48. Identify Z in the sequence:



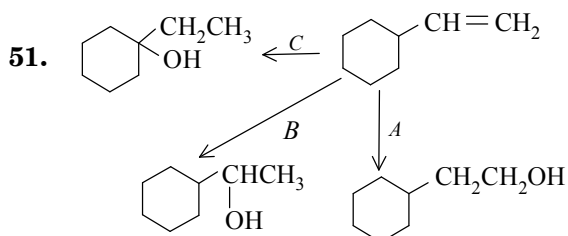
- (a) $(\text{CH}_3)_2\text{CHOCH}_2\text{CH}_3$
 (b) $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)-\text{O}-\text{CH}_2\text{CH}_3$
 (c) $\text{CH}_3(\text{CH}_2)_3-\text{O}-\text{CH}_2\text{CH}_3$
 (d) $\text{CH}_3(\text{CH}_2)_4-\text{O}-\text{CH}_3$

49.  $\xrightarrow{\text{LiAlH}_4} A$, A is

- (a) $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$
 (b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$



50. . In this diol,
 (a) —OH at C₂ is more basic than that of at C₅
 (b) —OH at C₂ is more acidic than at C₅
 (c) both behave as a base
 (d) both behave as an acid.



Schemes A, B, C are

I. acid-catalysed hydration

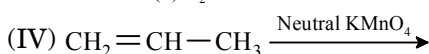
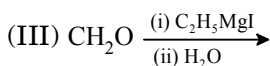
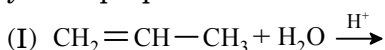
II. HBO

III. oxymercuration-demercuration

(a) I in all cases (b) I, II, III

(c) II, III, I (d) III, I, II

52. Which one/ones of the following reactions will yield 2-propanol?

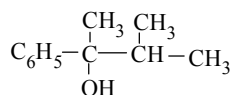


Choose the right answer.

(a) I and II (b) II and III

(c) III and I (d) II and IV

53. Which set of the following reagents (a to d) would you select to convert $\text{C}_6\text{H}_5\text{COCH}_3$ (acetophenone) to the following alcohol:



- (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{MgBr}$ and hydrolysis
 (b) $\text{CH}_3\text{CH}(\text{Br})\text{CH}_3$, AlCl_3
 (c) $(\text{CH}_3)_2\text{CHMgBr}$ and acid hydrolysis
 (d) $\text{CH}_3\text{CHOHCH}_3$, Zn.

54. Mild oxidation of glycerol with $\text{H}_2\text{O}_2/\text{FeSO}_4$ gives

- (a) glyceraldehyde only
 (b) dihydroxyacetone only
 (c) glycerose (d) none of these.

55. Methanol is industrially prepared by
 (a) oxidation of CH_4 by steam at 900°C
 (b) reduction of HCHO using LiAlH_4
 (c) reaction of HCHO with a solution of NaOH
 (d) reduction of CO using H_2 and $\text{ZnO}-\text{Cr}_2\text{O}_3$.

56. Which one of the following on oxidation gives a ketone?

- (a) Primary alcohol (b) Secondary alcohol
 (c) Tertiary alcohol (d) All of these.

57. What is formed when a primary alcohol undergoes catalytic dehydrogenation?

- (a) Aldehyde (b) Ketone
 (c) Alkene (d) Acid.

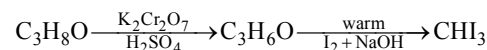
58. Dow's reaction involves

- (a) electrophilic addition
 (b) nucleophilic addition
 (c) electrophilic substitution
 (d) nucleophilic substitution.

59. Zerevitinov's determination of active hydrogen in a compound is based upon its reaction with

- (a) Na (b) CH_3MgI
 (c) Zn (d) Al

60. Identify X in the following sequence :



- (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (b) $\text{CH}_3\text{CHOHCH}_3$
 (c) $\text{CH}_3\text{OCH}_2\text{CH}_3$ (d) $\text{CH}_3\text{CH}_2\text{CHO}$

61. In Williamson's synthesis, ethoxyethane is prepared by

- (a) passing ethanol over heated alumina
 (b) heating sodium ethoxide with ethyl bromide
 (c) treating ethyl alcohol with excess of H_2SO_4 at $430-440\text{ K}$
 (d) heating ethanol with dry Ag_2O .

62. Which of the following reactants will react with phenol to give salicylaldehyde after hydrolysis?

- (a) Dichloromethane (b) Methyl chloride
 (c) Trichloromethane (d) None of these.

63. Which of the following does not give iodoform test?

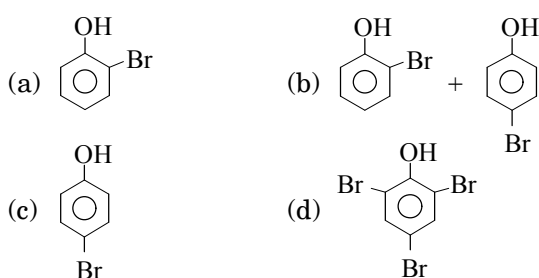
- (a) $\text{CH}_3\text{CH}_2\text{OH}$
 (b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
 (c) $(\text{CH}_3)_2\text{CHOH}$ (d) CH_3COCH_3

64. Conversion of cyclohexene to cyclohexanol can be conveniently achieved by

- (a) $\text{NaOH}-\text{H}_2\text{O}$ (b) $\text{Br}_2-\text{H}_2\text{O}$
 (c) hydroboration-oxidation
 (d) hydration-hydrolysis.

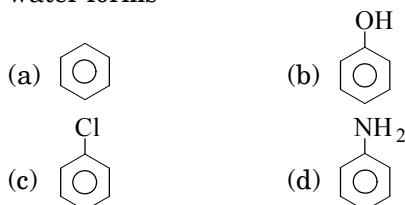
65. Aspirin is an acetylation product of
 (a) *p*-dihydroxybenzene
 (b) *o*-hydroxybenzoic acid
 (c) *o*-dihydroxybenzene
 (d) *m*-hydroxybenzoic acid.
66. Epichlorohydrin is
 (a) 3-chloropropane
 (b) 3-chloropropan-1-ol
 (c) 3-chloro-1, 2-epoxypropane
 (d) none of the above.
67. Which of the following has lowest solubility in water?
 (a) CH₃OH (b) C₂H₅OH
 (c) (CH₃)₂CHOH (d) (CH₃)₃COH

68. Phenol reacts with bromine water in carbon disulphide at low temperature to give

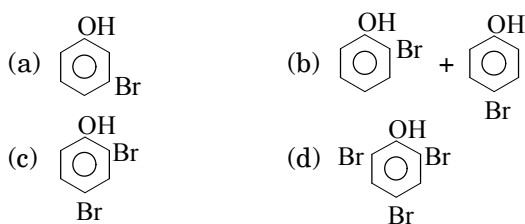


69. Which of the following is most acidic?
 (a) Phenol (b) Ethyl alcohol
 (c) Picric acid (d) *p*-Nitrophenol.
70. In the reaction of phenol with CHCl₃ and aqueous NaOH at 70°C (343 K), the electrophile attacking the ring is
 (a) CHCl₃ (b) •CHCl₂
 (c) :CCl₂ (d) COCl₂

71. Benzenediazonium chloride on boiling with water forms



72. When phenol is treated with excess bromine water, it gives



73. Picric acid is a name for a

- (a) phenol (b) carboxylic acid
 (c) trinitrophenol (d) nitroalkane.

74. Bakelite is a polymer of
 (a) HCHO + Phenol
 (b) HCHO + Acetaldehyde
 (c) H₂SO₄ + Phenol (d) none of these.
75. The reaction of aromatic acyl chloride and phenol in the presence of a base NaOH or pyridine is called
 (a) Kolbe's reaction
 (b) Perkin reaction
 (c) Sandmeyer's reaction
 (d) Schotten-Baumann reaction.

76. Ethyl alcohol is industrially prepared from ethylene by
 (a) permanganate oxidation
 (b) catalytic reduction
 (c) absorbing in H₂SO₄ followed by hydrolysis
 (d) fermentation.

77. How many isomers of C₅H₁₁OH will be primary alcohols?
 (a) 5 (b) 2
 (c) 4 (d) 3

78. The enzyme which can catalyse the conversion of glucose to ethanol is
 (a) zymase (b) invertase
 (c) maltase (d) diastase.

79. Which of the following can work as a dehydrating agent for alcohols?
 (a) H₂SO₄ (b) Al₂O₃
 (c) P₂O₅ (d) All of these.

80. In reaction of alcohols with alkali metal, which of the following alcohols will react fastest?
 (a) Secondary (b) Tertiary
 (c) Primary (d) All equally.

81. Which of the following statements is correct regarding ease of dehydration?
 (a) Primary > Secondary
 (b) Secondary > Tertiary
 (c) Tertiary > Primary
 (d) None of the above.

82. Grignard reagent on reaction with a ketone forms
 (a) tertiary alcohol (b) secondary alcohol
 (c) primary alcohol (d) carboxylic acid.

83. Ethyl alcohol on oxidation with K₂Cr₂O₇ gives
 (a) acetic acid (b) acetaldehyde
 (c) formaldehyde (d) formic acid.

84. Ethyl alcohol gives ethyl chloride with the help of
 (a) SOCl_2 (b) NaCl
 (c) Cl_2 (d) KCl
85. Which of the following isomers of butanol has a chiral structure?
 (a) $(\text{CH}_3)_3\text{COH}$ (b) $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\text{OH}$
 (c) $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$
 (d) $\text{CH}_3(\text{CH}_2)_3\text{OH}$
86. $\text{R} - \text{OH} + \text{HX} \rightarrow \text{RX} + \text{H}_2\text{O}$
 In the above reaction, the reactivity of alcohols is
 (a) tertiary > secondary > primary
 (b) tertiary < secondary < primary
 (c) tertiary > primary > secondary
 (d) secondary > primary > tertiary.
87. An organic compound (A) reacts with sodium metal and forms (B). On heating with conc. H_2SO_4 (A) gives diethyl ether. (A) and (B) are respectively
 (a) $\text{C}_2\text{H}_5\text{OH}$ and $\text{C}_2\text{H}_5\text{ONa}$
 (b) $\text{C}_3\text{H}_7\text{OH}$ and CH_3ONa
 (c) CH_3OH and CH_3ONa
 (d) $\text{C}_4\text{H}_9\text{OH}$ and $\text{C}_4\text{H}_9\text{ONa}$.
88. What is the product obtained when chlorine reacts with ethyl alcohol in the presence of NaOH ?
 (a) CH_3Cl (b) $\text{C}_2\text{H}_5\text{Cl}$
 (c) $\text{CCl}_3\cdot\text{CHO}$ (d) CHCl_3
89. A fruity smell is obtained by the reaction of ethanol with
 (a) PCl_5 (b) CH_3COCH_3
 (c) CH_3COOH (d) none of these.
90. Which of the following alcohols is used in beverages?
 (a) Propanol (b) 2-Butanol
 (c) Methanol (d) Ethanol.
91. 3 moles of ethanol react with one mole of phosphorus tribromide to form 3 moles of bromoethane and one mole of X. Which of the following is X?
 (a) H_3PO_4 (b) H_3PO_2
 (c) HPO_3 (d) H_3PO_3
92. A compound of the formula $\text{C}_4\text{H}_{10}\text{O}$ reacts with sodium and undergoes oxidation to give a carbonyl compound which does not reduce Tollen's reagent, the original compound is
 (a) diethyl ether (b) *n*-butyl alcohol
 (c) *iso*-butyl alcohol (d) *sec*-butyl alcohol.
93. Propan-1-ol can be prepared from propene by
 (a) $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$
 (b) $\text{Hg}(\text{OAc})_2/\text{H}_2\text{O}$ followed by NaBH_4
 (c) B_2H_6 followed by H_2O_2
 (d) $\text{CH}_3\text{CO}_2\text{H}/\text{H}_2\text{SO}_4$
94. When alcohol reacts with concentrated H_2SO_4 , intermediate formed is
 (a) carbonium ion (b) alkoxy ion
 (c) alkyl hydrogen sulphate
 (d) none of these.
95. The characteristic group of secondary alcohol is
 (a) $-\text{CH}_2\text{OH}$ (b) $\begin{array}{c} \diagup \\ \text{C} - \text{OH} \\ \diagdown \end{array}$
 (c) $>\text{CHOH}$ (d) $>\text{C}(\text{OH})_2$
96. Maximum number of active hydrogens are present in
 (a) acetic acid (b) glycerol
 (c) methane (d) methanol.
97. Action of nitrous acid on ethylamine gives
 (a) C_2H_6 and NH_3 (b) $\text{C}_2\text{H}_5\text{OH}$ and N_2
 (c) $\text{C}_2\text{H}_5\text{OH}$ and C_2H_4 (d) $\text{C}_2\text{H}_5\text{OH}$ and NH_3
98. The products of combustion of an aliphatic thiol (RSH) at 298 K are
 (a) $\text{CO}_{2(g)}$, $\text{H}_2\text{O}_{(g)}$ and $\text{SO}_{2(g)}$
 (b) $\text{CO}_{2(g)}$, $\text{H}_2\text{O}_{(l)}$ and $\text{SO}_{2(g)}$
 (c) $\text{CO}_{2(l)}$, $\text{H}_2\text{O}_{(l)}$ and $\text{SO}_{2(g)}$
 (d) $\text{CO}_{2(g)}$, $\text{H}_2\text{O}_{(l)}$ and $\text{SO}_{2(l)}$
99. 23 g of Na will react with ethanol to give
 (a) one mole of oxygen
 (b) one mole of H_2
 (c) $\frac{1}{2}$ Mole of H_2 (d) none of these.
100. Alcohols of low molecular weight are
 (a) soluble in water
 (b) soluble in water on heating
 (c) insoluble in water
 (d) insoluble in all solvents.
101. Primary and secondary alcohols on action of red hot copper give
 (a) aldehydes and ketones respectively
 (b) ketones and aldehydes respectively
 (c) only aldehydes
 (d) only ketones.
102. When primary alcohol is oxidised with Cl_2 , it gives
 (a) CH_3CHO (b) CH_3COCH_3
 (c) CH_3COCl (d) COCl_2

103. Which of the following is the most suitable method for removing the traces of water from ethanol?

- (a) Reacting with Na metal
 (b) Passing dry HCl through it
 (c) Distilling it (d) Reacting with Mg.

104. The reagent used to convert ethanoic acid to ethanol is

- (a) LiAlH_4 (b) BH_3
 (c) PCl_3 (d) $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$

105. A compound is soluble in conc. H_2SO_4 . It does not decolourise bromine in CCl_4 but is oxidised by chromic anhydride in aqueous sulphuric acid within two seconds, turning orange solution to blue-green, then opaque. The original solution contains

- (a) a secondary alcohol
 (b) an alkene
 (c) an ether (d) a primary alcohol.

106. *n*-Propyl alcohol and *iso*-propyl alcohol can be chemically distinguished by which reagent?

- (a) PCl_5 (b) Reduction
 (c) Oxidation with potassium dichromate
 (d) Ozonolysis.

107. The most suitable reagent for the conversion of $\text{RCH}_2\text{OH} \rightarrow \text{RCHO}$ is

- (a) KMnO_4 (b) $\text{K}_2\text{Cr}_2\text{O}_7$
 (c) CrO_3
 (d) PCC (pyridine chlorochromate).

108. $(\text{CH}_3)_2\text{CHOH} \xrightarrow{\text{Mild oxid.}} X \xrightarrow[\text{(ii) HOH}]{\text{(i) CH}_3\text{MgBr}} Y$.

Here, Y is

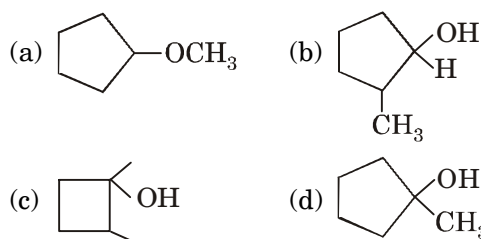
- (a) *iso*-butyl alcohol (b) *tert*-butyl alcohol
 (c) *iso*-butylene (d) *sec*-butyl alcohol.

109. Reaction of CH_2-CH_2 with RMgX

followed by hydrolysis will lead to the product

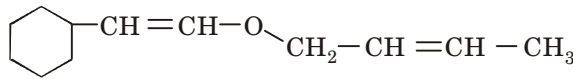
- (a) RCHOHR (b) RCHOHCH_3
 (c) $\text{R}_2\text{CHCH}_2\text{OH}$ (d) $\text{RCH}_2\text{CH}_2\text{OH}$

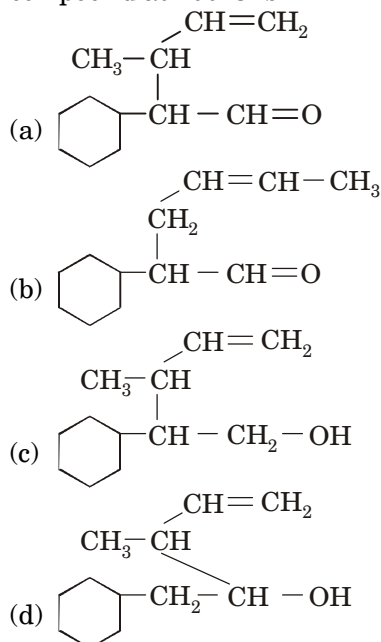
110. An organic compound A (molecular formula, $\text{C}_6\text{H}_{12}\text{O}$) doesn't decolourise the Bayer's reagent and, doesn't change the colour of acidic dichromate solution. Compound A on treatment with H_2SO_4 produces alkene, which on oxidative ozonolysis gives a molecule ($\text{C}_6\text{H}_{10}\text{O}_3$), which gives the positive iodoform test. The most appropriate molecular structure of A, is

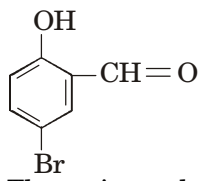


111. A compound $\text{C}_9\text{H}_{12}\text{O}$ (A), is oxidised under vigorous conditions to benzoic acid. It reacts with CrO_3 and gives a positive iodoform test. Mark out the incorrect statement about the compound (A).

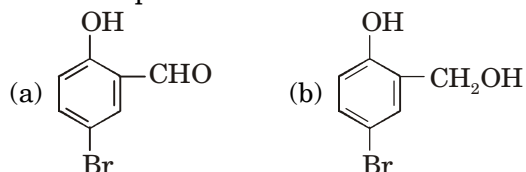
- (a) The compound is benzylic alcohol.
 (b) The compound is 2° alcohol.
 (c) The compound is chiral.
 (d) The compound doesn't give violet colour on treatment with FeCl_3 .

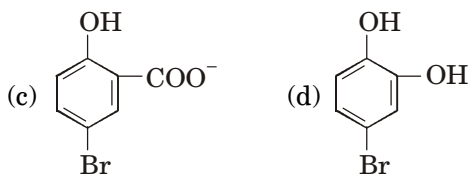
112. 
 The predominant product on heating the above compound at 200°C is



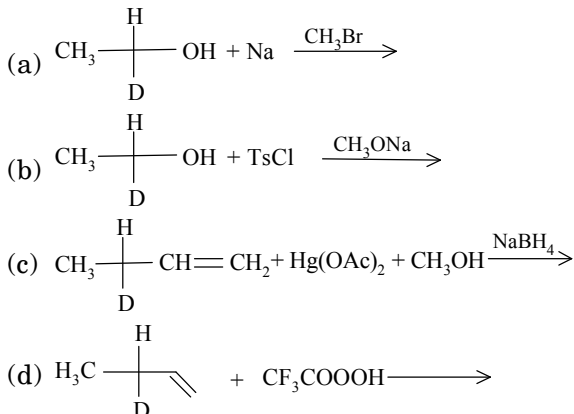
113.  $\xrightarrow[\text{H}^+]{\text{H}_2\text{O}_2, \bar{\text{O}}\text{H}}$ Product.

The main product is

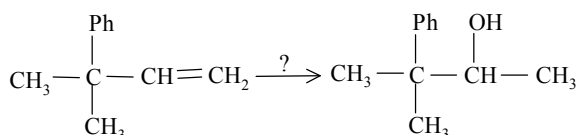




114. In which of the following preparations of ether, the configuration about chiral center is not retained?

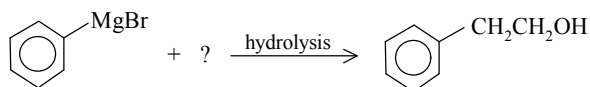



115. Which of the following reagent is most suitable for the following conversion?



- (a) $\text{H}^+/\text{HO}-\text{R}$ (b) TsCl, ROH
 (c) $\text{Hg}(\text{OCOCF}_3)_2, \text{ROH}, \text{NaBH}_4$
 (d) $\text{B}_2\text{H}_6/\text{THF}, \text{H}_2\text{O}_2/\text{OR}^-$

116. What is missing compound in the following transformation?

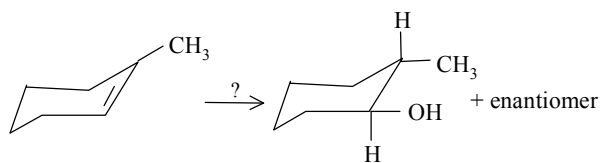


- (a) HCOOCH_3 (b) CH_3COCH_3
 (c) $\text{CH}_3\text{COOC}_2\text{H}_5$ (d) 

117. An ether is obtained when phenol is treated with which of the following reagent?

- (a) $(\text{CH}_3\text{CO})_2\text{O}/\text{CH}_3\text{COONa}$
 (b) $\text{C}_2\text{H}_5\text{I}/\text{NaOH}$ (c) $(\text{CH}_3)_3\text{CCl}/\text{HF}$
 (d) $\text{CHCl}_3/\text{NaOH}$

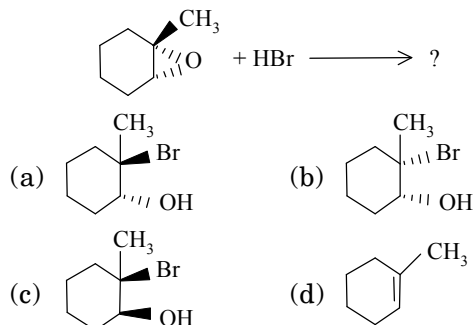
118. Which of the reagents would effect the conversion?



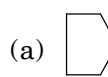

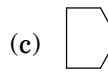
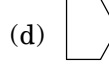
- (a) BH_3/THF , then $\text{H}_2\text{O}_2/\text{OH}^-$

- (b) $\text{H}_2\text{O}/\text{Hg}(\text{OAc})_2, \text{THF}$ then $\text{NaBH}_4/\text{OH}^-$
 (c) H_3O^+ , heat (d) none of these.

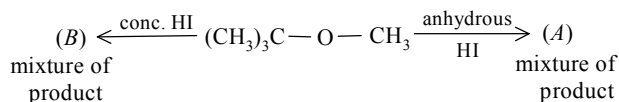
119. The product of the following reaction



120. Which of the following is most suitable method for the preparation of methyl cyclopentyl ether?

- (a)  + CH_3ONa (b)  + CH_3Br
 (c)  + CH_3F
 (d)  + $\text{CH}_3\text{CH}_2\text{Cl}$

121. Consider the following transformations:



- (a) A and B are identical mixture of CH_3I and $(\text{CH}_3)_3\text{C}-\text{OH}$
 (b) A and B are identical CH_3OH , $(\text{CH}_3)_3\text{CI}$
 (c) A is a mixture of CH_3I and $(\text{CH}_3)_3\text{COH}$ whereas B is a mixture of CH_3OH and $(\text{CH}_3)_3\text{CI}$
 (d) A is a mixture of $(\text{CH}_3)_3\text{CI}$ and CH_3OH where as B is a mixture of CH_3I and $(\text{CH}_3)_3\text{COH}$.

122. What happens when oxirane is heated with PCl_5 ?

- (a) A geminal dihalide is formed.
 (b) A vicinal dihalide is formed.
 (c) Mixture of vicinal and geminal dihalide is formed.
 (d) No reaction takes place.

123. What is the product of the reaction,



- (a) $\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{CH}_2\text{I}$, $\text{HOH}_2\text{C}-\text{C}_6\text{H}_4-\text{CH}_3$
 (b) $\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{CH}_2\text{OH}$, $\text{IH}_2\text{C}-\text{C}_6\text{H}_4-\text{CH}_3$
 (c) $\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{CH}_2\text{I}$, $\text{IH}_2\text{C}-\text{C}_6\text{H}_4-\text{CH}_3$
 (d) no reaction.

124. The action of HX on ether is in the order of
 (a) HBr > HCl > HI > HF
 (b) HI > HBr > HCl > HF
 (c) HCl > HI > HBr > HF
 (d) all are equal reactive.

125. In the reaction,
 $\text{PhMgBr} + \text{CH}_3 - \text{CH} - \text{CH}_2 \xrightarrow{\text{H}_2\text{O}}$, the major

product obtained is

- (a) Ph - CH₂ - CH(OH)CH₃
 (b) Ph - $\underset{\text{CH}_3}{\text{CH}}$ - CH₂OH
 (c) Ph - CH = CH₂
 (d) $\text{CH}_2 - \text{CH} - \text{CH}_2\text{Ph}$

126. Which of the following product is obtained in the following reaction?

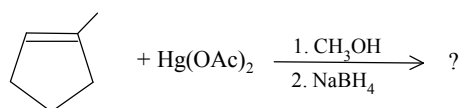


- (a) $\text{BrCH}_2 - \text{C}_6\text{H}_4 - \text{OCH}_3$
 (b) $\text{CH}_3 - \text{C}_6\text{H}_3(\text{Br}) - \text{OCH}_3$ (c) $\text{CH}_3 - \text{C}_6\text{H}_3(\text{Br}) - \text{OCH}_3$
 (d) No reaction.

127. In the reaction, $\text{Cyclopropane} + \text{PhOH} \xrightarrow{\text{H}^+}$, the product is

- (a) $\text{Cyclopropane} - \text{OH} - \text{Ph}$ (b) $\text{Cyclopropane} = \text{C} - \text{C} = \text{C}$
 (c) $\text{Cyclopropane} - \text{OH} - \text{CH}_2 - \text{Ph}$ (d) $\text{Cyclopropane} - \text{CH}_2 - \text{OH} - \text{Ph}$

128. Identify the product in the following reaction



- (a) $\text{Cyclopentane} - \text{H}_3\text{CO} - \text{H} - \text{H} - \text{CH}_3$ (b) $\text{Cyclopentane} - \text{CH}_3 - \text{OCH}_3$
 (c) $\text{Cyclopentane} - \text{CH}_3 - \text{OH}$ (d) $\text{Cyclopentane} - \text{CH}_3 - \text{CH}_3 - \text{OCH}_3$

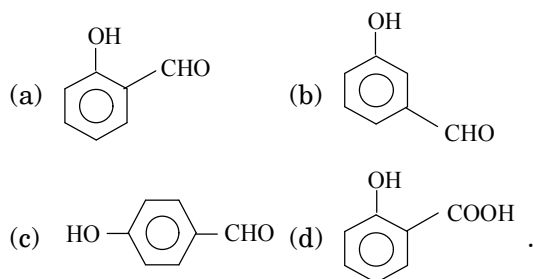
129. If a particular ether contains 60% carbon and 13.3% hydrogen, its formula could be
 (a) C₂H₆O (b) C₄H₁₀O
 (c) C₅H₁₂O (d) C₃H₈O

130. Electrophilic substitution in phenol generally occurs at
 (a) *o* and *p*-positions (b) *m*-position
 (c) only at *o*-position
 (d) only at *p*-position.

131. Which of the following is not true in case of reaction with heated copper at 300°C?

- (a) Phenol → Benzyl alcohol
 (b) Primary alcohol → Aldehyde
 (c) Secondary alcohol → Ketone
 (d) Tertiary alcohol → Olefin.

132. What is the major product obtained when phenol is treated with chloroform and aqueous alkali?



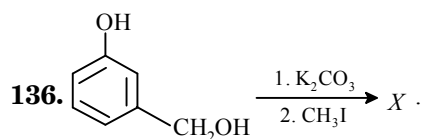
133. The strongest acid among the following aromatic compounds is

- (a) *o*-nitrophenol (b) *p*-chlorophenol
 (c) *p*-nitrophenol (d) *m*-nitrophenol.

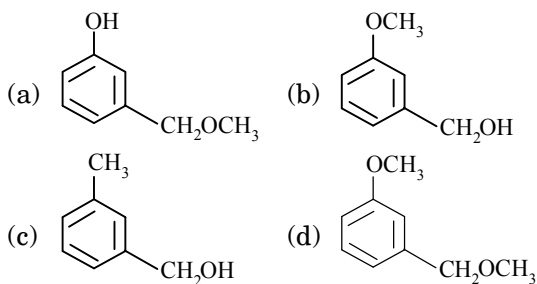
134. In the Liebermann's nitroso reaction, sequential changes in the colour of phenol occurs as

- (a) brown or red → green → deep blue
 (b) red → deep blue → green
 (c) red → green → white
 (d) white → red → green.

135. Na reacts with phenol to produce
 (a) H₂ gas (b) benzene
 (c) CO₂ gas (d) CO gas.



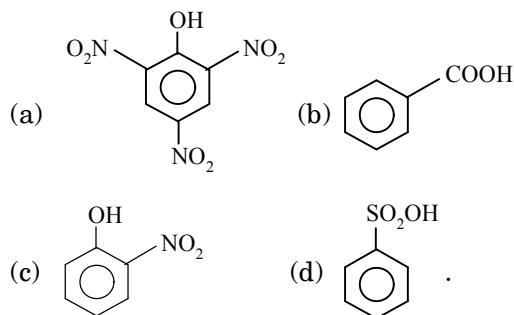
The product X is



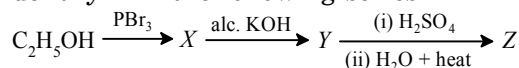
137. Salol can be used as
 (a) antiseptic (b) antipyretic
 (c) both (a) and (b) (d) none of these.
138. Which one of the following compounds gives characteristic deep colour with FeCl_3 solution?
 (a) Acetone (b) Ethanol
 (c) Phenol (d) Acetic acid.
139. Which of the following compounds is known as oil of winter green?
 (a) Phenyl benzoate (b) Phenyl salicylate
 (c) Phenyl acetate (d) Methyl salicylate.
140. Zinc powder + Ph - OH \rightarrow X. In the above reaction the product X will be
 (a) benzaldehyde (b) benzene
 (c) anisole (d) phenyl acetate.
141. Phenol on treatment with conc. HNO_3 gives
 (a) picric acid (b) styphnic acid
 (c) both (a) and (b) (d) none of these.
142. In order to get bakelite from phenol which of the following reagents is required?
 (a) HCHO (b) $\text{CHCl}_3/\text{NaOH}$
 (c) CCl_4/NaOH (d) HCHO/H^+ or OH^-
143. Phenol gives colour with neutral FeCl_3 solution.
 (a) violet (b) green
 (c) red (d) blue.
144. Vinyl carbinol is
 (a) $\text{HO} - \text{CH}_2\text{CH}=\text{CH}_2$
 (b) $\text{CH}_3\text{C}(\text{OH}) = \text{CH}_2$
 (c) $\text{CH}_3 - \text{CH}=\text{CH} - \text{OH}$
 (d) $\text{CH}_3\text{C}(\text{CH}_2\text{OH}) = \text{CH}_2$
145. Phenol is more readily soluble in
 (a) dil. HCl
 (b) NaOH solution
 (c) both NaOH and dil. HCl
 (d) sodium bicarbonate solution.
146. Benzylamine reacts with nitrous acid to form
 (a) azobenzene (b) benzene
 (c) benzyl alcohol (d) phenol.
147. Sodium phenoxide reacts with CO_2 at 400 K and 4.7 atm pressure to give

- (a) sodium salicylate (b) salicylaldehyde
 (c) catechol (d) benzoic acid.

148. The compound 'A' when treated with methyl alcohol and few drops of H_2SO_4 gave smell of winter green. The compound 'A' is
 (a) succinic acid (b) salicylic acid
 (c) tartaric acid (d) oxalic acid.
149. Which of the following will not be soluble in sodium carbonate solution?

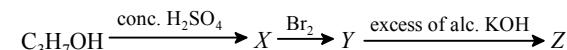


150. Identify Z in the following series.



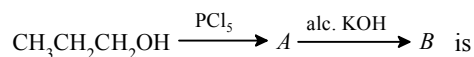
- (a) $\text{CH}_2=\text{CH}_2$ (b) $\text{CH}_3-\text{CH}_2\text{OH}$
 (c) $\text{CH}_3-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_3$
 (d) None of these.

151. Identify Z in the series.



- (a) $\text{CH}_3-\underset{\text{NH}_2}{\text{CH}}-\underset{\text{NH}_2}{\text{CH}_2}$ (b) $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\underset{\text{OH}}{\text{CH}_2}$
 (c) $\text{CH}_3-\underset{\text{OH}}{\text{C}}=\text{CH}_2$ (d) $\text{CH}_3-\text{C}\equiv\text{CH}$

152. The compound B formed in the following sequence of reaction



- (a) propyne (b) propene
 (c) propanal (d) propane.

153. Which of the following cannot be produced by acidic dehydration of alcohols?

- (a) Ether
 (b) Aldehyde
 (c) Alkyl hydrogen sulphate
 (d) Alkene.

154. Which one is primary alcohol?

- (a) Buten-2-ol (b) Propan-2-ol
 (c) Butan-1-ol
 (d) 2,3-Dimethylhexan-4-ol

155. Which of the following is not a characteristic of alcohol?
- They are lighter than water
 - Their boiling points rise fairly uniformly with rising molecular weight
 - Lower members are insoluble in water and organic solvents but the solubility regularly increases with molecular mass
 - Lower members have a pleasant smell and burning taste, higher members are colourless and tasteless.
156. Alcohol fermentation is brought about by the action of
- CO₂
 - O₂
 - invertase
 - yeast.
157. When vapours of an alcohol are passed over hot reduced copper, alcohol is converted into alkene, the alcohol is
- primary
 - secondary
 - tertiary
 - none of these.
158. Alkene $R - CH = CH_2$ reacts with B_2H_6 in the presence of H_2O_2 to give
- $R - \overset{\overset{O}{||}}{C} - CH_3$
 - $R - \overset{\overset{OH}{|}}{CH} - \overset{\overset{OH}{|}}{CH_2}$
 - $R - CH_2 - CHO$
 - $R - CH_2 - CH_2 - OH$
159. Which statement is not correct about alcohols?
- Ethyl alcohol is heavier than water.
 - Ethyl alcohol evaporates more quickly.
 - Alcohol with less number of carbon atoms is more soluble in water than alcohol with more number of carbon atoms.
 - Alcohol produces H_2 by reaction with sodium metal.
160. Which of the following processes is employed to convert alkyl halide into alcohol?
- Addition
 - Substitution
 - Dehydrohalogenation
 - Molecular rearrangement.
161. $R - CH_2 - CH_2 - OH$ can be converted into RCH_2CH_2COOH by the following sequence of steps
- PBr_3, KCN, H_3O^+
 - $PBr_3, KCN, H_2/Pt$
 - KCN, H_3O^+
 - HCN, PBr_3, H_3O^+
162. Which one has highest boiling point?
- Butan-2-ol
 - Ethane
 - Butane
 - Pentane.
163. Which of the following will not give iodoform test?
- Ethanol
 - Ethanal
 - Iso*-propyl alcohol
 - Benzyl alcohol.
164. Which of the following has maximum hydrogen bonding?
- Ethylamine
 - Ammonia
 - Ethyl alcohol
 - Diethyl ether.
165. The correct order of boiling point for primary (1°), secondary (2°) and tertiary (3°) alcohols is
- 1° > 2° > 3°
 - 3° > 2° > 1°
 - 2° > 1° > 3°
 - 2° > 3° > 1°
166. Which of the following is correct?
- Reduction of any aldehyde gives secondary alcohol.
 - Reaction of vegetable oil with H_2SO_4 gives glycerine.
 - Alcoholic iodine with NaOH gives iodoform.
 - Sucrose on reaction with NaCl gives invert sugar.
167. Order of esterification of alcohols is
- T > S > P
 - S > T > P
 - P > S > T
 - none of these.
168. The most reactive nucleophile among the following is
- CH_3O^-
 - $C_6H_5O^-$
 - $(CH_3)_2CHO^-$
 - $(CH_3)_3CO^-$
169. Final product formed on reduction of glycerol by hydriodic acid is
- propane
 - propanoic acid
 - propene
 - none of these.
170. The product $\begin{matrix} CH_2OCOCH_3 \\ | \\ CH_2OCOCH_3 \end{matrix}$ is obtained by the reaction of
- acetone and glycol
 - ethanal and ethanol
 - glycol and CH_3COCl
 - glycerol and $(CH_3CO)_2O$.
171. Dehydration of glycerol gives
- propane
 - propene
 - acrolein
 - benzene.
172. Glycerol is a
- primary alcohol
 - monohydric alcohol
 - secondary alcohol
 - trihydric alcohol.
173. Rectified spirit is a mixture of
- 95% ethyl alcohol + 5% water
 - 94% ethyl alcohol + 4.53% water
 - 94.4% ethyl alcohol + 5.43% water
 - 90% ethyl alcohol + 10% water.

174. Mild oxidation of glycerol with $\text{H}_2\text{O}_2/\text{FeSO}_4$ gives

- (a) glyceraldehyde (b) dihydroxy acetone
(c) glycerose (d) none of these.

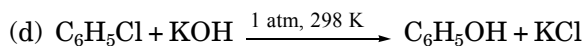
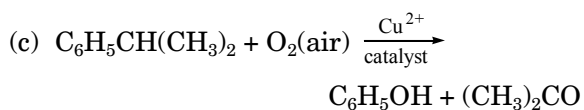
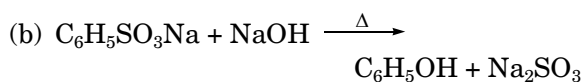
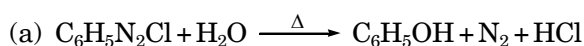
175. Ethanol containing some methanol is called

- (a) absolute spirit (b) rectified spirit
(c) power alcohol (d) methylated spirit.

176. Proof spirit (by volume) is a mixture of

- (a) 67.1% ethyl alcohol + 32.9% water
(b) 95.87% ethyl alcohol + 4.13% water
(c) 57.1% ethyl alcohol + 42.9% water
(d) None of the above.

177. For the preparation of phenol which one of the following reaction is not feasible?



178. Phenol gives *sym*-tribromophenol when treated with bromine in aqueous solution but only *o*- and *p*-bromophenols in CCl_4 solution because

- (a) in aqueous solution the bromine is ionised.
(b) in aqueous solution, phenol exists in equilibrium with phenoxide ion which has more activating effect.
(c) in CCl_4 , the electrophilicity of Br_2 increases.
(d) in CCl_4 , the other positions of benzene rings are blocked by the solvent.

179. Condensation of phenol with phthalic anhydride in presence of a drop of concentrated H_2SO_4 gives

- (a) phenolphthalein (b) methyl red
(c) bakelite (d) none of these.

180. The reaction of $\text{CH}_3-\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{OH}$ with HBr gives

- (a) $\text{CH}_3\text{CHBrCH}_2-\text{C}_6\text{H}_4-\text{OH}$
(b) $\text{CH}_3\text{CH}_2\text{CHBr}-\text{C}_6\text{H}_4-\text{OH}$
(c) $\text{CH}_3\text{CHBrCH}_2-\text{C}_6\text{H}_3(\text{Br})-\text{OH}$
(d) $\text{CH}_3\text{CH}_2\text{CHBr}-\text{C}_6\text{H}_3(\text{Br})-\text{OH}$

181. An organic compound with molecular formula, $\text{C}_7\text{H}_8\text{O}$ dissolves in NaOH and gives a

characteristic colour with FeCl_3 . On treatment with bromine, it gives a tribromoderivative, $\text{C}_7\text{H}_5\text{OBr}_3$. The compound is

- (a) benzyl alcohol (b) *o*-cresol
(c) *p*-cresol (d) none of these.

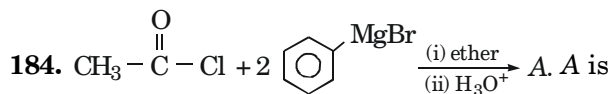
182. Dehydration of the following in increasing order is

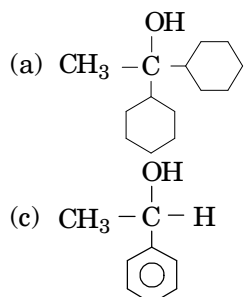
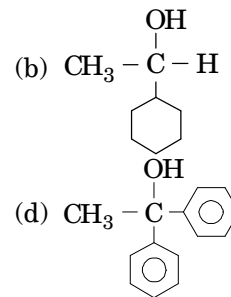
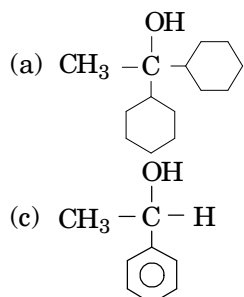
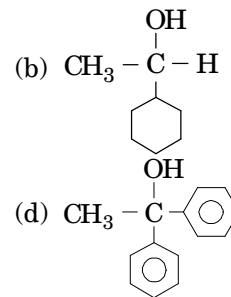


- (a) I < II < III < IV (b) II < III < IV < I
(c) I < III < IV < II (d) none of these.

183. When phenol reacts with benzenediazonium chloride, the product obtained is

- (a) phenyl hydrazine
(b) *p*-amino azobenzene
(c) phenol hydroxylamine
(d) *p*-hydroxy azobenzene.



- (a)  (b) 
(c)  (d) 

185. Phenol differs much from ethanol in its reaction towards

- (a) metallic sodium (b) acetyl chloride
(c) PCl_3 (d) nitric acid.

186. What amount of bromine will be required to convert 2 g of phenol into 2, 4, 6-tribromophenol?

- (a) 4.00 (b) 6.00
(c) 10.22 (d) 20.44

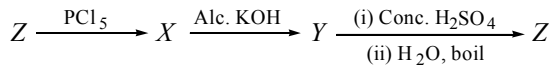
187. Which of the following has the highest boiling point?

- (a) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{OH}$
(b) $\text{CH}_3-\text{CH}_2-\underset{\text{OH}}{\text{CH}}-\text{CH}_3$
(c) $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2\text{OH}$
(d) $\text{CH}_3-\underset{\text{CH}_3}{\text{C}}-\text{CH}_3$

188. Cl_2 reacts with ethanol to give
 (a) $\text{C}_2\text{H}_5\text{Cl}$ (b) CHCl_3
 (c) CCl_3CHO (d) none of these.

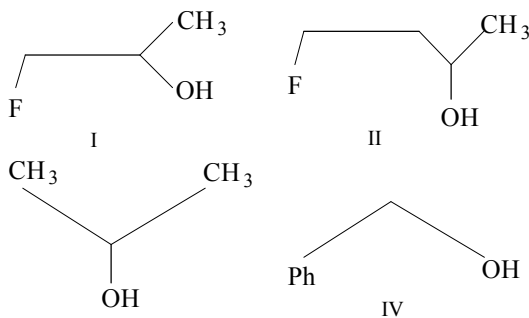
189. HBr reacts fastest with
 (a) 2-methylpropan-1-ol
 (b) 2-methylpropan-2-ol
 (c) propan-2-ol (d) propan-1-ol.

190. What is Z in the following sequence of reactions?



- (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (b) $\text{CH}_3\text{CHOHCH}_3$
 (c) $(\text{CH}_3\text{CH}_2)_2\text{CHOH}$ (d) $\text{CH}_3\text{CH}=\text{CH}_2$

191. The order of reactivity of the following alcohols towards concentrated HCl is

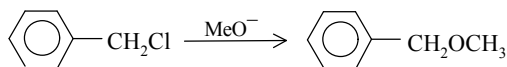


- (a) $\text{I} > \text{II} > \text{III} > \text{IV}$ (b) $\text{I} > \text{III} > \text{II} > \text{IV}$
 (c) $\text{IV} > \text{III} > \text{II} > \text{I}$ (d) $\text{IV} > \text{III} > \text{I} > \text{II}$

192. The compound that will react most readily with NaOH to form methanol is

- (a) $(\text{CH}_3)_4\text{N}^+\text{I}^-$ (b) CH_3OCH_3
 (c) $(\text{CH}_3)_3\text{S}^+\text{I}^-$ (d) $(\text{CH}_3)_3\text{CCl}$

193. The conversion of



preferably follows

- (a) $\text{S}_{\text{N}}1$ path (b) $\text{S}_{\text{N}}2$ path
 (c) $\text{S}_{\text{N}}1'$ path (d) $\text{S}_{\text{N}}\text{i}$ path.

194. Which of the reagents are not used in the preparation of anisole *via* Williamson's synthesis?

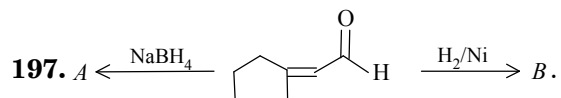
- (a) Na (b) $\text{CH}_3 - \text{Cl}$
 (c) (d)

195. Which of the following ethers form peroxide readily?

- (a) (b)
 (c) $(\text{CH}_3)_3\text{C} - \text{OC}(\text{CH}_3)_3$
 (d) $\text{CH}_3 - \text{O} - \text{CH}_3$

196. Which of the following could be employed to transform ethanol into 1-propanol?

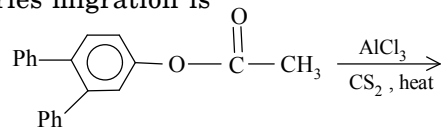
- (a) HBr , Mg /ether then H_3O^+
 (b) HBr , Mg /ether then HCHO then H_3O^+
 (c) H_2SO_4 at 140°C
 (d) $\text{H}_2\text{SO}_4/180^\circ\text{C}$ then



Compounds A and B are

- (a) ,
 (b) ,
 (c) ,
 (d) none of the above.

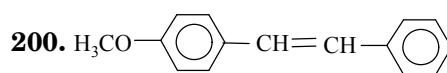
198. The product mainly obtained in the following Fries migration is



- (a) (b)
 (c) (d)

199. The correct order of decreasing strength of the following acid is

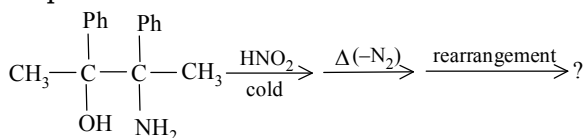
- (a) $\text{C}_6\text{H}_5\text{SO}_3\text{H} > \text{C}_6\text{H}_5\text{COOH} > \text{C}_6\text{H}_5\text{CH}_2\text{COOH} > \text{C}_6\text{H}_5\text{OH}$
 (b) $\text{C}_6\text{H}_5\text{SO}_3\text{H} > \text{C}_6\text{H}_5\text{COOH} > \text{C}_6\text{H}_5\text{OH} > \text{C}_6\text{H}_5\text{CH}_2\text{COOH}$
 (c) $\text{C}_6\text{H}_5\text{CH}_2\text{COOH} > \text{C}_6\text{H}_5\text{COOH} > \text{C}_6\text{H}_5\text{OH} > \text{C}_6\text{H}_5\text{SO}_3\text{H}$
 (d) $\text{C}_6\text{H}_5\text{OH} > \text{C}_6\text{H}_5\text{CH}_2\text{COOH} > \text{C}_6\text{H}_5\text{COOH} > \text{C}_6\text{H}_5\text{SO}_3\text{H}$



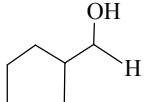
on hydroboration oxidation primarily gives

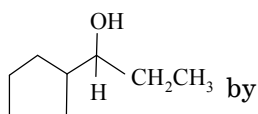
- (a) $\left(\text{H}_3\text{CO}-\text{CH}-\text{CH}_2\text{C}_6\text{H}_5 \right)_3 \text{B}$
- (b) $\text{H}_3\text{CO}-\text{C}_6\text{H}_4-\text{CH}_2-\text{CH}(\text{OH})-\text{C}_6\text{H}_5$
- (c) $\text{CH}_3\text{O}-\text{C}_6\text{H}_4-\text{CH}(\text{OH})-\text{CH}_2-\text{C}_6\text{H}_5$
- (d) $\text{CH}_3\text{OH} + \text{HO}-\text{C}_6\text{H}_4-\text{CH}=\text{CH}-\text{C}_6\text{H}_5$

201. The final product of the following reaction sequence is



- (a) $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CCH}_3(\text{Ph})_2$
- (b) $\text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{Ph}}{\text{C}}(\text{CH}_3)_2$
- (c) $\text{CH}_3-\overset{\text{H}}{\underset{\text{Ph}}{\text{C}}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{Ph}$
- (d) none of the above.

202.  can be effectively converted to

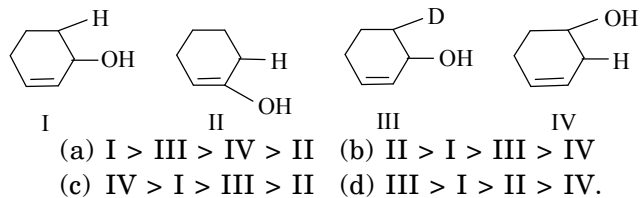


- (a) CrO_3 at 300°C , $\text{CH}_3\text{CH}_2\text{OH}$, $\text{H}_2\text{SO}_4/180^\circ\text{C}$
- (b) hot, conc. KMnO_4 followed by $\text{C}_2\text{H}_5\text{MgBr}$, H_3O^+
- (c) $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$, $\text{CH}_3\text{CH}_2\text{Br}$, $\text{C}_2\text{H}_5\text{O}^-$
- (d) Cu at 300°C , $\text{CH}_3\text{CH}_2\text{MgBr}$, H_3O^+ .

203. A compound (A), $\text{C}_7\text{H}_6\text{O}_2$ reacts with excess of CH_3MgBr followed by H_3O^+ gives an alcohol, which on dehydration gave an alkene which upon reductive ozonolysis gives an aldehyde which responds positively to the iodoform test. The ester may be

- (a) $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OC}_6\text{H}_5$ (b) $\text{C}_6\text{H}_5\text{COOH}$
- (c) $p\text{-OHC}_6\text{H}_4\text{CHO}$ (d) all of these.

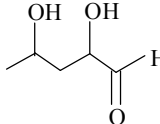
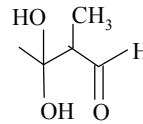
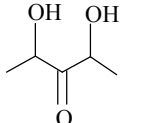
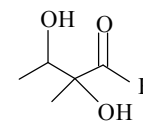
204. The ease of dehydration in the following compounds is



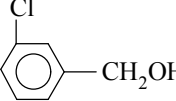
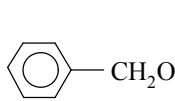
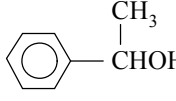
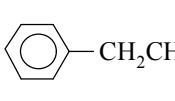
205. Compound (X), $\text{C}_5\text{H}_{10}\text{O}_3$

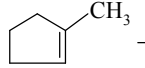
- $\xrightarrow{\text{Na}}$ evolves one equiv. H_2
- $\xrightarrow{\text{NaHCO}_3}$ no effervescence of CO_2
- $\xrightarrow[\text{Pb}(\text{OAc})_4]{\text{HIO}_4 \text{ or}}$ $\text{CH}_3\text{CHO} + \text{HCOOH} + \text{CH}_3\text{COOH}$
- $\xrightarrow{\text{HI/Red P}}$ $\text{CH}_3\text{CH}_2\text{CH} \begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix}$

Compound (X) is

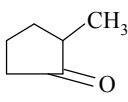
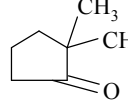
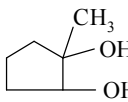
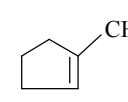
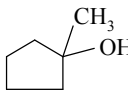
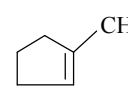
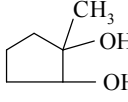
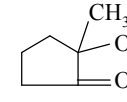
- (a) 
- (b) 
- (c) 
- (d) 

206. Which of the following is most reactive with HCl in presence of anhydrous ZnCl_2 (Lucas reagent)?

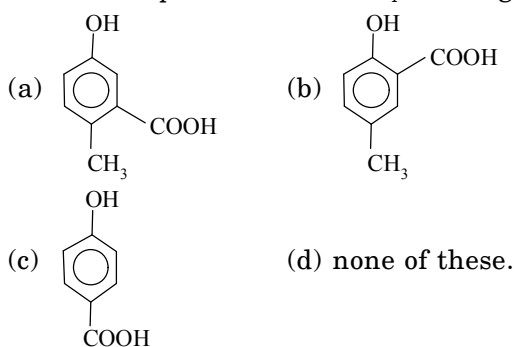
- (a)  (b) 
- (c)  (d) 

207.  $\xrightarrow[\text{cold, dil.}]{\text{KMnO}_4/\text{OH}^-}$ A $\xrightarrow[\text{CH}_3\text{COOH}]{\text{CrO}_3}$ B.

Compounds (A) and (B) are

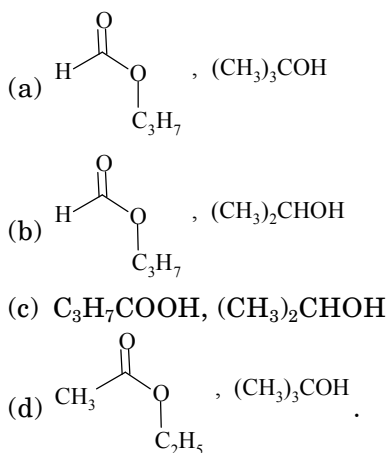
- (a) , 
- (b) , 
- (c) , 
- (d) , 

208. Reaction of *p*-cresol with CCl_4/NaOH gives

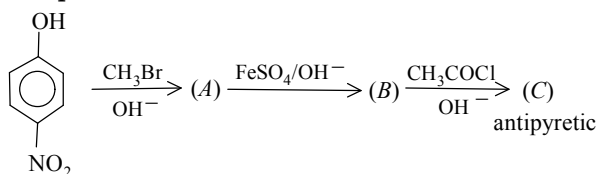


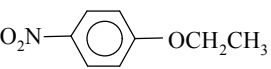
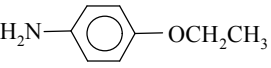
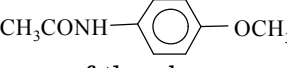
209. Ester $A(\text{C}_4\text{H}_8\text{O}_2) + \text{CH}_3\text{MgBr} \xrightarrow[\text{(excess)}]{\text{H}_3\text{O}^+} B(\text{C}_3\text{H}_8\text{O})$

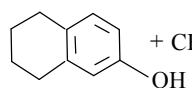
Alcohol (*B*) reacts appreciably faster with Lucas reagent. Hence, (*A*) and (*B*) are



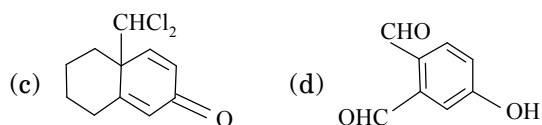
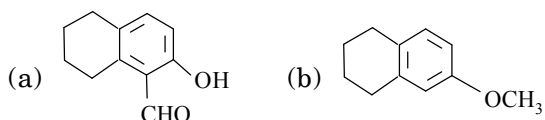
210. Identify the final product in the following sequence



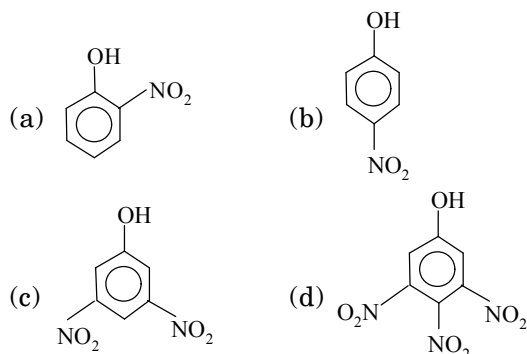
- (a) 
- (b) 
- (c) 
- (d) none of the above.

211.  + $\text{CHCl}_3 \xrightarrow{\text{KOH}} A$ (expected) + B (unexpected).

The unexpected product is



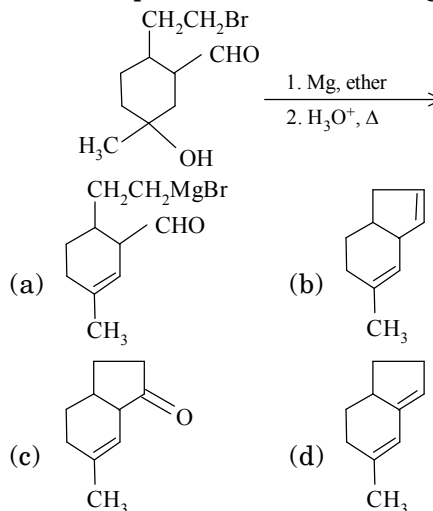
212. The most steam volatile compound is

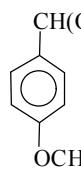


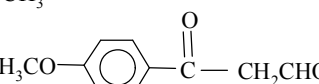
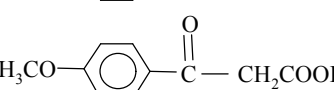
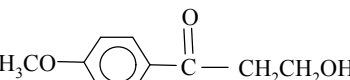
213. $R - \text{OH} \xrightarrow{\text{P} + \text{I}_2} \xrightarrow{\text{AgNO}_2} \xrightarrow{\text{HNO}_2} \text{blue colour.}$

- Which of the following is $R - \text{OH}$?
- (a) Primary (b) Secondary
(c) Tertiary (d) Any of these.

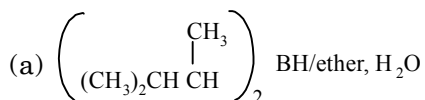
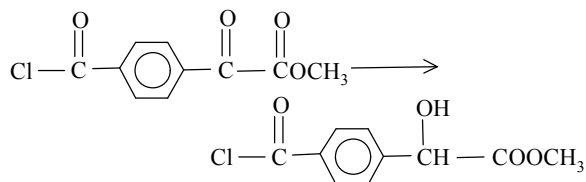
214. The final product in the following reaction is



215.  $\xrightarrow[\text{acetone, } 25^\circ\text{C}]{\text{MnO}_2} A$. Compound (*A*) is

- (a) 
- (b) 
- (c) 
- (d) none of the above.

216. Which of the following is used for the following conversion?



- (b) AlH₃
 (c) NaBH₄ (d) [((CH₃)₃C)₃SnH]

217. When a 1° alkyl halide reacts with an alkoxide, the product is

- (a) hydrocarbon (b) ether
 (c) unsaturated hydrocarbon
 (d) alcohol.

218. Acetic anhydride reacts with diethyl ether in the presence of anhydrous AlCl₃ to give

- (a) CH₃COOCH₃ (b) CH₃CH₂COOCH₃
 (c) CH₃COOCH₂CH₃ (d) CH₃CH₂OH

219. When diethyl ether is treated with excess of Cl₂ in the presence of sunlight, the product formed is

- (a) CH₃CHCl - O - CH₂CH₃
 (b) CH₃CHCl - O - CHClCH₃
 (c) CCl₃CCl₂ - O - CCl₂CCl₃
 (d) CH₃CCl₂ - O - CHClCH₃

220. An organic compound of molecular formula C₃H₆O does not produce any precipitate with 2,3-dinitrophenyl hydrazine and does not react with sodium metal. This compound is

- (a) CH₃COCH₃ (b) CH₂=CH - OCH₃
 (c) CH₃CH₂CHO (d) CH₂=CHCH₂OH.

221. Ether which is liquid at room temperature is

- (a) C₂H₅OCH₃ (b) CH₃OCH₃
 (c) C₂H₅OC₂H₅ (d) none of these.

222. Alcohols are isomeric with

- (a) acids (b) ethers
 (c) esters (d) aldehydes.

223. An organic compound of molecular formula C₄H₁₀O does not react with sodium. With excess of HI, it gives only two types of alkyl halide. The compound is

- (a) ethoxyethane
 (b) 2-methylpropane-2-ol
 (c) 1-methoxypropane (d) 1-butanol.

224. Which one of the following reactions does not yield an alkyl halide?

- (a) Diethyl ether + Cl₂ (in the dark)
 (b) Diethyl ether + HI
 (c) Diethyl ether + PCl₅
 (d) Divinyl ether $\xrightarrow{\text{Reduction}} X \xrightarrow{\text{SOCl}_2}$

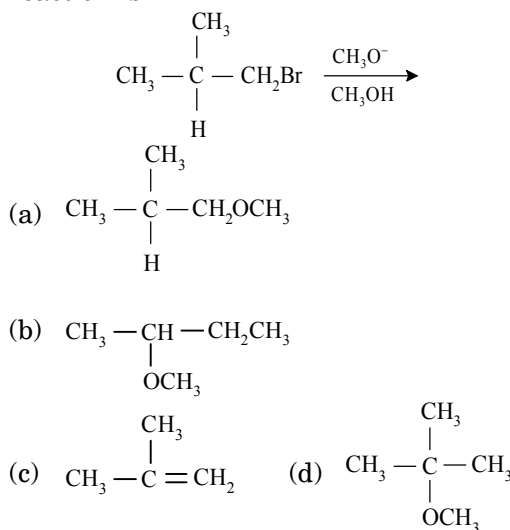
225. An aromatic ether is not cleaved by HI even at 525 K. The compound is

- (a) C₆H₅OCH₃ (b) C₆H₅O - C₆H₄(CH₃)
 (c) C₆H₅OC₃H₇ (d) tetrahydrofuran.

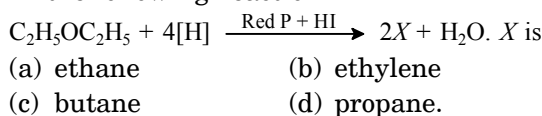
226. Which of the following compounds is resistant to nucleophilic attack by OH⁻ ions?

- (a) Urea (b) Acetonitrile
 (c) Acetamide (d) Diethyl ether.

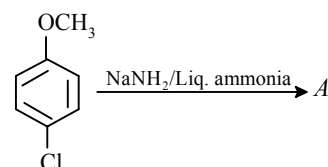
227. The major product formed in the following reaction is



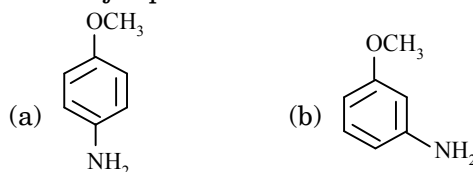
228. In the following reaction

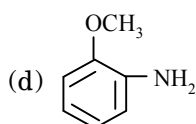
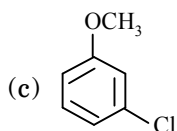


229. In the reaction



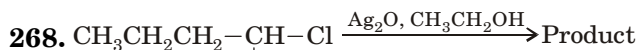
The major product A is





230. On boiling with concentrated HBr, phenyl ethyl ether will give
 (a) phenol and ethyl bromide
 (b) bromobenzene and ethanol
 (c) phenol and ethane
 (d) bromobenzene and ethane.
231. In Williamson's synthesis, ethoxyethane is prepared by
 (a) passing ethanol over alumina
 (b) heating ethanol with dry Ag_2O
 (c) heating sodium ethoxide with ethyl bromide
 (d) treating ethyl alcohol with excess of H_2SO_4 at 443 K.
232. The ether that undergoes electrophilic substitution reactions is
 (a) $\text{CH}_3\text{OC}_2\text{H}_5$ (b) $\text{C}_6\text{H}_5\text{OCH}_3$
 (c) CH_3OCH_3 (d) $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$
233. Ether is obtained from ethyl alcohol in presence of H_2SO_4 at
 (a) 413 K (b) 473 K
 (c) 383 K (d) 273 K
234. Ethers are quite stable towards
 (a) oxidising agents (b) reducing agents
 (c) Na metal (d) bases.
235. *tert*-Butyl methyl ether on heating with HI gives a mixture of
 (a) *tert*-butyl alcohol and methyl iodide
 (b) *tert*-butyl iodide and methanol
 (c) *iso*-butylene and methyl iodide
 (d) *iso*-butylene and methanol.
236. The number of ether metamers represented by molecular formula $\text{C}_4\text{H}_{10}\text{O}$ is
 (a) 4 (b) 3
 (c) 2 (d) 1
237. Salicylic acid on heating with sodalime forms
 (a) phenol (b) benzyl alcohol
 (c) benzene (d) benzoic acid.
238. Picric acid and benzoic acid can be distinguished by
 (a) aqueous NaHCO_3 (b) aqueous NaOH
 (c) aqueous FeCl_3 (d) aqueous Na_2CO_3 .
239. When phenol is treated with NH_3 and ZnCl_2 , it changes to
 (a) aniline (b) salicylic acid
 (c) cyclohexanol (d) none of these.
240. Intramolecular rearrangement of phenyl esters to give *o*- and *p*-derivative in presence of AlCl_3 is known as
 (a) Friedel Crafts reaction
 (b) Fries rearrangement
 (c) esterification (d) coupling.
241. Which of the following has lowest boiling point?
 (a) Phenol (b) *o*-Nitrophenol
 (c) *m*-Nitrophenol (d) *p*-Nitrophenol.
242. Phenol is less soluble in water. It is due to
 (a) non-polar nature of phenol
 (b) acidic nature of $-\text{OH}$ group
 (c) non-polar hydrocarbon part in it
 (d) none of the above.
243. The functional group present in cresol is
 (a) phenolic group (b) ketonic group
 (c) ether group (d) amino group.
244. Phthalein test is a characteristic of
 (a) alcohols (b) phenols
 (c) aldehydes (d) ketones.
245. Which of the following is soluble in dilute aqueous NaOH?
 (a) $\text{C}_6\text{H}_5\text{OH}$ (b) C_6H_6
 (c) $\text{C}_2\text{H}_5\text{OH}$ (d) $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$
246. One of the following statements regarding Reimer-Tiemann reaction is false.
 (a) Reaction of phenol with CHCl_3 and KOH
 (b) CCl_2 acts as a nucleophile
 (c) Reaction of phenol with CCl_4 and NaOH
 (d) Reaction of phenol with formaldehyde to form bakelite.
247. The compound required for the formation of thermosetting polymer with methanal is
 (a) phenol (b) benzene
 (c) benzaldehyde (d) all of these.
248. Which of the following is most acidic?
 (a) *p*-Cresol (b) *p*-Chlorophenol
 (c) *p*-Nitrophenol (d) *p*-Aminophenol.
249. The formula of phenoxy benzene is
 (a) $\text{C}_6\text{H}_5\text{C}_6\text{H}_5$ (b) $\text{C}_6\text{H}_5 - \text{O} - \text{C}_6\text{H}_5$
 (c) $\text{C}_6\text{H}_6 - \text{O} - \text{C}_6\text{H}_6$ (d) none of these.
250. Phenol and cyclohexanol can be distinguished by using
 (a) FeCl_3 (b) Na
 (c) PCl_5 (d) CH_3COCl
251. Which of the following is most volatile?
 (a) *o*-Nitrophenol (b) *p*-Nitrophenol
 (c) *m*-Nitrophenol (d) All of these.
252. Resorcinol and conc. H_2SO_4 in presence of phthalic anhydride produces a compound which is
 (a) a dye (b) an antiseptic
 (c) an indicator (d) a detergent.
253. Phenol on hydrogenation in presence of nickel catalyst at 160°C gives

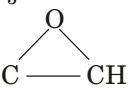
- (a) HBr, Δ ; *t*-butoxide
 (b) H₃PO₄, Δ ; conc. OH⁻
 (c) CH₃COOH; Heat
 (d) Al₂O₃, Pyridine, 250°C



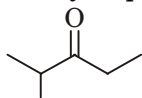
The main product is

- (a) $\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_3$
 (b) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{OCH}_2-\text{CH}_3$
 (c) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{OH}$
 (d) $\text{CH}_3\text{CH}_2\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2\text{CH}_2\text{CH}_3$

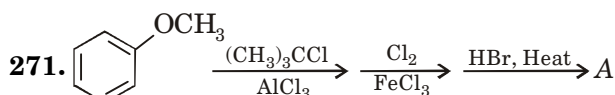
269. An organic compound *B* is formed by the reaction of ethyl magnesium iodide (CH₃CH₂MgI) with a substance *A*, followed by treatment with a dilute aqueous acid. Compound *B* does not react with PCC or PDC in dichloromethane. Which of the following is the most suitable as *A*?

- (a) CH₃-CH=O (b) HCH=O
 (c)  (d) $\text{CH}_3\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$

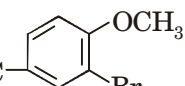
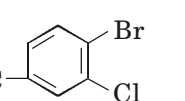
270. Which sequence of steps describes the best synthesis of 2-methyl-3-pentanone?

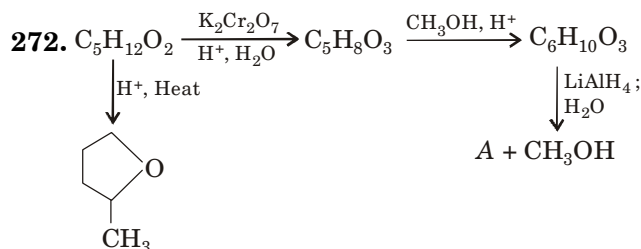
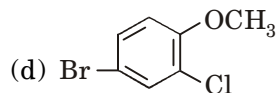
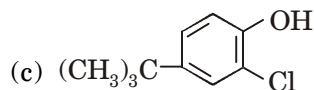


- (a) I. 1-propanol + (CH₃)₂CHMgBr, diethyl ether
 II. H₃O⁺ III. PCC, CH₂Cl₂
 (b) I. 1-propanol + PCC, CH₂Cl₂
 II. SOCl₂ III. (CH₃)₂CHCl, AlCl₃
 (c) I. 1-propanol + PCC, CH₂Cl₂
 II. (CH₃)₂CHLi, diethyl ether
 III. H₃O⁺
 IV. Na₂Cr₂O₇, H₂SO₄, H₂O, Heat
 (d) I. 2-propanol + Na₂Cr₂O₇ + H₂SO₄, H₂O, Heat
 II. CH₃CH₂CH₂Li, dimethyl ether
 III. H₃O⁺ IV. PCC, CH₂Cl₂

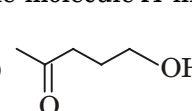
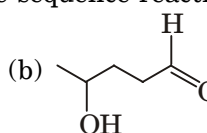
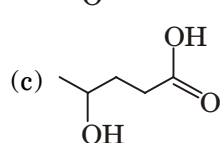
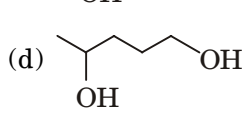


The final product *A*, is

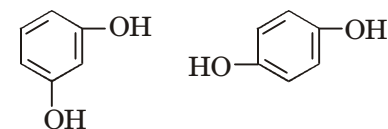
- (a) 
 (b) 



The molecule *A* in the sequence reaction, is

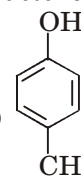
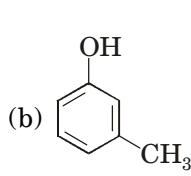
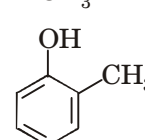
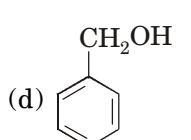
- (a)  (b) 
 (c)  (d) 

273. The resorcinol, meta isomer of hydroquinone doesn't undergo a facile reversible two *e*⁻ oxidation because



- Resorcinol Quinol or hydroquinone
 (a) two -OH groups at meta position (1, 3) are highly stable
 (b) being at meta, intramolecular coupling of two electrons cannot take place
 (c) being meta, oxygen containing pair of *e*⁻ have strong delocalising interaction
 (d) resorcinol is more acidic than hydroquinone.

274. A compound (*A*) has molecular formula C₇H₈O. It reacts with Na and NaOH and gives violet colour with FeCl₃, but doesn't decompose NaHCO₃. Upon oxidation *A* gives *B* which reacts with Na, NaOH, NaHCO₃ and gives violet colour with FeCl₃. *A* on nitration gives mononitro-derivative. The molecular structure of *A* is

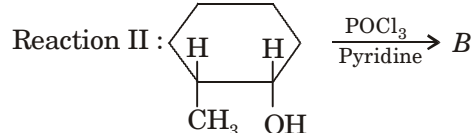
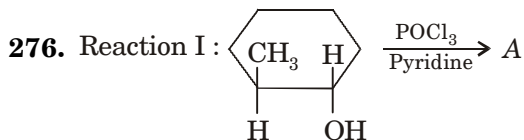
- (a)  (b) 
 (c)  (d) 

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

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

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

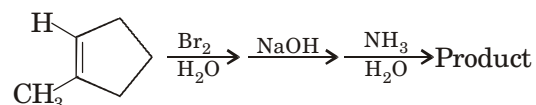
- (a) $X = \text{CH}_3\text{CH}=\text{CHCH}_2\text{OH}$; $Y = \text{CH}_3\text{CH}_2\text{CH}=\text{CHOH}$
 (b) $X = \text{CH}_2=\text{CHCH}_2\text{CH}_2\text{OH}$; $Y = \text{Cyclobutanol}$
 (c) $X = \text{CH}_3\text{C}(\text{OH})=\text{CHCH}_3$; $Y = \text{Cyclohexanone}$
 (d) $X = \text{CH}_2=\text{CHCH}_2\text{CH}_2\text{OH}$; $Y = \text{Cyclohexanone}$



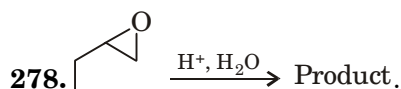
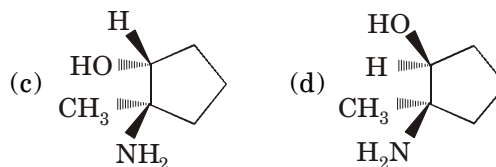
Products A and B are respectively

- (a) $A = \text{1-methylcyclohexene}$; $B = \text{3-methylcyclohexene}$
 (b) $A = \text{1-methylcyclohexene}$ = B
 (c) $A = \text{3-methylcyclohexene}$; $B = \text{1-methylcyclohexene}$
 (d) $A = \text{1-methylcyclohexene}$ = B

277. Choose the correct final product with stereochemistry.



- (a)
- (b)

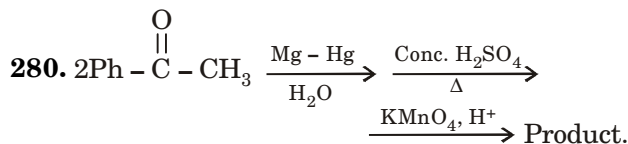


The main product is

- (a)
- (b)
- (c)
- (d)

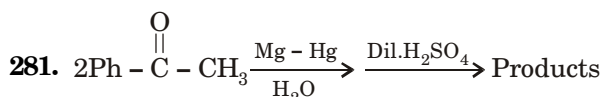
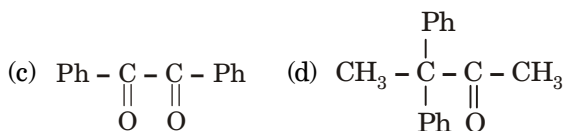
279. An organic compound A (molecular formula, $C_6H_{12}O_4$) on treatment with Na metal liberates H_2 gas and on treatment with HIO_4 , gives $2CH_3CH=O$, $HCOOH$ and CO_2 . The molecular structure of compound A is

- (a)
- (b)
- (c)
- (d)

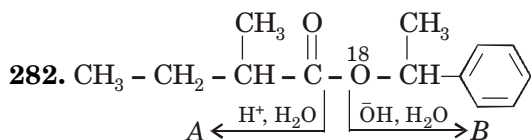
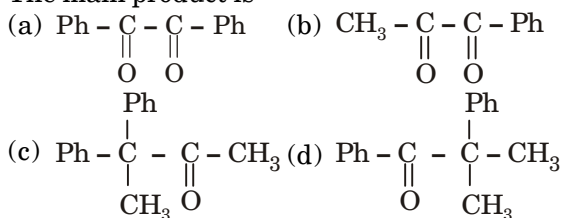


The final product is

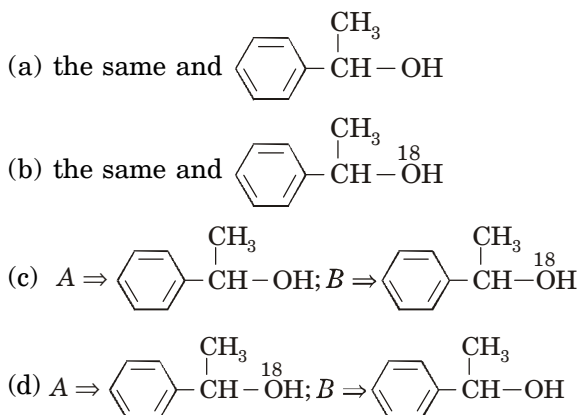
- (a) $CH_3-C(Ph)(OH)-C(Ph)(OH)-CH_3$
- (b) $CH_3-C(=O)-C(=O)-CH_3$



The main product is



Hydrolysis of ester gives acid and alcohol. The alcohols in A and B are respectively,



283. Glycerol can be obtained from

- (a) fats (b) propylene
 (c) both (a) and (b) (d) none of these.

284. Which is used as an antifreeze?

- (a) Glycol (b) Formic acid
 (c) Water (d) Methanol.

285. Which of the following reagents will convert glycerol to acrolein?

- (a) P_2O_5 (b) Conc. H_2SO_4
 (c) KHSO_4 (d) All of these.

286. In glycerine,

- (a) one primary - OH group is present
 (b) one tertiary - OH group is present
 (c) two secondary - OH groups are present
 (d) one secondary - OH group is present.

287. The boiling point of glycerol is more than propanal because of

- (a) hybridisation (b) H-bonding
 (c) resonance (d) all of these.

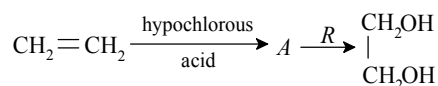
288. Iso-propyl alcohol on oxidation gives

- (a) acetone (b) ether
 (c) ethylene (d) acetaldehyde.

289. The wrong statement about glycerol is

- (a) it is a trihydric alcohol
 (b) acidified KMnO_4 converts it to oxalic acid
 (c) used in the manufacture of explosives
 (d) it is a tertiary alcohol.

290. In the reaction sequence,



A and R respectively are

- (a) $\text{CH}_2 - \text{CH}_2$ and heat
 (b) $\text{CH}_3\text{CH}_2\text{Cl}$ and NaOH
 (c) $\text{CH}_3\text{CH}_2\text{OH}$ and H_2SO_4
 (d) $\text{CH}_2\text{Cl} \cdot \text{CH}_2\text{OH}$ and NaHCO_3

291. When ethylene glycol is heated with acidified potassium permanganate, the main organic compound obtained is

- (a) oxalic acid (b) glyoxal
 (c) formic acid (d) acetaldehyde.

292. Absolute alcohol (100% alcohol) is prepared by distilling rectified spirit over

- (a) Na (b) CaCl_2
 (c) Mg (d) $\text{Mg}(\text{OC}_2\text{H}_5)_2$

293. When wine is kept in air, it becomes sour due to

- (a) bacteria
 (b) oxidation of $\text{C}_2\text{H}_5\text{OH}$ into CH_3COOH
 (c) virus
 (d) formic acid formation.

294. To prepare 3-ethylpentan-3-ol, the reagents needed are

- (a) $\text{CH}_3\text{CH}_2\text{MgBr} + \text{CH}_3\text{COCH}_2\text{CH}_3$
 (b) $\text{CH}_3\text{MgBr} + \text{CH}_3\text{CH}_2\text{CH}_2\text{COCH}_2\text{CH}_3$
 (c) $\text{CH}_3\text{CH}_2\text{MgBr} + \text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$
 (d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{MgBr} + \text{CH}_3\text{COCH}_2\text{CH}_3$

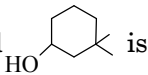
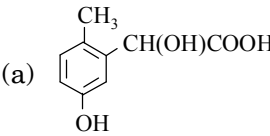
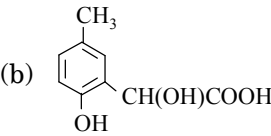
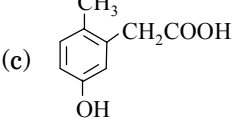
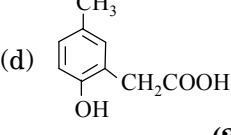
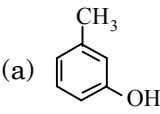
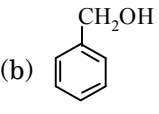
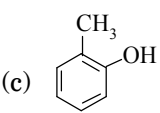
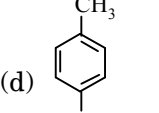
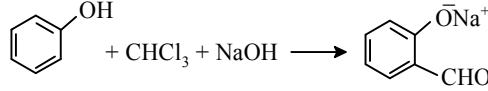
295. In the synthesis of glycerol from propene, the steps involved are

- (a) glycerol- β -chlorohydrin and allyl chloride
 (b) glyceryl trichloride and glycerol- α -chlorohydrin
 (c) allyl alcohol and glycerol- β -chlorohydrin
 (d) allyl alcohol and monosodium glycerolate.

296. An organic compound A reacts with methyl magnesium iodide to form an addition product which on hydrolysis forms the compound B. Compound B gives blue colour salt in Victor Meyer's test. The compounds A and B respectively are

- (a) acetaldehyde, *t*-butyl alcohol
 (b) acetaldehyde, ethyl alcohol
 (c) acetaldehyde, *iso*-propyl alcohol
 (d) acetone, *iso*-propyl alcohol.
- 297.** Scientific study of fermentation was first made by
 (a) Buchner (b) Liebig
 (c) Biot (d) Pasteur.
- 298.** The reaction between alcohol and carboxylic acids is called
 (a) esterification (b) hydrolysis
 (c) saponification (d) hydrogenation.
- 299.** C₂H₅OH can be differentiated from CH₃OH by
 (a) reaction with HCl (b) reaction with NH₃
 (c) iodoform test (d) solubility in water.
- 300.** The reaction of ethanol with H₂SO₄ does not give
 (a) ethylene
 (b) diethyl ether
 (c) acetylene
 (d) ethylhydrogen sulphate.
- 301.** Which of the following does not give yellow ppt. with I₂/NaOH?
 (a) C₂H₅OH (b) CH₃CHO
 (c) CH₃COCH₃ (d) HCHO.
- 302.** The order of reactivity of halogen acids for reaction with C₂H₅OH is
 (a) HCl > HBr > HI (b) HI > HBr > HCl
 (c) HBr > HI > HCl (d) HBr > HCl > HI
- 303.** Which of the following compounds is obtained on passing ethanol vapours on heated Al₂O₃?
 (a) Ethyl ether (b) Acetone
 (c) Ethane (d) Ethanol.
- 304.** Ethylene may be obtained by the treatment of concentrated H₂SO₄ and X at 160-170°C. X is
 (a) C₂H₅OH (b) CH₃OH
 (c) C₃H₇OH (d) (CH₃)₂CHCH₂OH
- 305.** Glycol is added to aviation petrol because
 (a) it prevents freezing of petrol
 (b) it minimises the loss of petrol
 (c) it increases the efficiency of fuel
 (d) it prevents the engine from heating up.
- 306.** When ethyl hydrogen sulphate is heated with excess of alcohol at 410 K, the product obtained is
 (a) ethane (b) ethylene
 (c) diethyl ether (d) diethyl sulphate.
- 307.** Anisole with conc. HNO₃ and conc. H₂SO₄ gives
 (a) phenol
 (b) nitrobenzene
 (c) *o*- and *p*-nitroanisole
 (d) *m*-nitroanisole.
- 308.** Which of the following compounds on boiling with alkaline KMnO₄ and subsequent acidification will not give benzoic acid?
 (a) Toluene (b) Acetophenone
 (c) Anisole (d) Benzyl alcohol.
- 309.** Grignard reagent is not prepared in aqueous medium but it is prepared in ether medium, because
 (a) the reagent forms complex with water
 (b) the reagent becomes inactive in water
 (c) it is insoluble in water
 (d) the reagent is highly reactive in water.
- 310.** The C - O - C angle in ether is about
 (a) 180° (b) 190° 28'
 (c) 110° (d) 105°
- 311.** When methyl-*t*-butyl ether is formed?
 (a) (C₂H₅)₃CONa + CH₃Cl
 (b) CH₃ONa + (CH₃)₃CCl
 (c) (CH₃)₃CONa + C₂H₅Cl
 (d) (CH₃)₃CONa + CH₃Cl
- 312.** Which of the following cannot be prepared by using Williamson's synthesis?
 (a) Methoxybenzene
 (b) Benzyl-*p*-nitrophenyl ether
 (c) Methyl-*tert*-butyl ether
 (d) Di-*tert* butyl ether.
- 313.** Increasing order of reactivity of the following alkyl halides in the Williamson's synthesis is
 I. CH₂ = CHCH₂Cl II. CH₃CH₂CH₂Br
 III. (CH₃)₃CCH₂Br IV. CH₃CH₂CH₂Cl
 (a) II < III < IV < I
 (b) III < II < IV < I
 (c) IV < III < I < II
 (d) III < IV < II < I
- 314.** Which of the following is best method to prepare phenyl-*t*-butyl ether?
 (a) (CH₃)₃C - O⁻Na⁺ + C₆H₅Br
 (b) C₆H₅ONa + (CH₃)₃CCl
 (c) (CH₃)₂C = CH₂ $\xrightarrow[\text{C}_6\text{H}_5\text{OH}]{\text{Hg}(\text{OCOCH}_3)_2}$ $\xrightarrow{\text{NaBH}_4}$
 (d) None of the above.
- 315.** Diethyl ether on heating with conc. HI gives two moles of
 (a) ethanol (b) iodoform
 (c) ethyl iodide (d) methyl iodide.

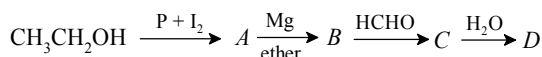
QUESTIONS FROM PREVIOUS YEARS AIEEE/JEE MAIN

1. An ether is more volatile than an alcohol having the same molecular formula. This is due to
 (a) dipolar character of ethers
 (b) alcohols having resonance structures
 (c) intermolecular hydrogen bonding in ethers
 (d) intermolecular hydrogen bonding in alcohols.
(2003)
2. During dehydration of alcohols to alkenes by heating with concentrated H_2SO_4 , the initiation step is
 (a) protonation of alcohol molecule
 (b) formation of carbocation
 (c) elimination of water
 (d) formation of an ester.
(2003)
3. For which of the following parameters the structural isomers C_2H_5OH and CH_3OCH_3 would be expected to have the same values? (Assume ideal behaviour)
 (a) Heat of vaporisation
 (b) Vapour pressure at the same temperature
 (c) Boiling points
 (d) Gaseous densities at the same temperature and pressure.
(2004)
4. The IUPAC name of the compound  is
 (a) 3,3-dimethyl-1-hydroxy cyclohexane
 (b) 1,1-dimethyl-3-hydroxy cyclohexane
 (c) 3,3-dimethyl-1-cyclohexanol
 (d) 1,1-dimethyl-3-cyclohexanol.
(2004)
5. Among the following compounds which can be dehydrated very easily?
 (a) $CH_3CH_2CH_2CH_2CH_2OH$
 (b) $CH_3CH_2CH_2\overset{OH}{\underset{|}{C}}HCH_3$
 (c) $CH_3CH_2\overset{CH_3}{\underset{|}{C}}CH_2CH_3$
 $\quad \quad \quad |$
 $\quad \quad \quad OH$
 (d) $CH_3CH_2\overset{CH_3}{\underset{|}{C}}HCH_2CH_2OH$
 $\quad \quad \quad |$
 $\quad \quad \quad CH_3$
(2004)
6. The best reagent to convert pent-3-en-2-ol into pent-3-en-2-one is
 (a) acidic permanganate
 (b) acidic dichromate
 (c) chromic anhydride in glacial acetic acid
 (d) pyridinium chlorochromate.
(2005)
7. *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
 (a) 
 (b) 
 (c) 
 (d) 
(2005)
8. The structure of the compound that gives a tribromoderivative on treatment with bromine water is
 (a) 
 (b) 
 (c) 
 (d) 
(2006)
9. 
 The electrophile involved in the above reaction is
 (a) dichloromethyl cation ($\overset{\oplus}{C}HCl_2$)
 (b) dichlorocarbene ($:CCl_2$)
 (c) trichloromethyl anion ($\overset{\ominus}{C}Cl_3$)
 (d) formyl cation ($\overset{\oplus}{C}HO$).
(2006)
10. HBr reacts with $CH_2 = CH - OCH_3$ under anhydrous conditions at room temperature to give
 (a) CH_3CHO and CH_3Br
 (b) $BrCH_2CHO$ and CH_3OH

- (c) $\text{BrCH}_2 - \text{CH}_2 - \text{OCH}_3$
 (d) $\text{H}_3\text{C} - \text{CHBr} - \text{OCH}_3$

(2006)

11. In the following sequence of reactions,



the compound *D* is

- (a) propanal (b) butanal
 (c) *n*-butyl alcohol (d) *n*-propyl alcohol.

(2007)

12. Phenol, when it first reacts with concentrated sulphuric acid and then with concentrated nitric acid, gives

- (a) nitrobenzene
 (b) 2, 4, 6-trinitrobenzene
 (c) *o*-nitrophenol (d) *p*-nitrophenol.

(2008)

13. The major product obtained on interaction of phenol with sodium hydroxide and carbon dioxide is

- (a) benzoic acid (b) salicylaldehyde
 (c) salicylic acid (d) phthalic acid.

(2009)

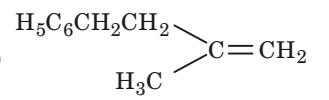
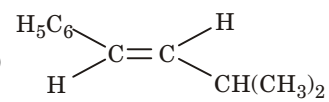
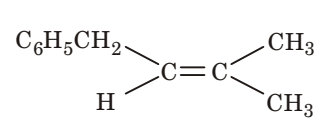
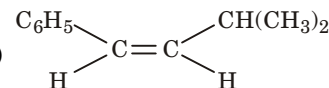
14. From amongst the following alcohols the one that would react fastest with conc.HCl and anhydrous ZnCl_2 , is

- (a) 1-Butanol
 (b) 2-Butanol
 (c) 2-Methylpropan-2-ol
 (d) 2-Methylpropanol.

(2010)

15. The main product of the following reaction is



- (a) 
- (b) 
- (c) 
- (d) 

(2010)

16. Phenol is heated with a solution of mixture of KBr and KBrO_3 . The major product obtained in the above reaction is

- (a) 2-bromophenol (b) 3-bromophenol
 (c) 4-bromophenol
 (d) 2,4,6-tribromophenol

(2011)

17. Sodium ethoxide has reacted with ethanoyl chloride. The compound that is produced in this reaction is

- (a) diethyl ether (b) 2-butanone
 (c) ethyl chloride (d) ethyl ethanoate

(2011)

18. *Ortho*-nitrophenol is less soluble in water than *p*- and *m*-nitrophenols because

- (a) *o*-nitrophenol shows intramolecular H-bonding
 (b) *o*-nitrophenol shows intermolecular H-bonding
 (c) melting point of *o*-nitrophenol is lower than those of *m*- and *p*-isomers
 (d) *o*-nitrophenol is more volatile in steam than those of *m*- and *p*-isomers

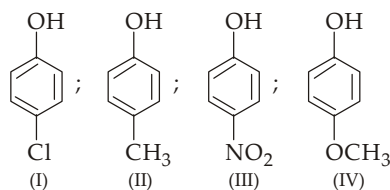
(2012)

19. 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?

- (a) tertiary alcohol by $\text{S}_{\text{N}}2$
 (b) secondary alcohol by $\text{S}_{\text{N}}1$
 (c) tertiary alcohol by $\text{S}_{\text{N}}1$
 (d) secondary alcohol by $\text{S}_{\text{N}}2$

(JEE Main 2013)

20. Arrange the following compounds in order of decreasing acidity.



- (a) $\text{IV} > \text{III} > \text{I} > \text{II}$ (b) $\text{II} > \text{IV} > \text{I} > \text{III}$
 (c) $\text{I} > \text{II} > \text{III} > \text{IV}$ (d) $\text{III} > \text{I} > \text{II} > \text{IV}$

(JEE Main 2013)

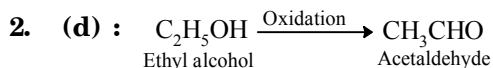
21. The most suitable reagent for the conversion of $\text{R}-\text{CH}_2-\text{OH} \rightarrow \text{R}-\text{CHO}$ is

- (a) PCC (Pyridinium chlorochromate)
 (b) KMnO_4
 (c) $\text{K}_2\text{Cr}_2\text{O}_7$
 (d) CrO_3

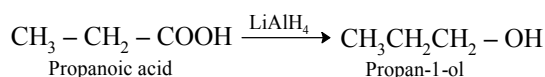
(JEE Main 2014)

HINTS & SOLUTIONS

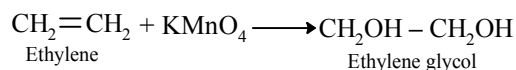
1. (d) : All the given compounds can be prepared from ethyl alcohol.



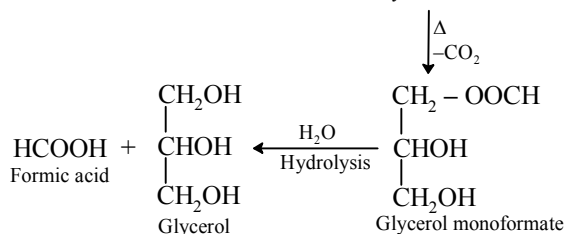
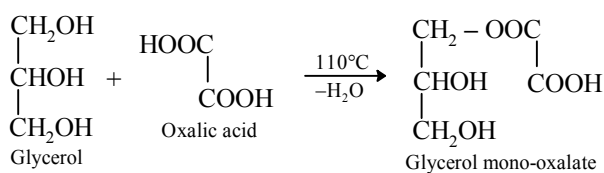
3. (d) :



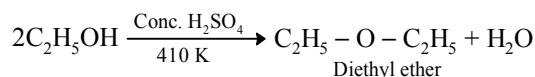
4. (c) :



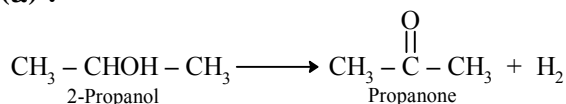
5. (b) :



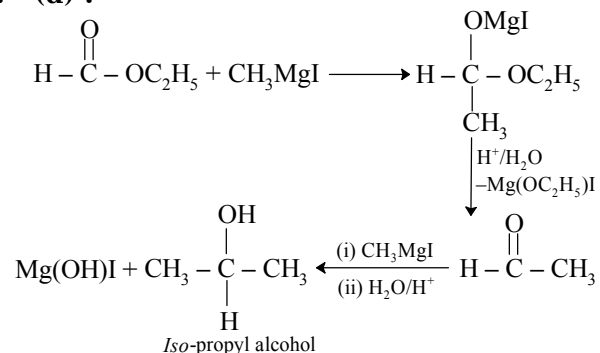
6. (c) :



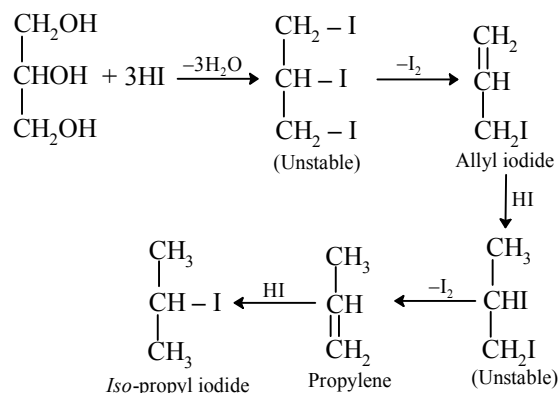
7. (a) :



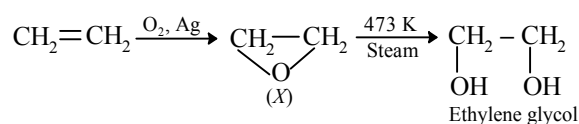
8. (d) :



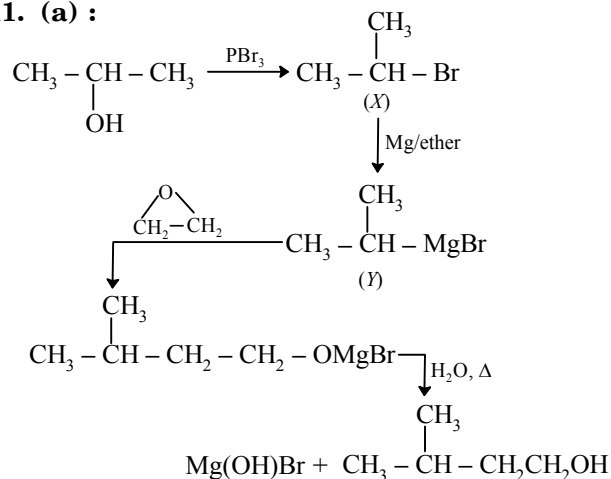
9. (b) : During the reaction of glycerol with HI, all are formed except $\text{CH}_2\text{OH} - \text{CHI} - \text{CH}_2\text{OH}$.



10. (d) :

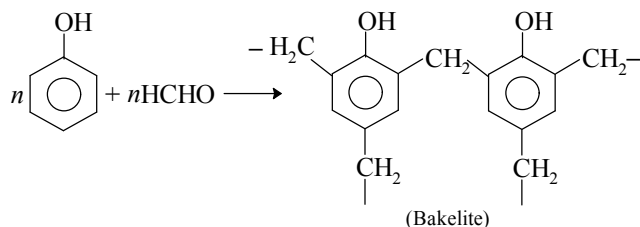


11. (a) :



12. (a) : Phenols get coupled with diazonium salts to form dyes.

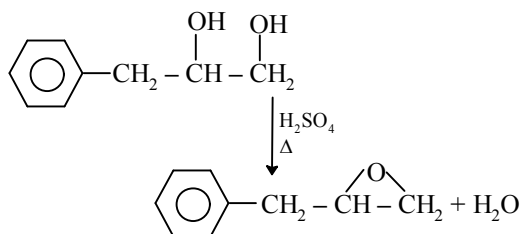
13. (b) : Bakelite is a polymer formed by reaction of phenol with formaldehyde.



14. (c) : Electron releasing inductive effect of $-\text{OCH}_3$ group facilitates the protonation of alcohol involved in dehydration mechanism.

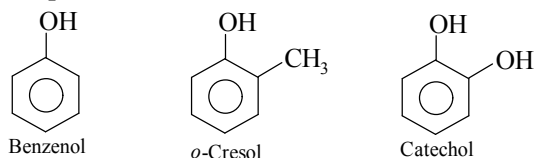
15. (b) : $-\text{OH}$ group present in phenols activates the benzene ring towards electrophilic substitution reaction (*i.e.* S_E reaction).

16. (d) :



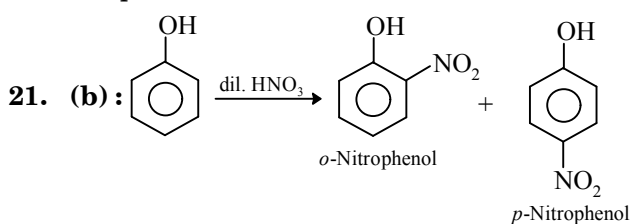
17. (c) : Phenol is a weaker acid than carbonic acid.

18. (d) : Compounds containing $-\text{OH}$ group directly attached to benzene ring are called phenolic compounds.



19. (b) : Phenol is also known as carboic acid.

20. (b) : Compounds containing $-\text{OH}$ group directly attached to the benzene ring are called phenolic compounds.



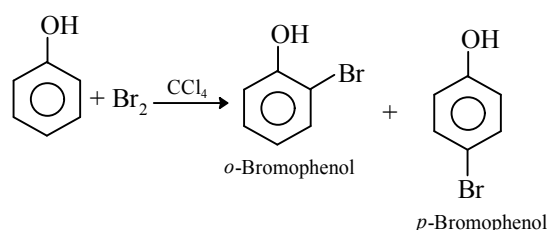
22. (d) : 2,4,6-Trinitrophenol also known as picric acid is slightly explosive in nature.

23. (b) : *p*-nitrophenol exhibits intermolecular hydrogen bonding and thus remains associated. Whereas, *o*-nitrophenol exhibits intramolecular hydrogen bonding which does not result in association.

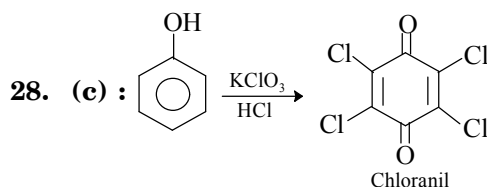
24. (b) : *p*-nitrophenol is stronger acid than salicylaldehyde due to strong electron withdrawing inductive effect of $-\text{NO}_2$ group. Being a stronger acid, *p*-nitrophenol is more soluble in base.

25. (a) : Phenol reacts with chloroform in presence of base (KOH or NaOH) to yield salicylaldehyde. Reaction is known as Reimer-Tiemann reaction.

26. (b) :

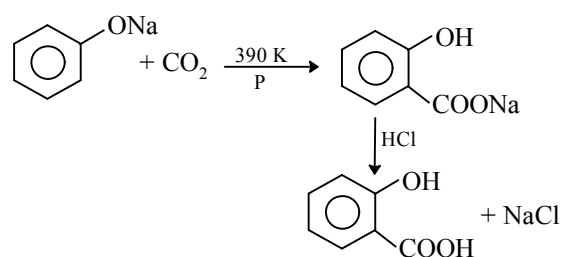


27. (b) : Phenols and alcohols are weaker acids (weaker than carboxylic acids) and do not react with NaHCO_3 .



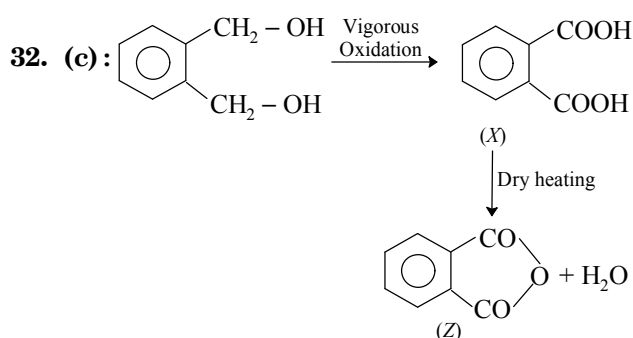
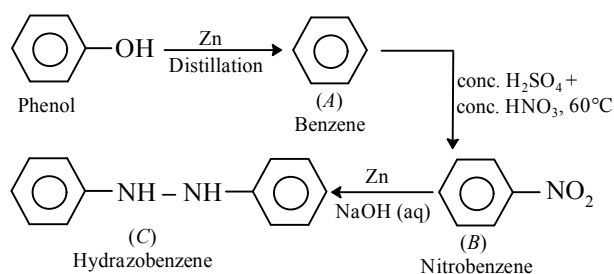
Phenol on oxidation with $\text{K}_2\text{S}_2\text{O}_8$ yields quinol and with KMnO_4 , *meso*-tartaric acid is produced.

29. (d) :



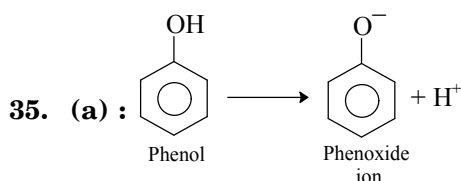
30. (c) : Phenols are soluble in NaOH but not in NaHCO_3 .

31. (d) :



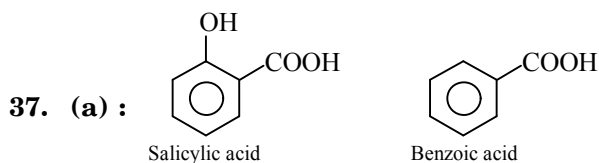
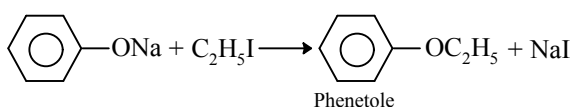
33. (d) : All the mentioned tests indicate the presence of phenolic group.

34. (c) : Nitro group ($-\text{NO}_2$) being electron withdrawing increases the acidic strength of phenol. Thus, *p*-nitrophenol is more acidic than phenol.



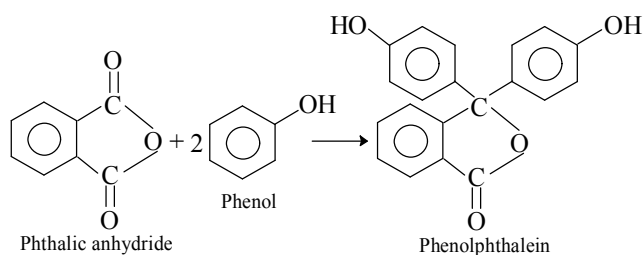
Since phenoxide ion is resonance stabilised and more stable than phenol, the above reaction has more urge towards right hand side.

36. (a) :

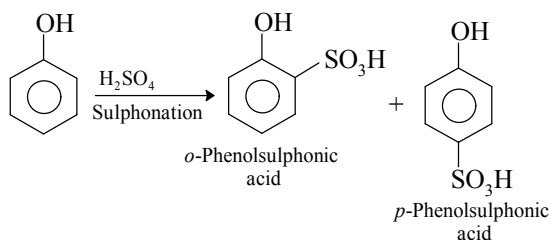


Due to *ortho*-effect, $-\text{OH}$ group increases the acidic strength.

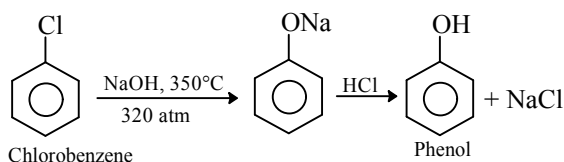
38. (b) :



39. (d) :

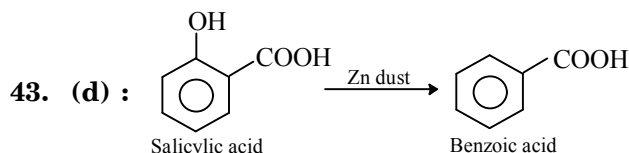
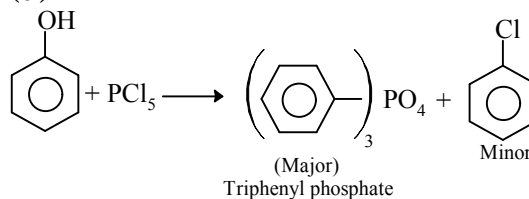


40. (c) :



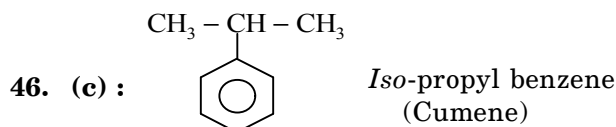
41. (b) : Phenol shows highest boiling point among the given compounds due to hydrogen bonding.

42. (d) :

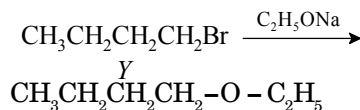
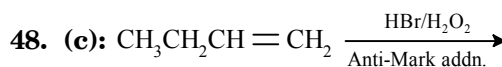


44. (a) : Benzoic acid reacts with NaHCO_3 while phenol being weak acid does not react with NaHCO_3 .

45. (c) : Because of intramolecular hydrogen bonding, *o*-nitrophenol possesses low melting point.



47. (d) : Electron donating groups ($-\text{OC}_2\text{H}_5$, $-\text{CH}_3$, etc.) tend to decrease and electron withdrawing groups ($-\text{NO}_2$, $-\text{CN}$, etc.) tend to increase the acidic character of phenols. Since $-\text{OCH}_3$ is a more powerful electron donating group than $-\text{CH}_3$ group, therefore, *p*-methylphenol is slightly more acidic than that *p*-methoxyphenol while *p*-nitrophenol is the strongest acid.

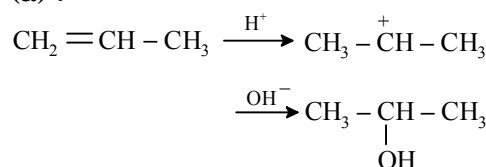


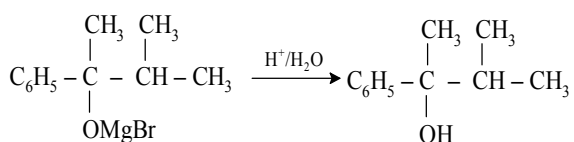
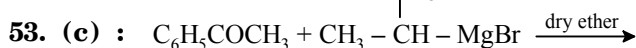
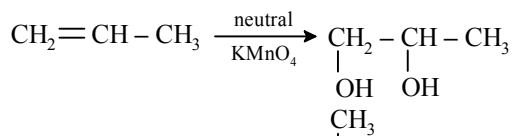
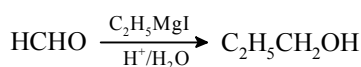
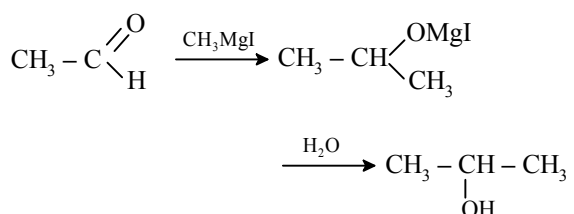
49. (c)

50. (a) : Group having $+I$ effect increases the basicity and $-I$ effect decreases the basicity. C_2 is joined with two methyl groups whereas C_5 is joined with one ethyl group. Hence $-\text{OH}$ at C_2 is more basic than $-\text{OH}$ at C_5 .

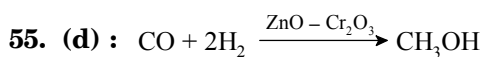
51. (c)

52. (a) :





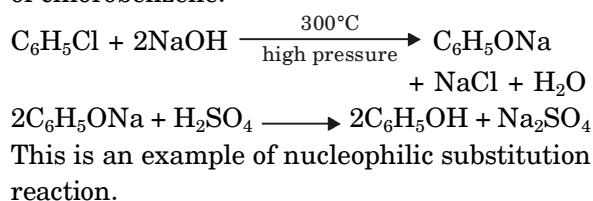
54. (c) : Glycerol on oxidation with $\text{H}_2\text{O}_2/\text{FeSO}_4$ gives glycerose which is a mixture of glyceraldehyde and dihydroxyacetone.



56. (b) : Secondary alcohols on oxidation give ketones.

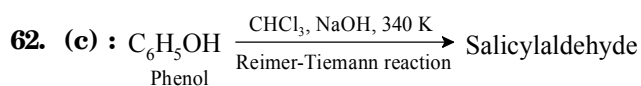
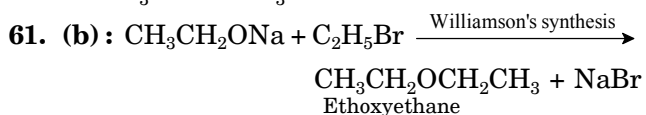
57. (a) : 1° alcohols on catalytic dehydrogenation give aldehydes.

58. (d) : Dow's reaction involves alkaline hydrolysis of chlorobenzene.

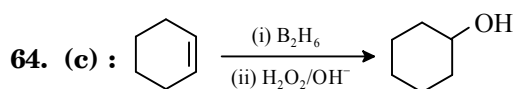


59. (b) : Zerevitinov's active hydrogen determination involves the reaction of a compound containing an active hydrogen (*i.e.* alcohols, amines, mercaptans, terminal alkynes, etc.) with CH_3MgI and the number of active hydrogens corresponds to the number of moles of CH_4 evolved per mole of the compound.

60. (b) : Since $\text{C}_3\text{H}_8\text{O}$ on treatment with $\text{I}_2 + \text{NaOH}$ gives CHI_3 , therefore, $\text{C}_3\text{H}_8\text{O}$ must be a methyl ketone, *i.e.* CH_3COCH_3 . If this is so then, X must be $\text{CH}_3\text{CHOHCH}_3$.



63. (b) : $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ does not give iodoform test since it does not contain the grouping $\text{CH}_3\text{CHOH}-$ or $\text{CH}_3\text{CO}-$.

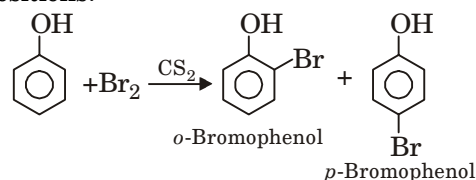


65. (b)

66. (c)

67. (d) : Solubility decreases as the length of carbon chain or hydrocarbon part increases. Thus, $(\text{CH}_3)_3\text{COH}$ has the lowest solubility.

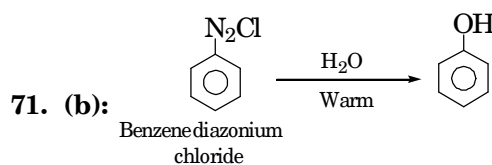
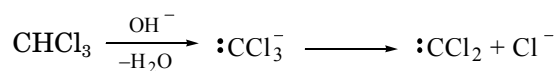
68. (b) : As compared to H_2O , in CS_2 , the ionization of phenol is suppressed. As a result, the benzene nucleus is much less activated than in water and hence only monobromination occurs at *o*- and *p*-positions.



69. (c) : Presence of electron withdrawing group, on the benzene ring increases the acidity of phenol as it enables the ring to draw more electrons from the phenoxy oxygen and thus releasing easily the proton.

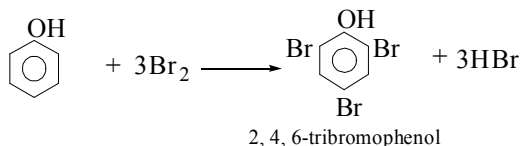
Picric acid containing three electron withdrawing $-\text{NO}_2$ group is most acidic.

70. (c) : During the reaction of phenol with CHCl_3 , dichlorocarbene ($:\text{CCl}_2$) is the electrophile, *i.e.*

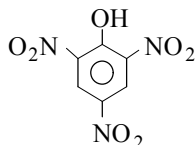


When benzenediazonium chloride solution is warmed, phenol is formed with evolution of nitrogen. The phenol from solution is recovered by steam distillation. This is also a laboratory method.

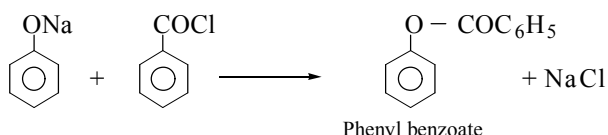
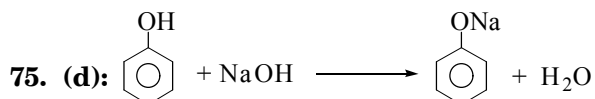
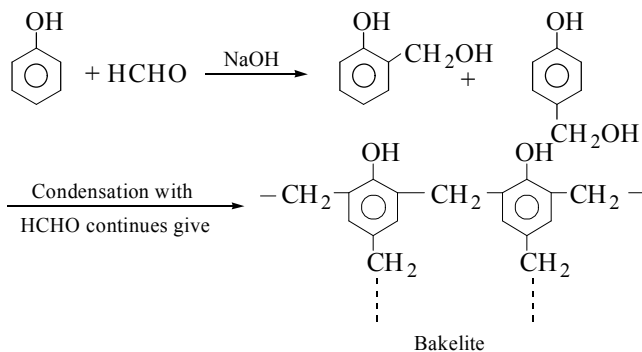
72. (d) : Phenol forms a white precipitate with excess of bromine water yielding 2, 4, 6-tribromophenol.



73. (c): Picric acid is 2, 4, 6-trinitrophenol.

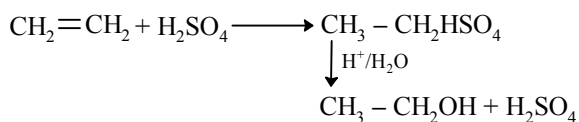


74. (a):

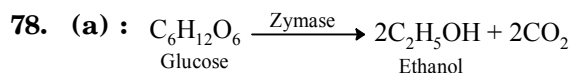
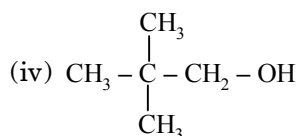
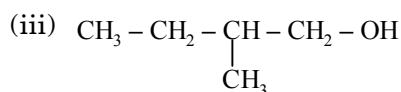
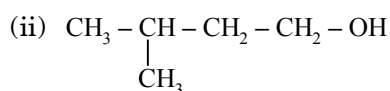
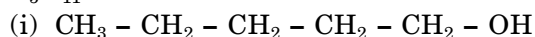


This reaction is called as Schotten-Baumann reaction.

76. (c):



77. (c): Isomeric primary alcohol of formula $\text{C}_5\text{H}_{11}\text{OH}$ are:



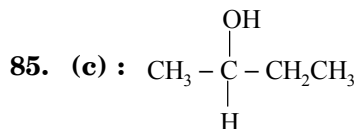
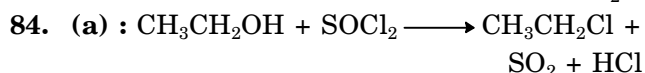
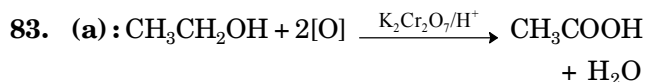
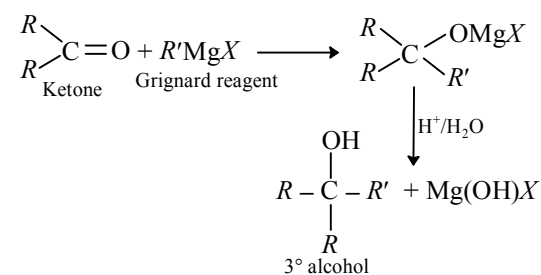
79. (d): All the given reagents can act as dehydrating agents for alcohols.

80. (c): Reaction of alcohols with alkali metal reflects the acidic character of alcohols and their acidic strength *i.e.* activity towards alkali metals follows the order:

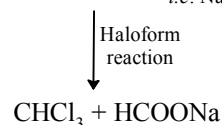
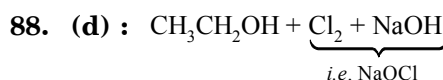
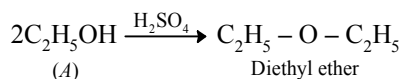
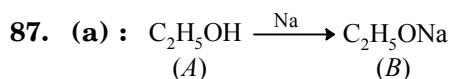
$\text{CH}_3\text{OH} >$ primary alcohol $>$ secondary alcohol $>$ tertiary alcohol.

81. (c): Order of ease of dehydration of alcohols is: 3° alcohol $>$ 2° alcohol $>$ 1° alcohol

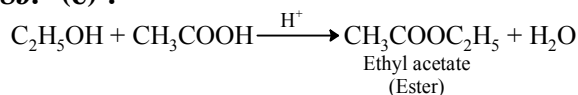
82. (a):



86. (a): Reactions of alcohols involving cleavage of C – OH bond follow the reactivity order: Tertiary $>$ secondary $>$ primary, according to the stability of carbocation intermediate.

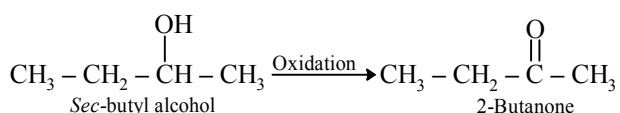


89. (c):

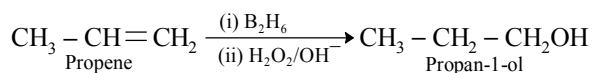


Esters have characteristic fruity smell.

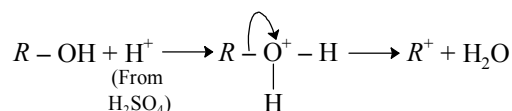
90. (d) : Ethanol is used in beverages.
91. (d) : $3\text{C}_2\text{H}_5\text{OH} + \text{PBr}_3 \longrightarrow 3\text{C}_2\text{H}_5\text{Br} + \text{H}_3\text{PO}_3$
92. (d) : Since the compound reacts with sodium, it must be either alcohol or carboxylic acid. Given compound on oxidation gives carbonyl compound which does not reduce Tollen's reagent, it means oxidation product must be a ketone. Only secondary alcohols yield ketone on oxidation, thus original compound should be *sec*-butyl alcohol.



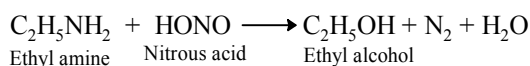
93. (c) : Hydroboration-oxidation gives anti-Markownikoff's product.



94. (a) :

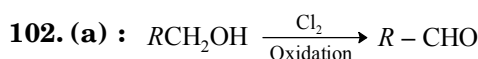
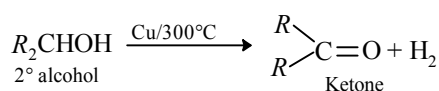
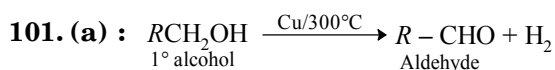


95. (c) : Secondary alcohols : $-\underset{\text{OH}}{\text{CH}}-$
96. (b) : Glycerol has three -OH groups and thus maximum number of active hydrogens among the given compounds.
97. (b) :

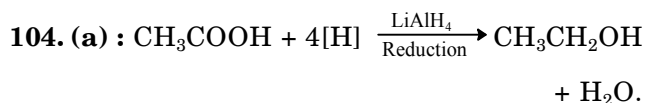
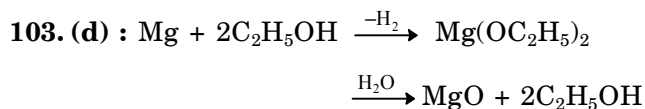


98. (b) : $\text{RSH} + \text{O}_2 \longrightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) + \text{SO}_2(\text{g})$
99. (c) : $\text{C}_2\text{H}_5\text{OH} + \text{Na} \longrightarrow \text{C}_2\text{H}_5\text{ONa} + 1/2\text{H}_2$
i.e. one mole of sodium or 23 g reacts with ethanol to give $\frac{1}{2}$ mole of H₂.

100. (a) : Alcohols of low molecular weight are soluble in water due to H-bonding.

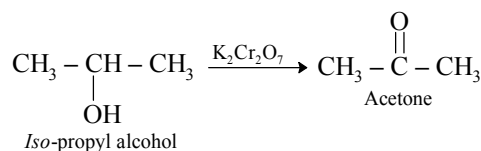
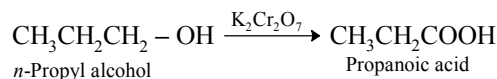


Primary alcohols yield aldehydes (CH₃CHO) on oxidation with Cl₂.



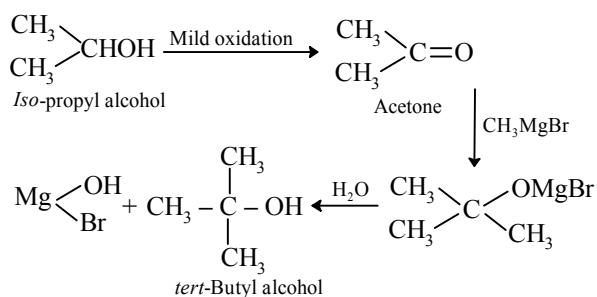
105. (d) : Since the given compound is soluble in H₂SO₄, the compound should be either alkene, alcohol or ether. It does not decolourise bromine, which shows that compound cannot be alkene. Compound is oxidised by chromic anhydride in aqueous H₂SO₄ i.e. compound cannot be an ether. As the oxidation is very fast, the compound (alcohol) may be a primary alcohol.

106. (c) : *n*-Propyl alcohol (1° alcohol) is oxidised to propanoic acid with K₂Cr₂O₇ and gives green colour immediately. *Iso*-propyl alcohol (2° alcohol) is oxidised to acetone with K₂Cr₂O₇ and gives green colour slowly.

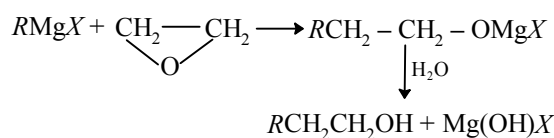


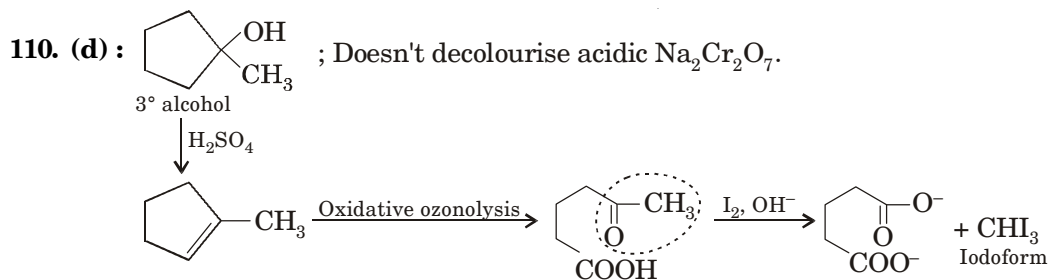
107. (d) : PCC (CrO₃·C₅H₅N·HCl) is the best reagent to oxidise alcohols till aldehyde stage.

108. (b) :

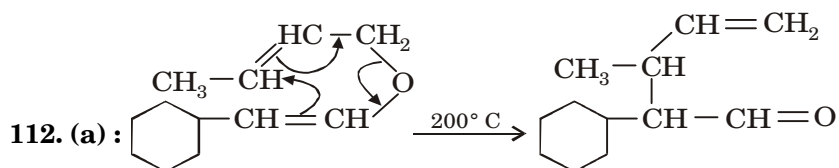
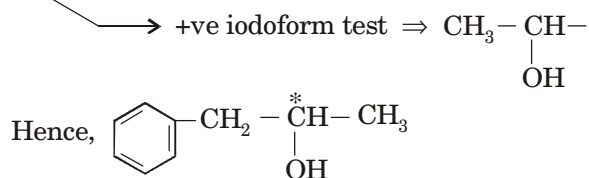


109. (d) :

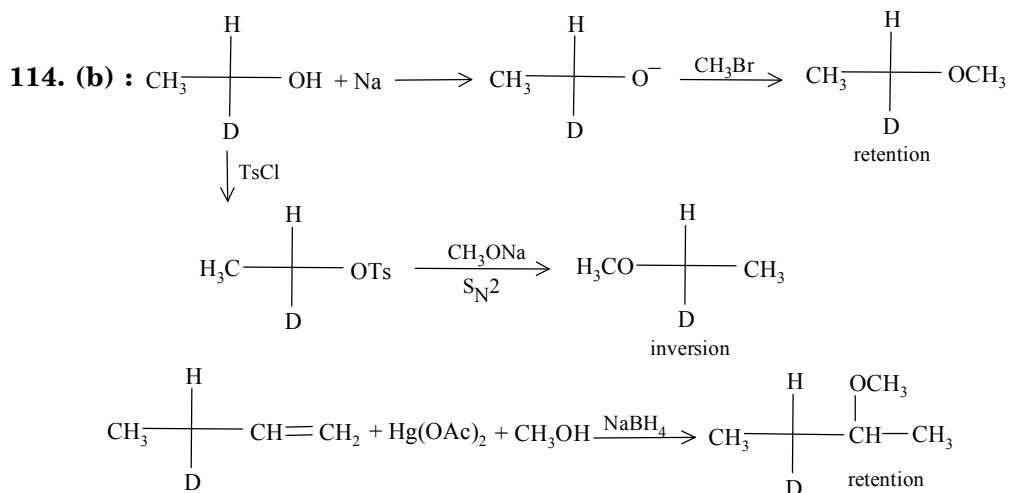
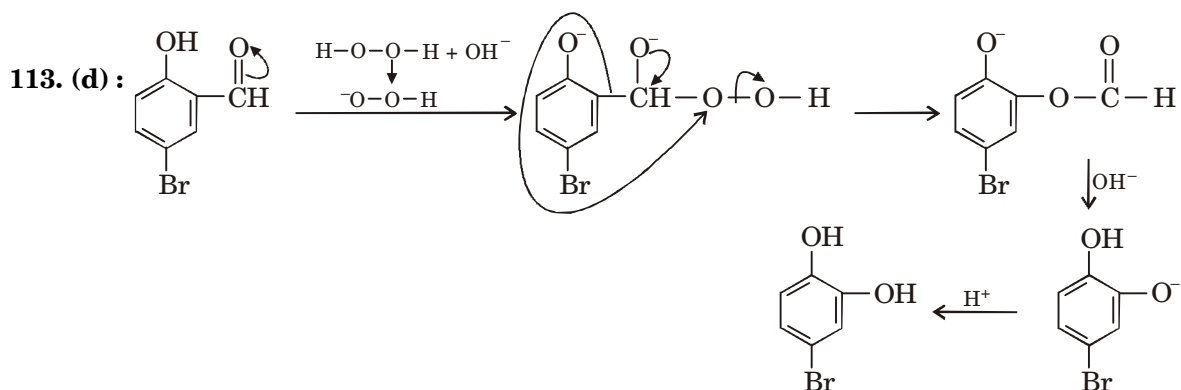


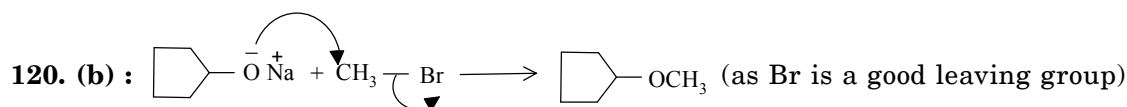
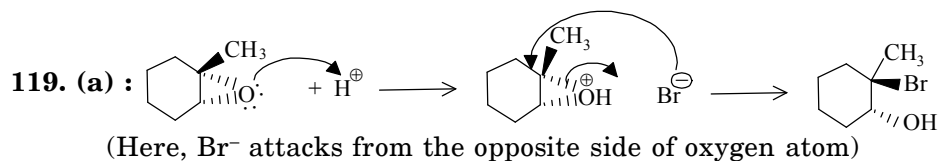
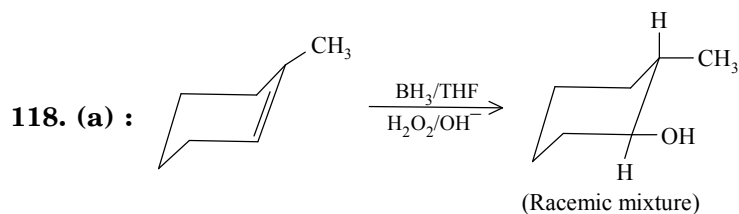
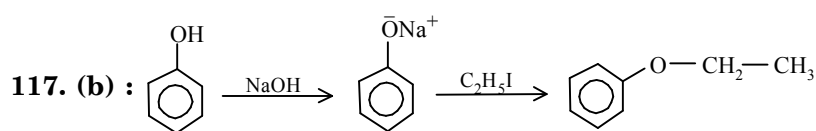
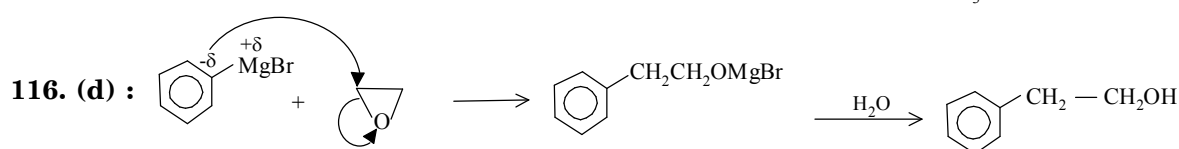
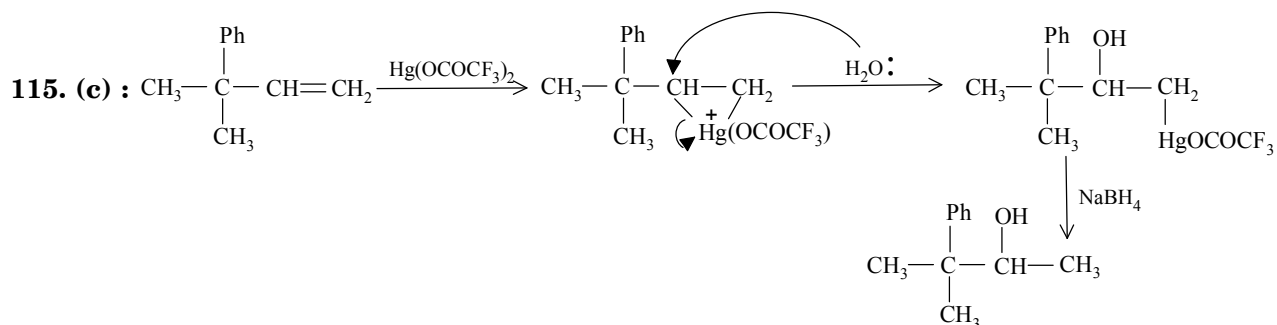
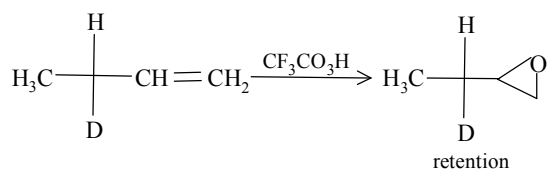


111. (a) : $\text{C}_9\text{H}_{12}\text{O}$ (A) \longrightarrow Benzoic acid \Rightarrow Monosubstituted benzene

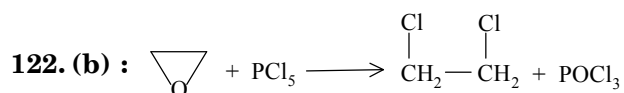


Claisen rearrangement type reaction with allyl-vinyl ether.

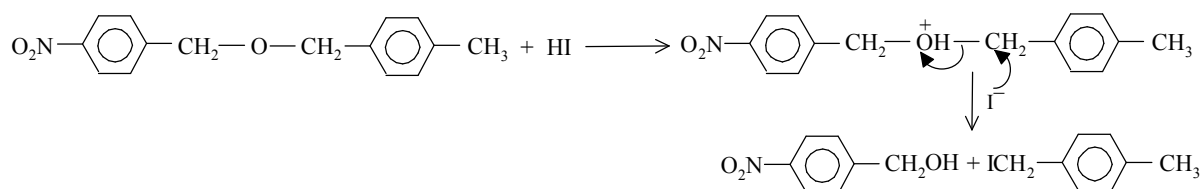




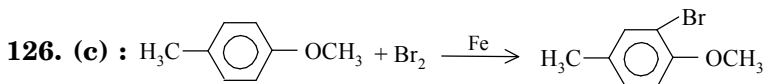
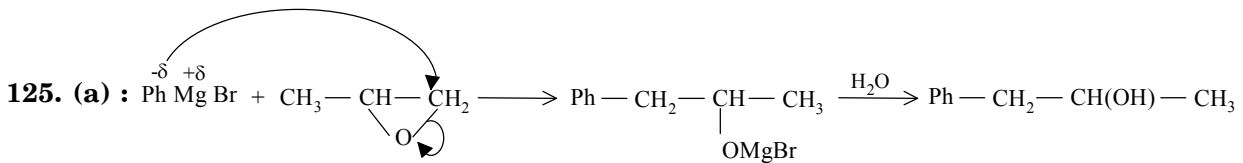
121. (c) : When conc. HI is used the reaction follows S_N1 but when anhydrous HI is used the reaction follows S_N2.



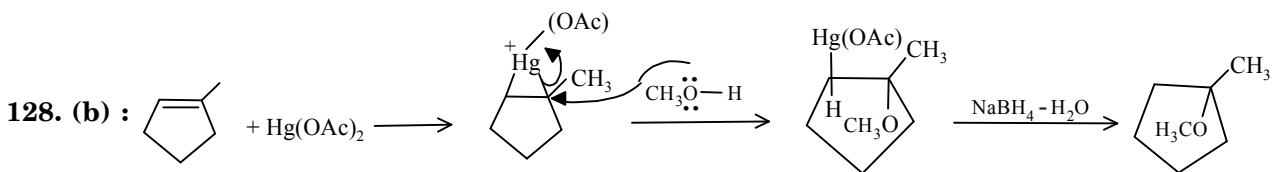
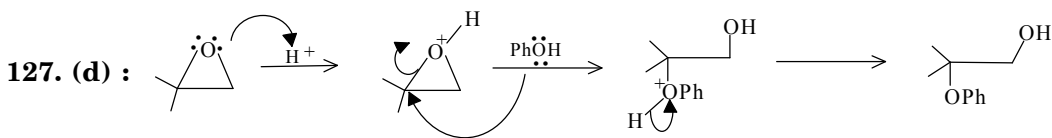
123. (b) : -NO₂ is electron withdrawing, whereas -CH₃ is electron donating group.



124. (b) : The order of reactivity depends upon the strength of nucleophile to attack. The order of nucleophilic character is given as $I^- > Br^- > Cl^- > F^-$. Hence, the correct order of reactivity is $HI > HBr > HCl > HF$.



(\therefore $-OCH_3$ is strong activating group than $-CH_3$ towards electrophilic aromatic substitution).



129. (d) : Let the formula be $C_xH_yO_z$

$$\text{Molecular weight} = 12x + y + 16z;$$

$$\% \text{ of oxygen} = 100 - [\% \text{ of carbon} + \% \text{ of hydrogen}] = 100 - [60 + 13.3] = 26.7\%$$

$$\% \text{ of carbon} = \frac{12x}{12x + y + 16z} \times 100 = 60\%$$

$$\% \text{ of hydrogen} = \frac{y}{12x + y + 16z} \times 100 = 13.3\%$$

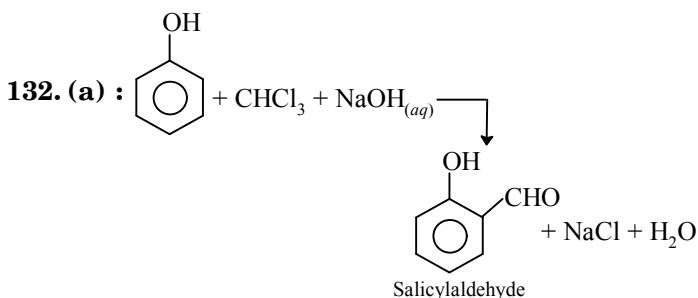
$$\% \text{ of oxygen} = \frac{16z}{12x + y + 16z} \times 100 = 26.7\%$$

On solving the above equations, we get the ratio of $x : y : z = 3 : 8 : 1$ (approximate)

\therefore Formula of compound is C_3H_8O .

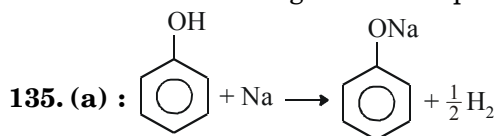
130. (a) : $-OH$ is *o/p*-directing group.

131. (a) : Phenols do not give benzyl alcohol on reaction with heated copper.

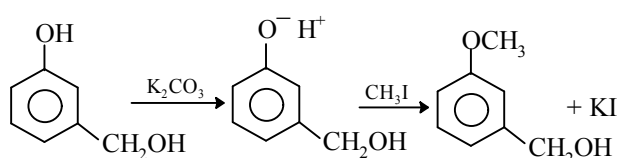


133. (c) : $-NO_2$ is stronger electron withdrawing group which increases the acidic strength of phenol to higher extent. *p*-nitrophenol is more acidic than *o*-nitrophenol because of intramolecular H-bonding in *o*-isomer.

134. (a) : Phenol on reaction with sodium nitrite (NaNO_2) and conc. H_2SO_4 gives a sequential change in colour as
Brown or red \rightarrow green \rightarrow deep blue.

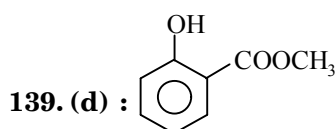
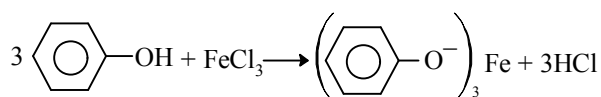


136. (b) : Given reagents K_2CO_3 and CH_3I react with $-\text{OH}$ group to give ether. Phenolic $-\text{OH}$ group is more reactive than benzylic $-\text{OH}$ due to higher acidic strength of phenols than alcohols. Hence, reaction would take place as follows.

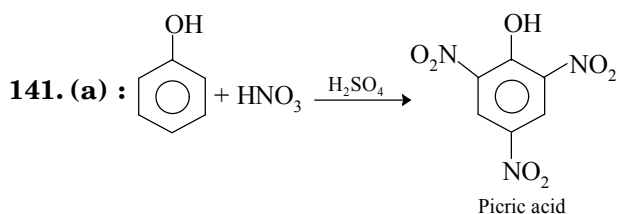
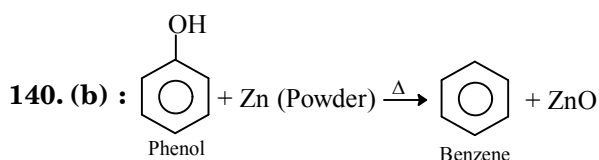


137. (a) : Salol is used as antiseptic.

138. (c) : Phenols give characteristic deep blue colour with FeCl_3 solution. Alcohols do not give this reaction.



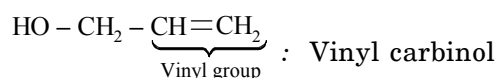
Methyl salicylate is also known as oil of winter green.



142. (d) : Acid or base-catalysed condensation of phenol with formaldehyde yields the polymer bakelite.

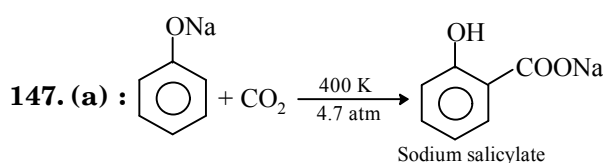
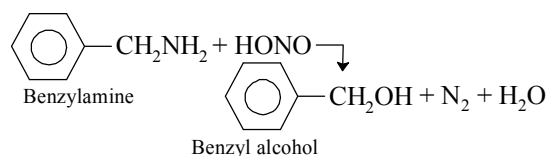
143. (a) : Phenol gives violet colour with neutral FeCl_3 solution.

144. (a) : Methyl alcohol is known as carbinol. Methyl alcohol substituted with vinylic group is called vinyl carbinol.



145. (c) : Phenol is soluble in both NaOH and dil. HCl .

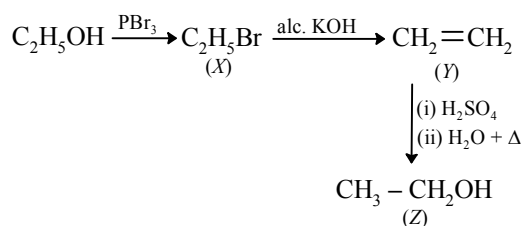
146. (c) :



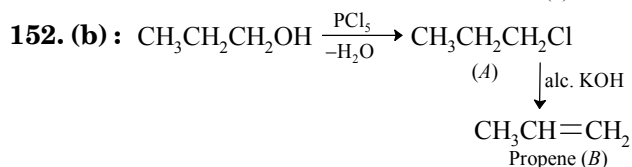
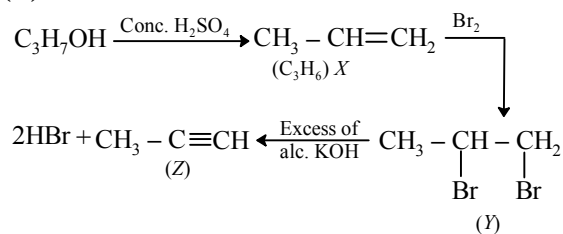
148. (b) : Salicylic acid on treatment with methyl alcohol in presence of H_2SO_4 yields oil of winter green.

149. (c) : Phenols being weak acids do not dissolve in sodium carbonate. Large number of electron withdrawing groups attached to phenol increases the acidic strength and thus reactivity to an appreciable extent.

150. (b) :



151. (d) :



153. (b) : Aldehydes can be produced by oxidation of alcohols.

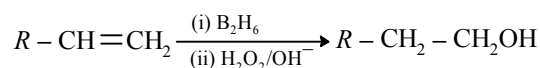
154. (c) : $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-OH}$, Butan-1-ol is a 1° alcohol.

155. (c) : Lower members of alcohols are soluble in water and solubility regularly decreases with molecular mass.

156. (d) : Yeast brings about the fermentation of alcohol.

157. (c) : Tertiary alcohols are not oxidised easily, they undergo dehydration by the action of hot copper to form alkenes.

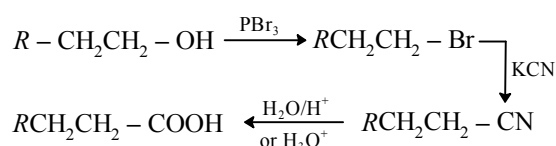
158. (d) :



159. (a) : Ethyl alcohol is lighter than water.

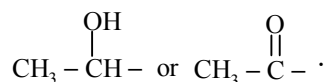
160. (b) : $R-\text{Cl} + \text{OH}^- \xrightarrow[\text{substitution}]{\text{Nucleophilic}} R-\text{OH} + \text{Cl}^-$

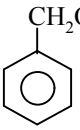
161. (a) :



162. (a) : Alcohols have higher boiling points than corresponding hydrocarbons due to intermolecular H-bonding.

163. (d) : To give iodoform test, compounds should have any of the following two groups.



Benzyl alcohol  does not have any of the required groups for iodoform test.

164. (c) : Ethyl alcohol shows hydrogen bonding to maximum extent among the given compounds.

165. (a) : Boiling point for isomeric alcohols follows the order $1^\circ > 2^\circ > 3^\circ$, because larger the surface area more will be boiling point.

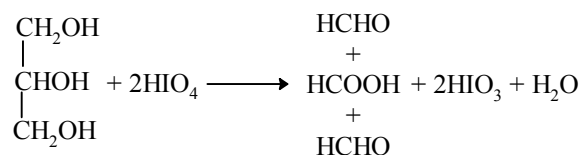
166. (c) : $\text{CH}_3\text{CH}_2\text{OH} + 3\text{I}_2 + 4\text{NaOH}$



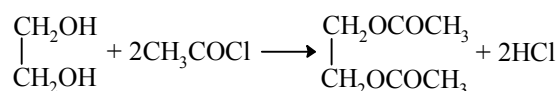
167. (c) : Order of reactivity of different alcohols towards esterification is 1° alcohol $>$ 2° alcohol $>$ 3° alcohol due to increased steric hindrance in 2° and 3° alcohols.

168. (a) : CH_3O^- is most reactive nucleophile among the given nucleophiles because it is least sterically hindered.

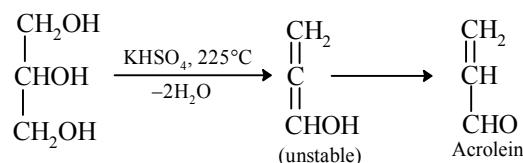
169. (d) :



170. (c) :



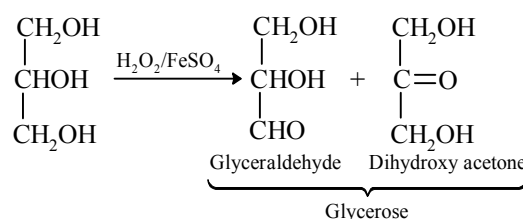
171. (c) :



172. (d) : Glycerol contains three $-\text{OH}$ groups, *i.e.* $\text{CH}_2\text{OH} - \text{CHOH} - \text{CH}_2\text{OH}$.

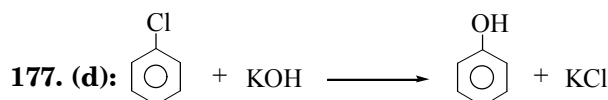
173. (a) : Rectified spirit is 95.87% aqueous solution of ethyl alcohol.

174. (c) : Mild oxidation of glycerol with $\text{H}_2\text{O}_2/\text{FeSO}_4$ (Fenton's reagent) gives a mixture of glyceraldehyde and dihydroxy acetone which is known as glycerose.



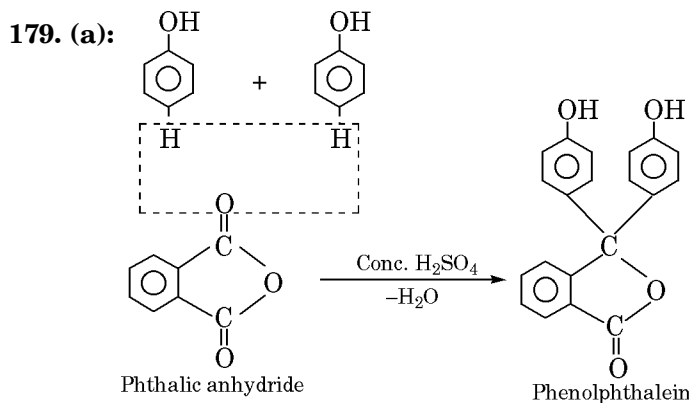
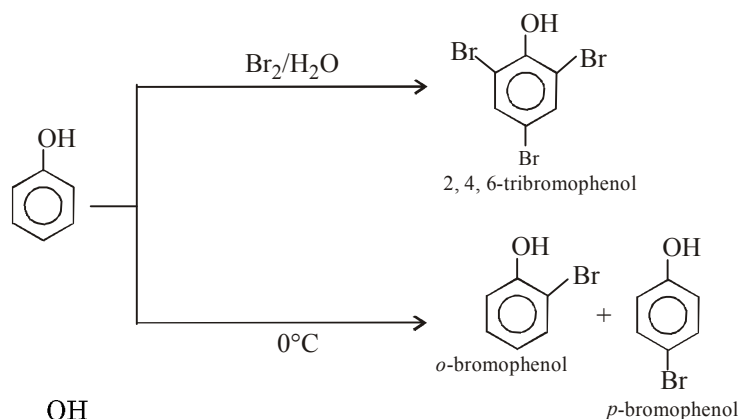
175. (d) : Ethanol mixed with some amount of methanol is known as methylated spirit.

176. (c) : Proof spirit is 57.1% aqueous solution of ethanol.

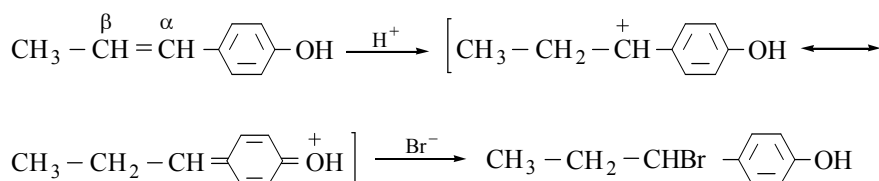


This nucleophilic substitution reaction of chlorobenzene is not possible in normal temperature and pressure conditions. It requires 200 atm pressure and 300°C temperature, as chlorobenzene is less reactive for nucleophilic substitution.

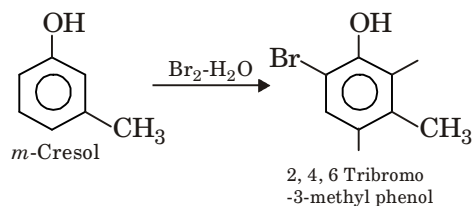
178. (b): In phenol –OH group has activating and ortho-para-directing effect, in aqueous solution due to the presence of phenoxide ion this effect is enhanced and 2, 4, 6-tribromophenol is obtained on the reaction with bromine. But in presence of non-polar (CCl_4) medium, the activity of phenol is decreased and only ortho and para-bromophenols are obtained.



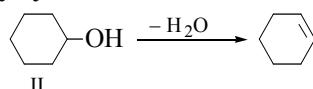
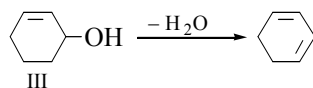
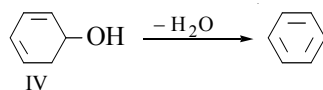
180. (b): Addition of a proton at β -carbon gives carbocation (I) which is stabilized by resonance because of the electron donating effect of the –OH group. The addition of Br^- ion to this carbocation gives the addition product (II).



181. (d): Since the compound dissolves in NaOH , it must be an acid or a phenol. Since it gives a characteristic colour with FeCl_3 , it must be a phenol. Now, three phenols having the molecular formula $\text{C}_7\text{H}_8\text{O}$ are *o*-, *m*- or *p*- cresol. Since the compound on treatment with Br_2 gives a tribromoderivative, therefore, two *o*- and one *p*- position with respect to –OH group is free. That is the phenol is *m*-cresol.

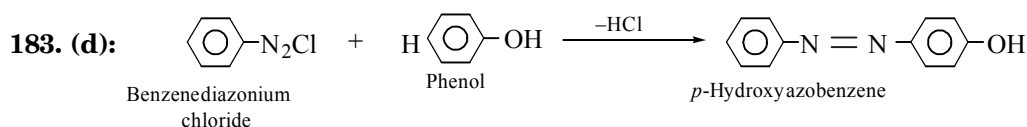


182. (a): Dehydration of IV is most facile since, it gives an aromatic compound. Dehydration of III gives a conjugated diene which is stabilized by resonance.

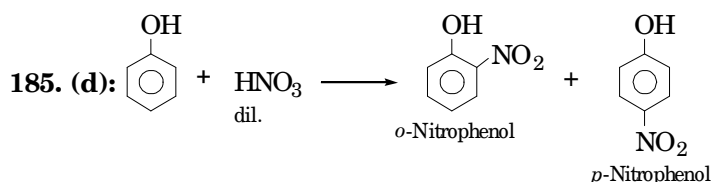
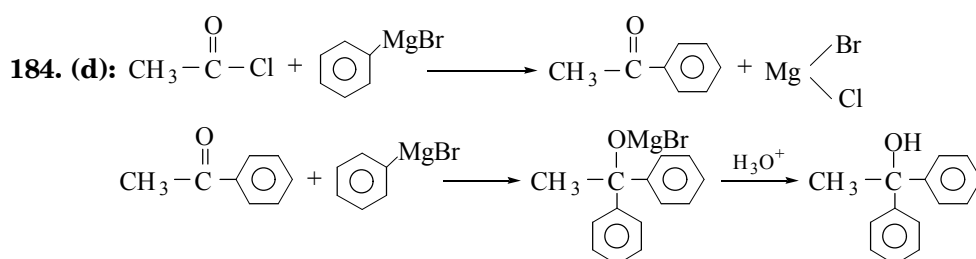


Dehydration of II gives only cyclohexene which is not stabilized by resonance.

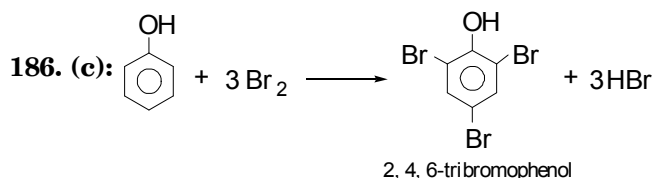
In contrast, phenol (I) does not undergo dehydration. Thus, the ease of dehydration is:
IV > III > II > I.



This is an example of coupling reaction, which results in the formation of an orange dye.



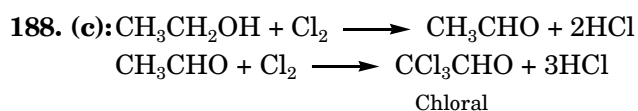
However, ethanol is oxidised by dilute HNO₃ to an aldehyde and then to an acid in following manner.



∴ 94 grams of phenol require bromine = 480 g

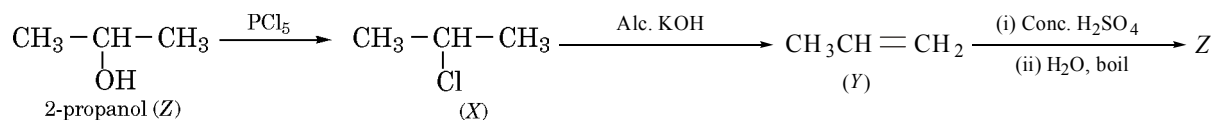
∴ 2 grams of phenol require amount of bromine = $\frac{480}{94} \times 2 = 10.22$ g

187. (a): In isomeric alcohols, the boiling point has the order primary > secondary > tertiary, and on branching the boiling point decreases. Therefore, among the given alcohols the boiling point of 1-butanol is highest.



189. (b): Greater the stability of the intermediate carbocation, more reactive is the alcohol. Since 2-methylpropan-2-ol generates 3° carbocation, therefore, it reacts fastest with HBr.

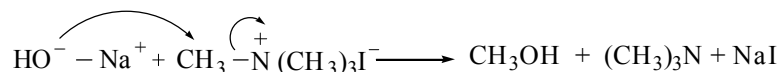
190. (b): The most important clue to solve this problem is the conversion of $Y \longrightarrow Z$. Since addition of H_2SO_4 followed by hydrolysis, *i.e.* hydration of alkenes follows Markownikoff's rule, therefore, Z can be only 2-propanol and not 1-propanol.



191. (c): The order of reactivity depends upon the stability of the carbocations formed, *i.e.*, $\overset{+}{\text{FCH}_2\text{CHCH}_3}$, $\overset{+}{\text{FCH}_2\text{CH}_2\text{CHCH}_3}$, $\overset{+}{\text{CH}_3\text{CHCH}_3}$ and $\overset{+}{\text{PhCH}_2}$. Since the relative stability of these carbocations follow the order:

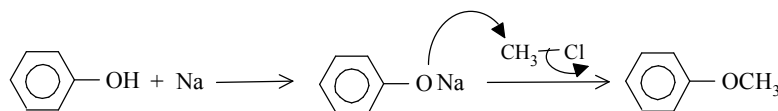
$\overset{+}{\text{PhCH}_2} > \overset{+}{\text{CH}_3\text{CHCH}_3} > \overset{+}{\text{FCH}_2\text{CH}_2\text{CHCH}_3} > \overset{+}{\text{FCH}_2\text{CHCH}_3}$, therefore, the order of reactivity of the alcohols (I, II, III and IV) follows the sequence: IV > III > II > I.

192. (a): Due to greater electronegativity of N over S, +ve charge on N will make $-\text{CH}_3$ group more electron deficient than +ve charge on less electronegative S. Therefore, $(\text{CH}_3)_4\text{N}^+\text{I}^-$ will undergo nucleophilic substitution more readily than $(\text{CH}_3)_3\text{S}^+\text{I}^-$.



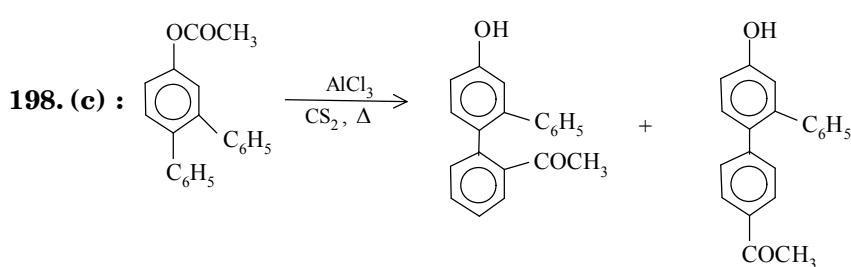
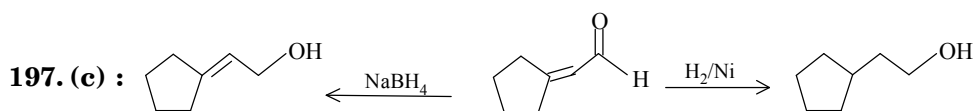
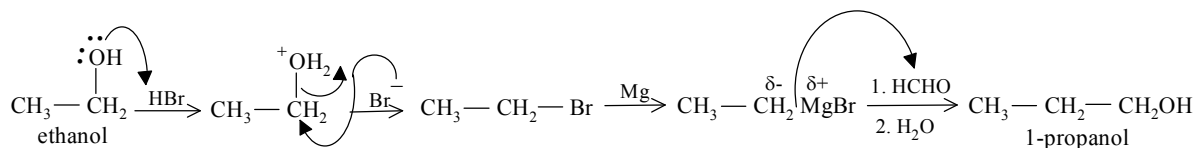
193. (a): As $\text{C}_6\text{H}_5\text{CH}_2^+$, benzylic carbocation is stable hence the conversion preferably follows S_N1 path.

194. (c): Williamson's synthesis of anisole

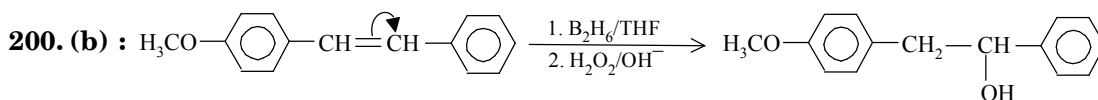


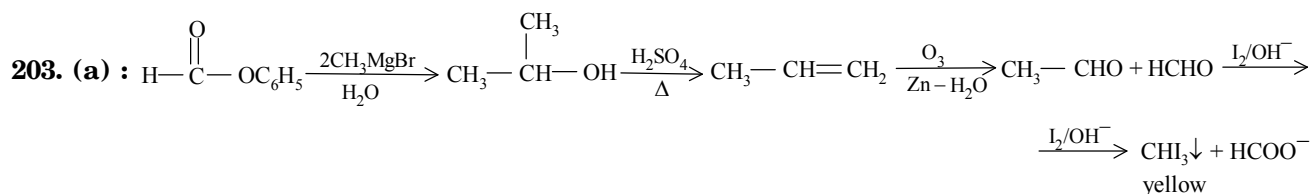
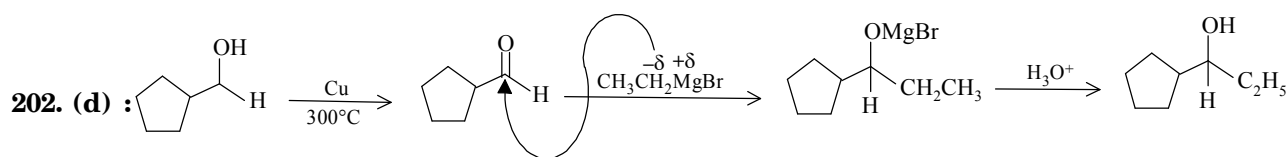
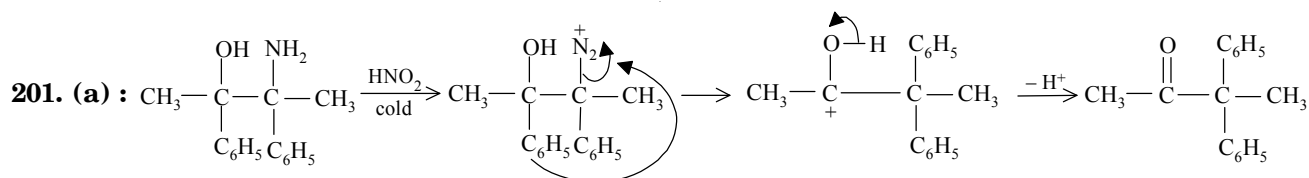
195. (b): Ether with α -hydrogen atom forms peroxide readily.

196. (b):

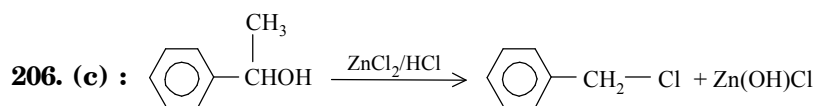
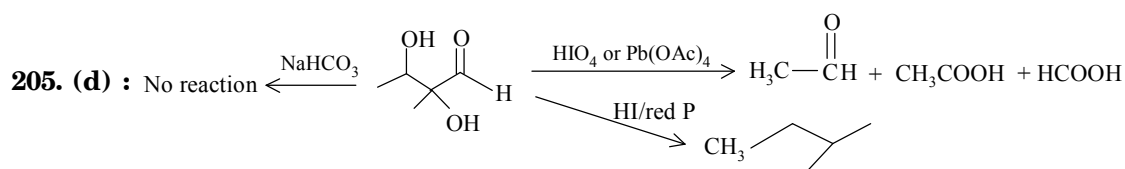


199. (a)

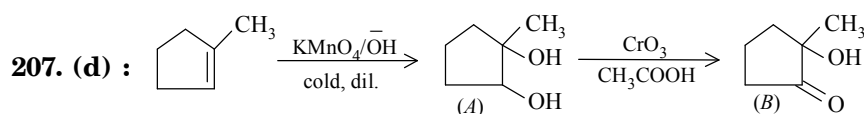




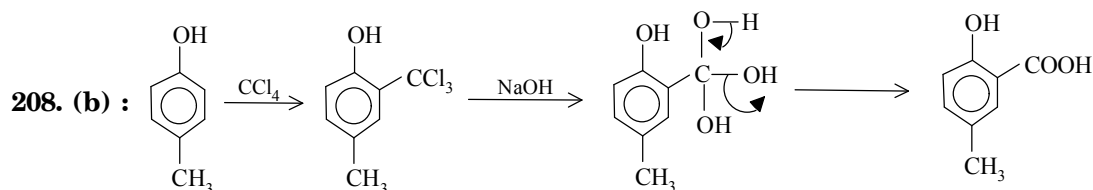
204. (a) : Allylic carbocation is more stable and C—H bond is easily broken compared to C—D bond. Hence I > III > IV > II.



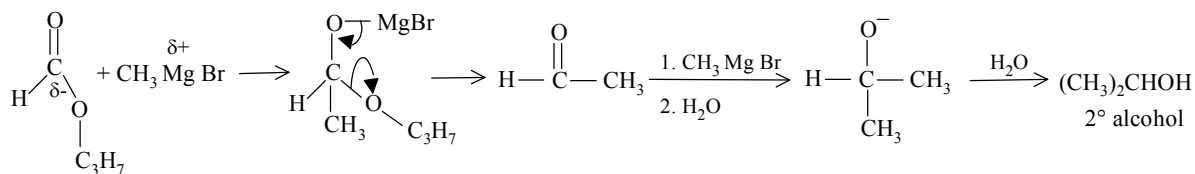
Since it is a secondary alcohol, it reacts vigorously with Lucas reagent.

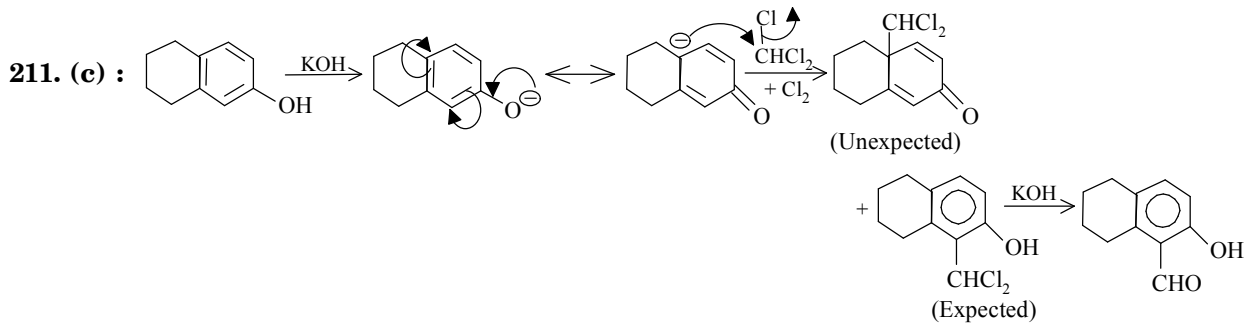
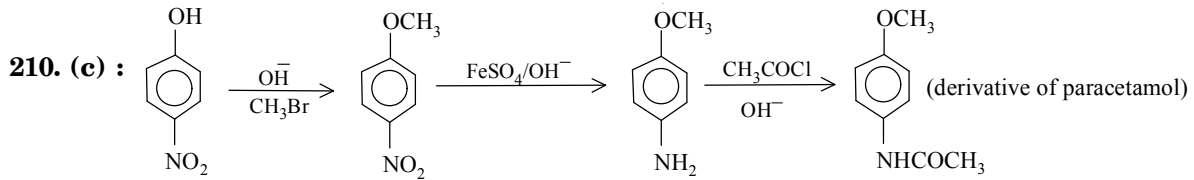


(Only 2° and 1° alcohols undergo oxidation using chromic acid).

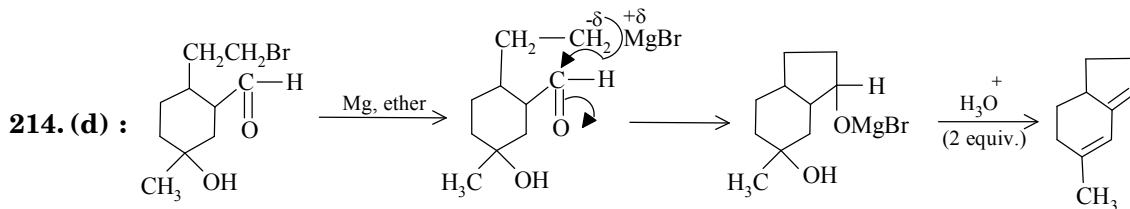
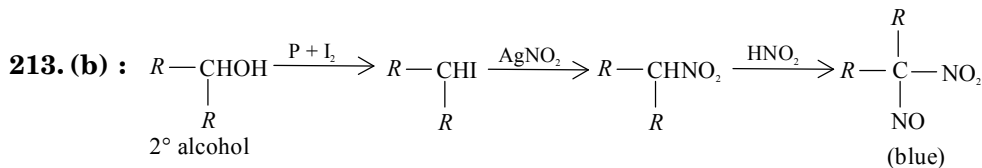


209. (b) : B reacts appreciably faster with Lucas reagent, so it is a secondary alcohol. $\therefore \text{B} = \text{CH}_3-\text{C}(\text{OH})(\text{CH}_3)-\text{H}$

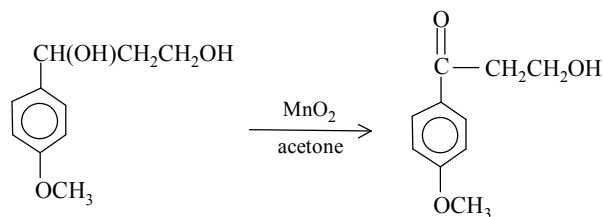




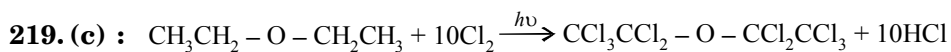
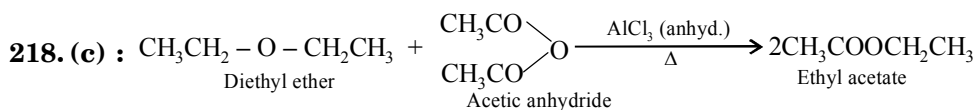
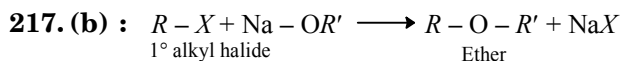
212. (a) : In *ortho*-nitrophenol, $-\text{OH}$ is linked to $-\text{NO}_2$ by means of intramolecular H-bonding. So, it is highly volatile.



215. (c) : $\text{MnO}_2/\text{acetone}$ is selectively used to oxidize allylic and benzylic alcohols.



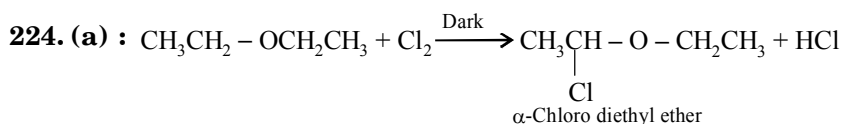
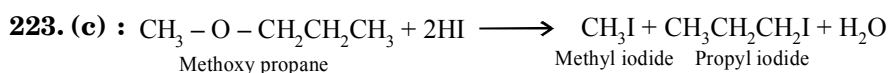
216. (a) : $\left((\text{CH}_3)_2\text{CH}-\overset{\text{CH}_3}{\text{CH}} \right)_2$ BH/ether; H_2O reduces aldehydes, ketones but not acid halides and esters.

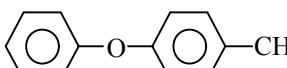


220. (b) : Since the compound does not react with 2,3-dinitrophenyl hydrazine, it can not be carbonyl compound. No reaction with sodium metal indicates that compound cannot be an alcohol. Hence it could only be $\text{CH}_2 = \text{CH} - \text{O} - \text{CH}_3$.

221. (c) : Only dimethyl ether and ethyl methyl ethers are gases at room temperature, whereas all other ethers are colourless liquids at room temperature.

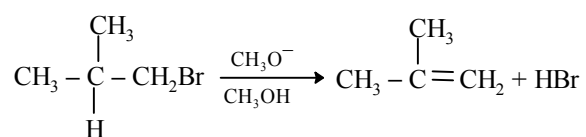
222. (b) : Alcohols are isomeric with ethers.



225. (b) :  : Diaryl ethers are not cleaved by HI.

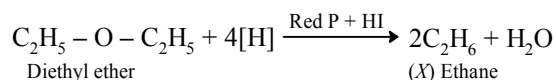
226. (d) : Ethers are quite inert towards the attack of nucleophiles due to lack of any reactive site.

227. (c) :

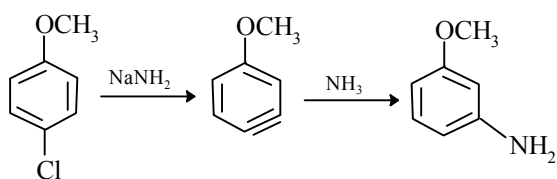


3° alkyl halides readily undergo E2 elimination in presence of some base like alkoxide ion rather than substitution.

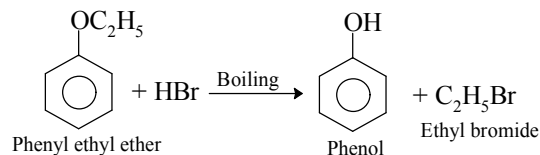
228. (a) :



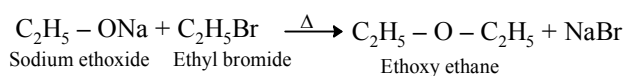
229. (b) :



230. (a) :

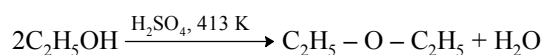


231. (c) :



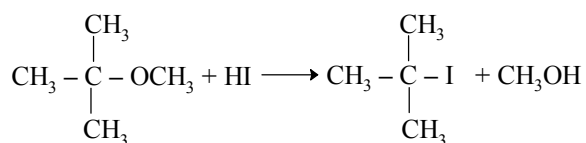
232. (b) : Alkyl aryl ethers undergo electrophilic substitution reaction.

233. (a) :

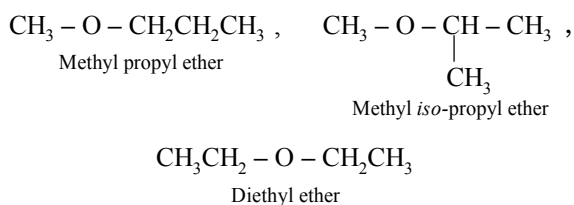


234. (a) : Ethers are quite inert towards the action of oxidising agent.

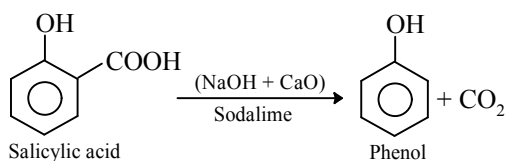
235. (b) :



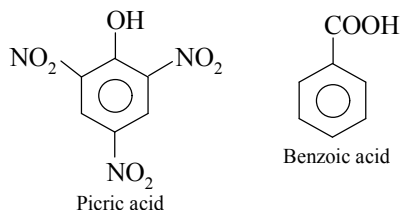
236. (b) : $\text{C}_4\text{H}_{10}\text{O}$:



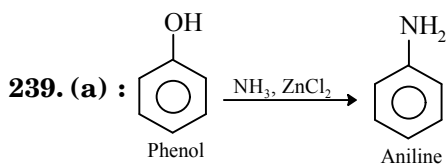
237. (a) :



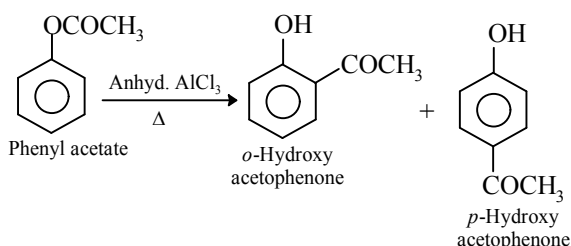
238. (c) :



Picric acid having $-\text{OH}$ group reacts with aqueous FeCl_3 to form brown solution, whereas benzoic acid does not give such reaction.

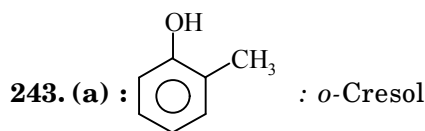


240. (b) : Fries rearrangement is the intramolecular rearrangement of phenyl esters to give mixture of *o*- and *p*-hydroxy ketones in presence of AlCl_3 . *e.g.*,



241. (b) : *o*-Nitrophenol exhibits intramolecular H-bonding and thus does not get associated as a result of which has low boiling point.

242. (c) : Because of large non-polar hydrocarbon part ($-\text{C}_6\text{H}_5$), phenol is less soluble in water.



244. (b) : Phthalein reaction is a characteristic test for phenols.

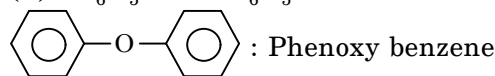
245. (a) : Phenol being strongest acid among the given compounds is soluble in dilute aqueous NaOH .

246. (d) : Reaction of phenol with formaldehyde is a polymerization reaction.

247. (a) : Phenol on reaction with methanal (HCHO) gives a thermosetting polymer, bakelite.

248. (c) : An electron withdrawing group increases the acidic strength of phenol.

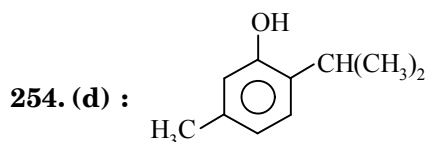
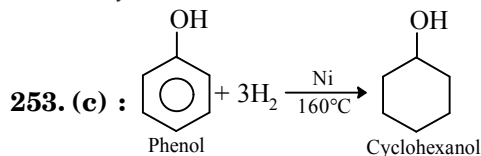
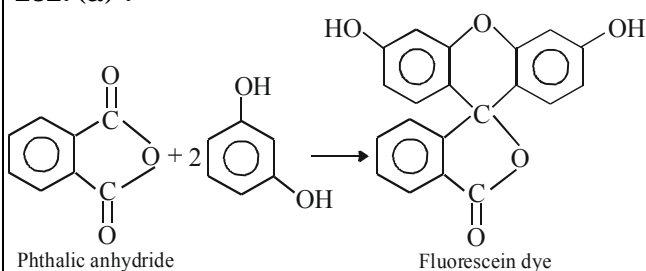
249. (b) : $\text{C}_6\text{H}_5 - \text{O} - \text{C}_6\text{H}_5$ *i.e.*



250. (a) : Alcohols do not react with FeCl_3 whereas phenols give brown coloured complexes with FeCl_3 .

251. (a) : *o*-Nitrophenol shows low melting point *i.e.* has volatile nature because of intramolecular hydrogen bonding.

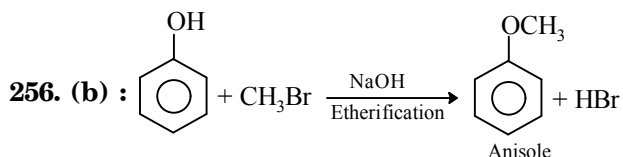
252. (a) :



Thymol (Oil of thyme and mint)

Thymol is white crystalline phenol derivative, occurs in many essential oils. It is used as fragrant material as well as mild antiseptic.

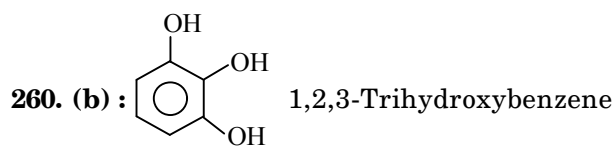
255. (c) : Phenols are more acidic than alcohols.



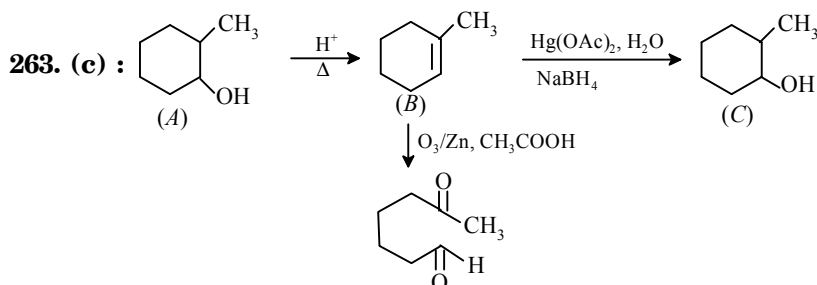
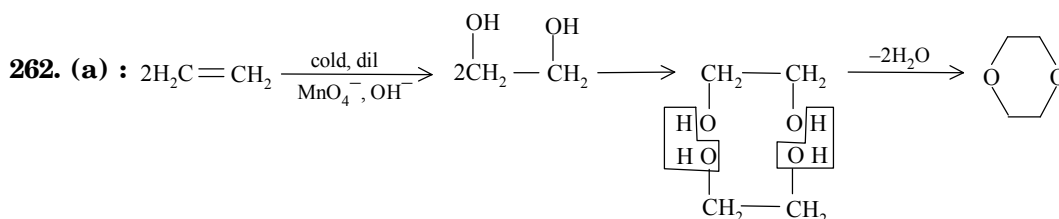
257. (a) : Phenol has a benzene ring which gets involved in resonance stabilization.

258. (c) : All the given compounds can be prepared from phenol.

259. (a) : Phenol has antiseptic action.



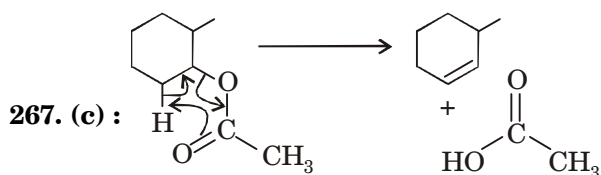
261. (c) : Phenol is used in such cases due to its antiseptic property.



264. (b) : $-\text{NO}_2$ shows $-I$, $-M$ at *ortho*, *para* and only $-I$ at *meta* position. $-\text{CH}_3$ group shows $+I$, hyperconjugation at *ortho*, *para* and shows only $+I$ at *meta*.

265. (c) : NaBH_4 cannot reduce lactones but can reduce aldehydes.

266. (d) : Higher the E° value, higher the reduction potential and greater the tendency to be reduced. II on reduction gives two aromatic rings which together have more resonance energy and stability than the present diketone compound. Reduction of I gives a simple aromatic ring having two $-\text{OH}$ groups at *ortho* position-relatively less stable than *para* form.



(Pyrolysis of ester prefers less substituted alkene)

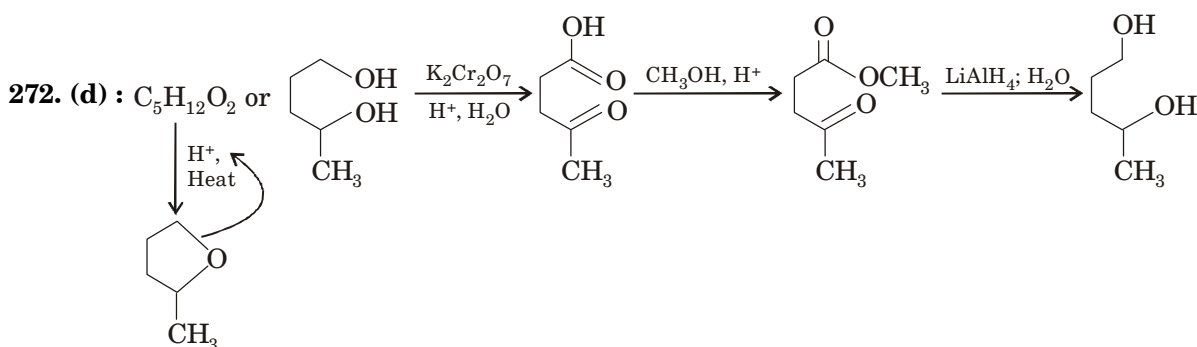
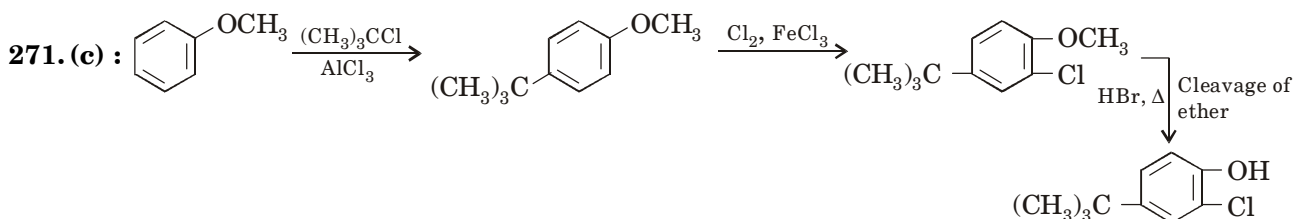
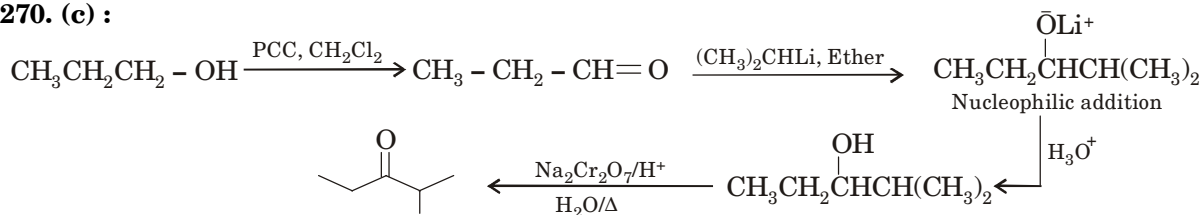
268. (b) : Ag_2O increases the leaving tendency of Cl^- and stabilises the ion. The $-\text{OH}$ group of ROH is then strong enough nucleophilic to displace $-\text{Cl}$.

269. (d) : $\text{A} + \text{CH}_3\text{CH}_2\text{MgI} \xrightarrow{\text{H}^+} \text{B}$; no reaction with PCC or PDC. It suggests A should be a ketone

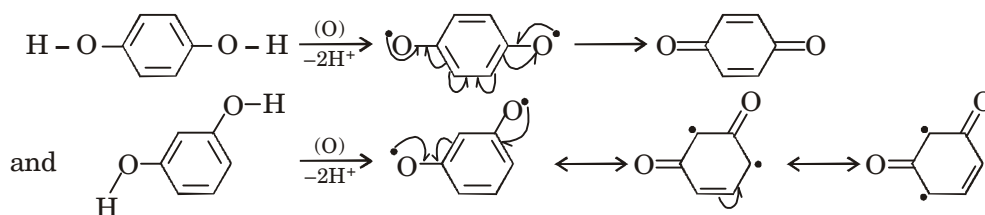
which on reaction with Grignard reagent gives 3° alcohol.

3° alcohol does not respond to mild oxidising agents.

270. (c) :

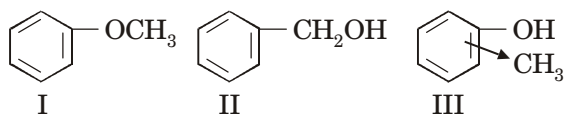


273. (b) : Basically in quinol two unpaired electrons at two oxygen atoms interact together and are coupled to impart greater stability in the form of quinone but unpaired electrons in resorcinol do not have interaction, and no coupling, thus no oxidation into stable one. Compare

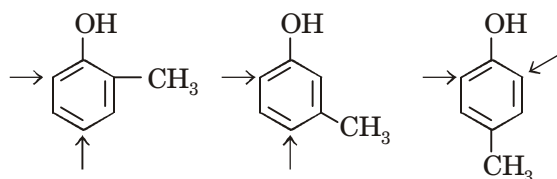


274. (a) : Molecular formula = $\text{C}_7\text{H}_8\text{O}$, Degree of unsaturation = 4 \Rightarrow One benzene ring

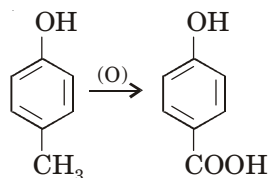
Hence possible forms are



I and II will not react with Na and NaOH, hence III is possible but three isomers are possible for III.



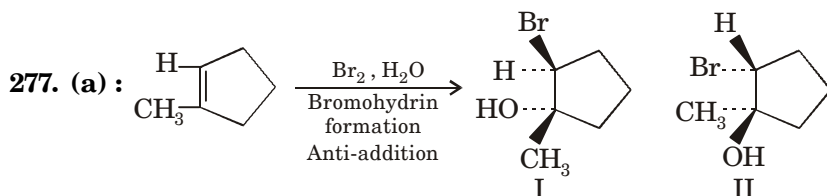
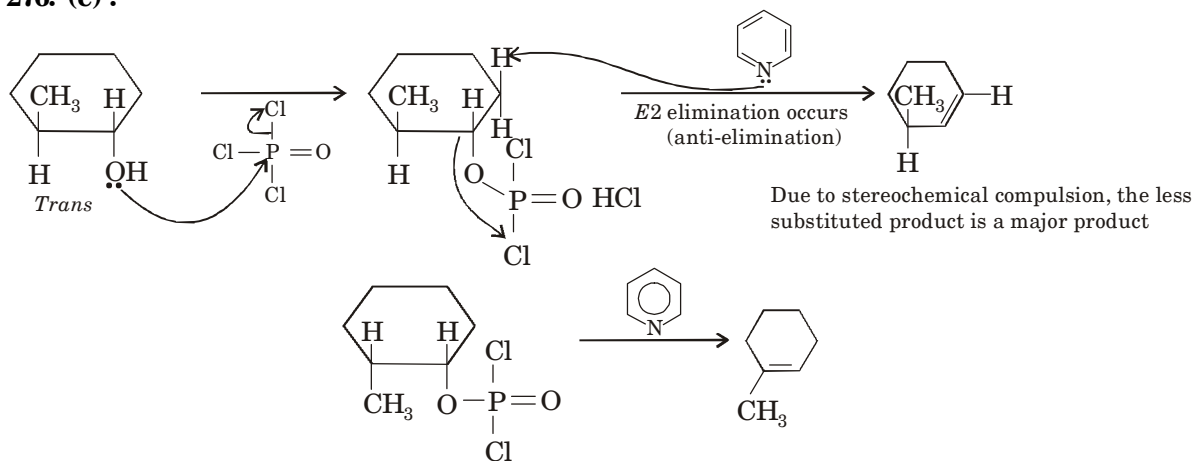
Only *p*-cresol will give a mono nitroderivative.



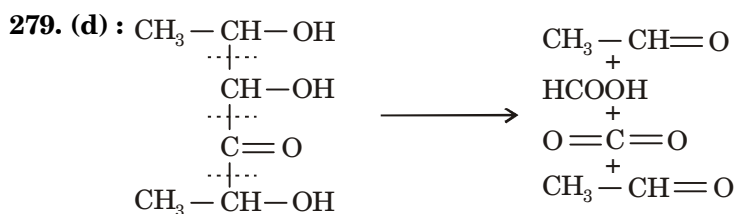
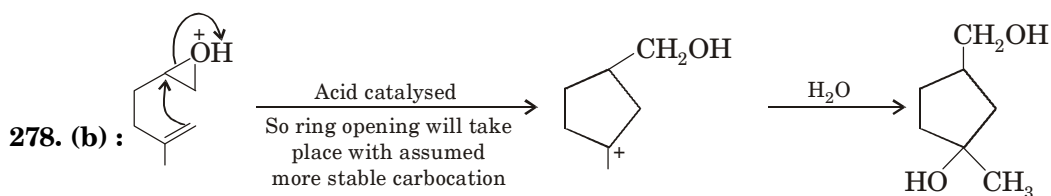
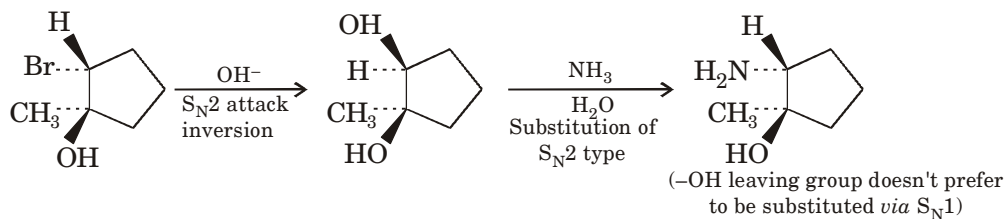
275. (d) : *X* does not give Lucas test, it means 1° alcohol. Bromine decolourises ⇒ unsaturation double or triple bond. Na metal bubbles ⇒ acidic hydrogen.

Hence, correct structures are $X = \text{CH}_2=\text{CHCH}_2\text{CH}_2\text{OH}$ and $Y = \text{C}_4\text{H}_8\text{O}$

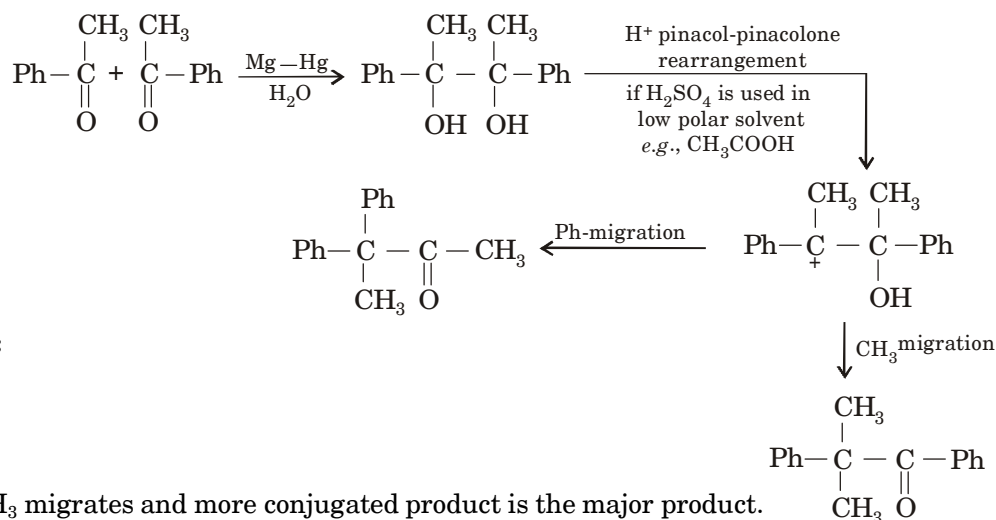
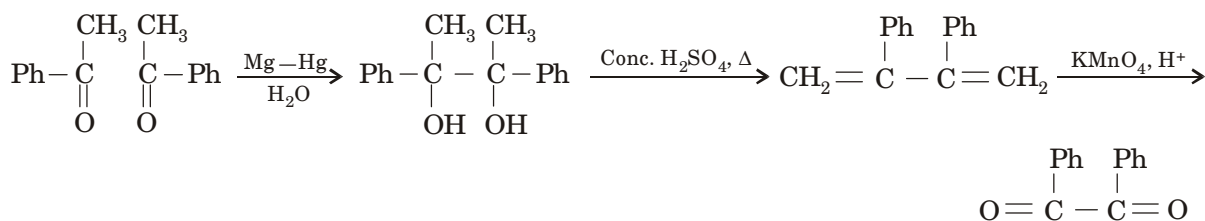
276. (c) :



(H_2O attacks at more substituted carbon atom) Take any one molecule for the next step.

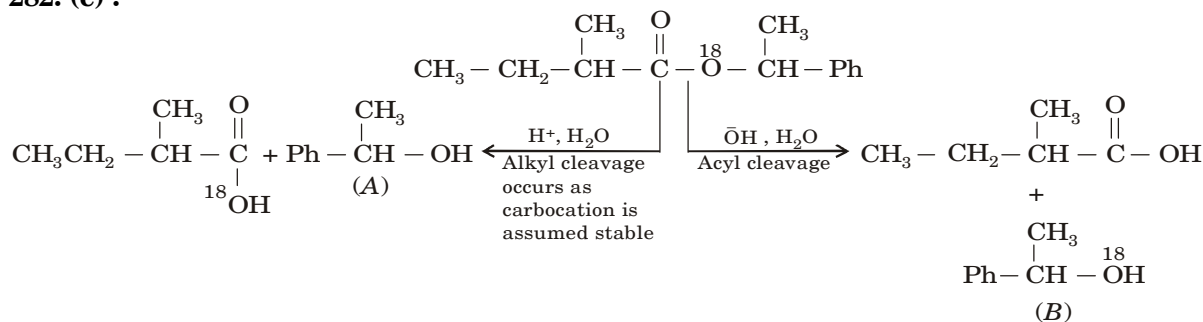


280. (c) :



281. (c) :

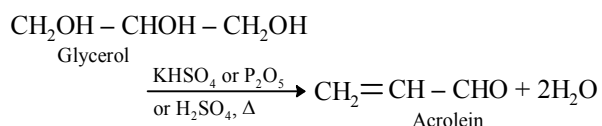
282. (c) :



283. (c) : Glycerol can be obtained both from fats and propylene.

284. (a) : Glycol is used as antifreeze in automobile radiator.

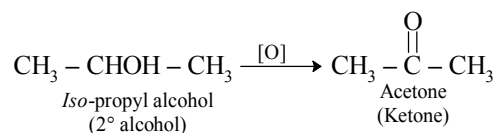
285. (d) : Glycerol can be dehydrated to acrolein by any of the given reagents.



286. (d) : Glycerine contains three –OH groups out of which two are primary and one is secondary.

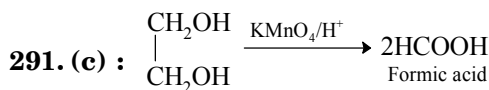
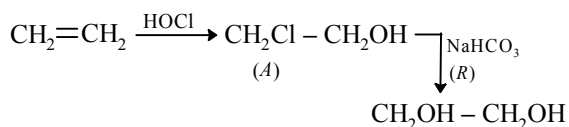
287. (b) : Glycerol has extensive H-bonding due to the presence of three –OH groups.

288. (a) : Secondary alcohols yield ketones on oxidation.

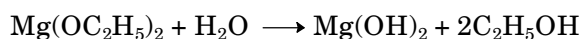


289. (d) : Glycerol has two primary and one secondary hydroxyl group.

290. (d) :

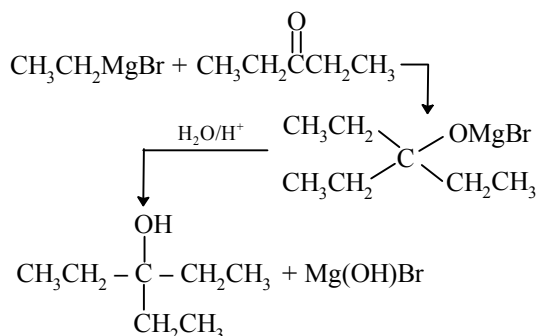


292. (d) : Water traces present in rectified spirit are removed by distilling it with $\text{Mg}(\text{OC}_2\text{H}_5)_2$.

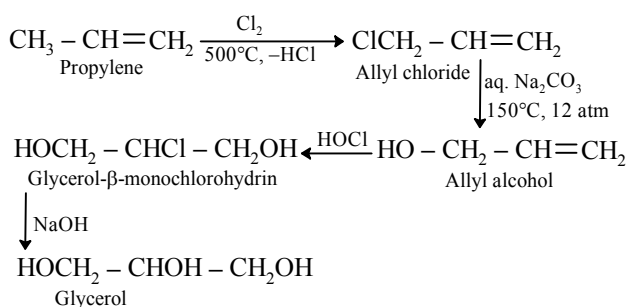


293. (b) : In air, ethanol ($\text{C}_2\text{H}_5\text{OH}$) gets oxidised to acetic acid (CH_3COOH).

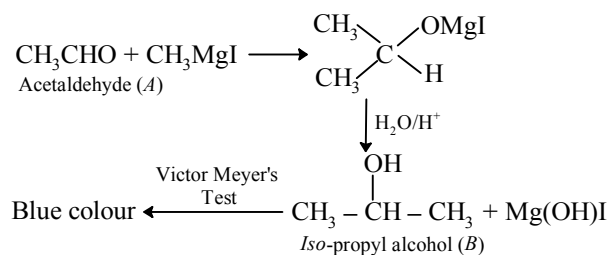
294. (c) :



295. (c) :

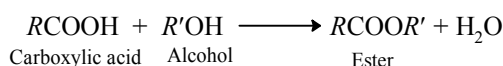


296. (c) : In Victor Meyer's test, blue colour salt is given by secondary alcohols. It means compound *B* must be a secondary alcohol. Only aldehydes with Grignard reagent yield secondary alcohols. Aldehyde should have one carbon less than the secondary alcohol since Grignard reagent contains methyl group. These conditions are satisfied by acetaldehyde and *iso*-propyl alcohol.



297. (d) : Louis Pasteur conducted first scientific study of fermentation.

298. (a) : Reaction between alcohol and carboxylic acid yields ester, hence the reaction is known as esterification.

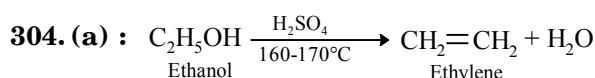
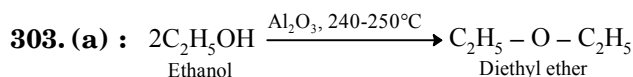


299. (c) : $\text{C}_2\text{H}_5\text{OH}$ gives iodoform test whereas CH_3OH does not.

300. (c) : Reaction of ethanol with H_2SO_4 does not yield acetylene at any condition.

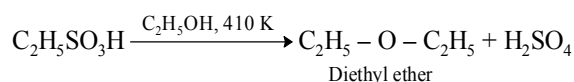
301. (d) : HCHO does not give yellow precipitate of iodoform with I_2/NaOH .

302. (b) : Since the bond strength of halogen acids follows the order, $\text{H}-\text{Cl} > \text{H}-\text{Br} > \text{H}-\text{I}$. The order of their reactivity for reaction with $\text{C}_2\text{H}_5\text{OH}$ is $\text{HI} > \text{HBr} > \text{HCl}$.

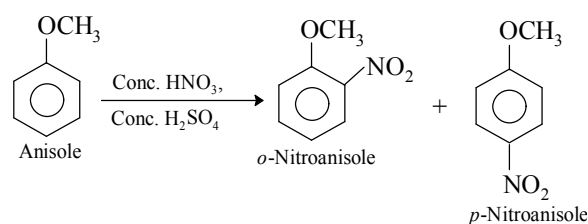


305. (a) : Glycol serves as an antifreeze for petrol.

306. (c) :



307. (c) :

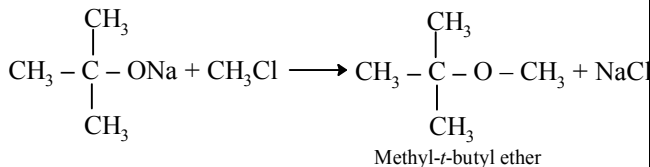


308. (c) : Ethers are quite stable or inert towards oxidising agents.

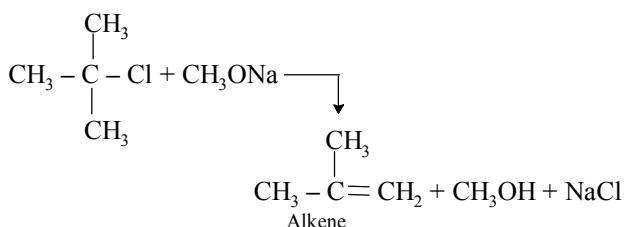
309. (d) : Grignard reagent is prepared in ether not in aqueous medium because it is highly reactive in water.

310. (c) : C - O - C angle in ether is about 110°.

311. (d) :



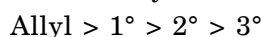
whereas,



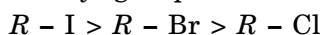
Secondary and tertiary alkyl halides readily undergo elimination reaction rather than ether formation in the presence of alkoxide.

312. (d) : Formation of di-*tertiary*-butyl ether requires the reaction of sodium *t*-butoxide with *t*-butyl halide. But tertiary alkyl halides prefer to undergo elimination reaction rather than Williamson's reaction in presence of alkoxide ion.

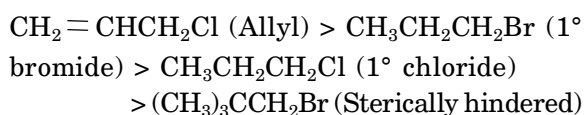
313. (d) : Order of reactivity of different alkyl halides towards Williamson's synthesis is



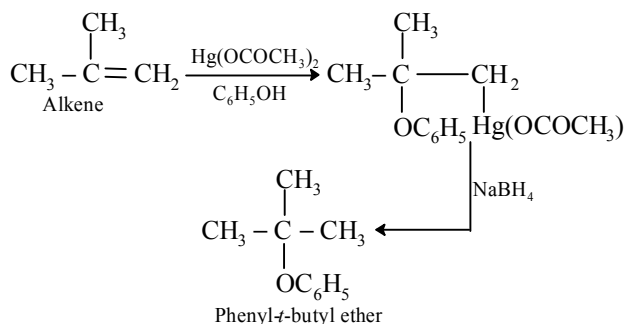
For same alkyl group order of reactivity is



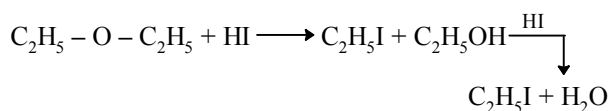
Thus, order of reactivity of given alkyl halides towards Williamson's synthesis can be given as



314. (c) :

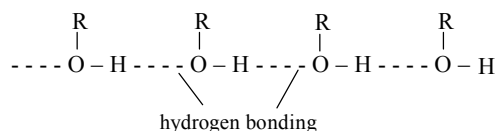


315. (c) :



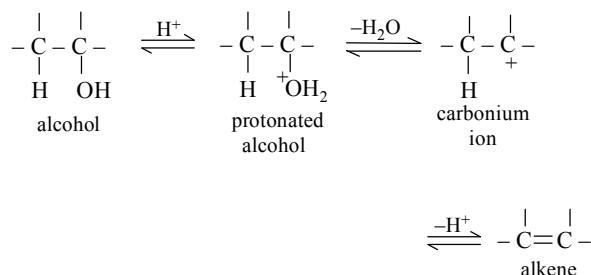
QUESTIONS FROM PREVIOUS YEARS AIEEE/JEE MAIN

1. (d) : The reason for the lesser volatility of alcohols than ethers is the intermolecular association of a large number of molecules due to hydrogen bonding as -OH group is highly polarised.



No such hydrogen bonding is present in ethers.

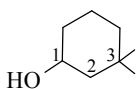
2. (a) : Dehydration of alcohol to alkene in presence of concentrated H_2SO_4 involves following steps :



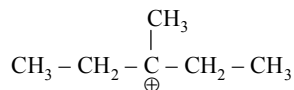
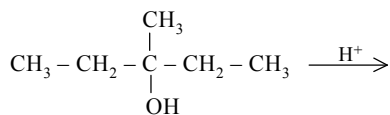
Thus, the initiation step is protonation of alcohol.

3. (d) : Vapour density = $\frac{\text{Molecular weight}}{2}$

As both the compounds have same molecular weights, both will have the same vapour density. Hence, gaseous density of both ethanol and dimethyl ether would be same under identical conditions of temperature and pressure. The rest of these three properties; vapour pressure, boiling point and heat of vaporization will differ as ethanol has hydrogen bonding whereas ether does not.

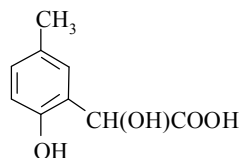
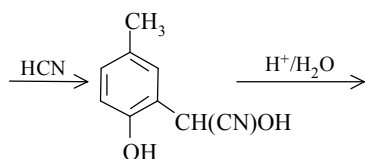
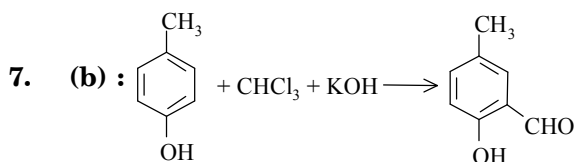
4. (c) :  → 3,3-dimethyl-1-cyclohexanol

5. (c) : The ease of dehydration of alcohols is tertiary > secondary > primary according to the order of stability of the carbocations.

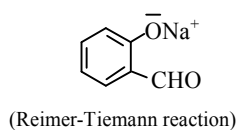
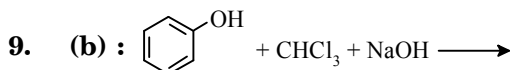
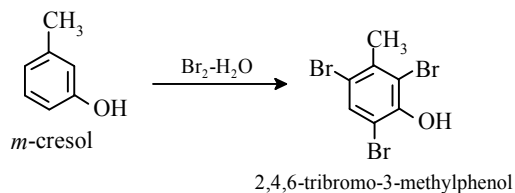


The more stable carbocation is generated thus more easily it will be dehydrated.

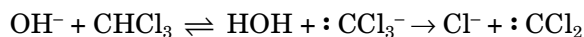
6. (d) : Pyridinium chlorochromate oxidises an alcoholic group selectively in the presence of carbon-carbon double bond.



8. (a) : Since the compound on treatment with Br_2 -water gives a tribromoderivative, therefore it must be *m*-cresol, because it has two *ortho* and one *para* position free with respect to OH group and hence can give tribromoderivative.

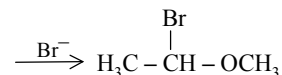
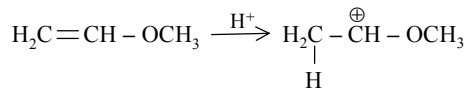


The electrophile is dichlorocarbene, $:\text{CCl}_2$ generated from chloroform by the action of a base.

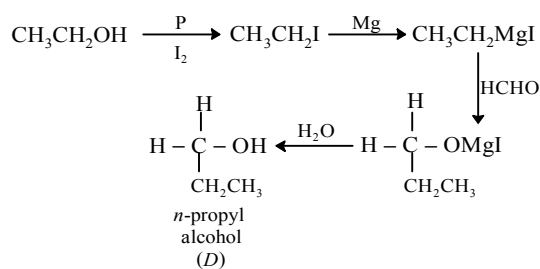


10. (d) : Methyl vinyl ether is a very reactive gas. It is hydrolysed rapidly by dilute acids at room temperature to give methanol and aldehyde.

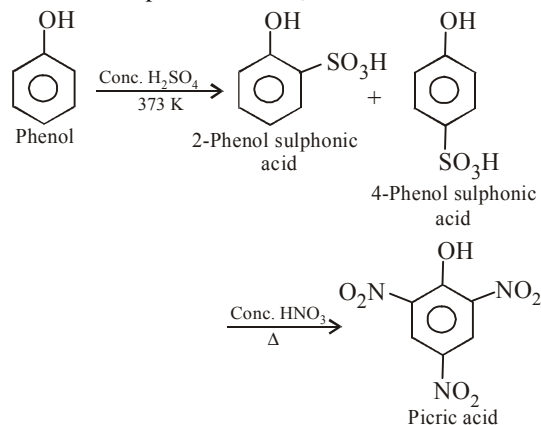
However, under anhydrous conditions at room temperature, it undergoes many addition reactions at the double bond.



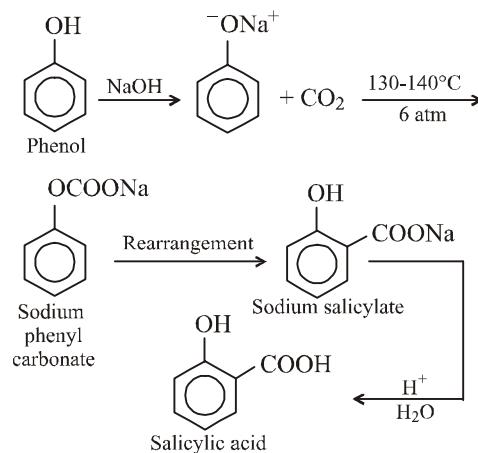
11. (d) :



12. : (None of the option is correct)



13. (c) : The reaction of phenol with NaOH and CO_2 is known as Kolbe-Schmidt or Kolbe's reaction. The product formed is salicylic acid.

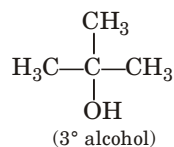


14. (c) : The reagent, conc. HCl and anhydrous ZnCl₂ is Lucas reagent, which is used to distinguish between 1°, 2° and 3° alcohols.

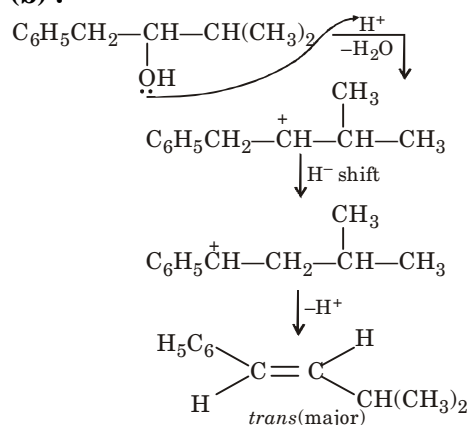
3° alcohol + Lucas reagent → Immediate turbidity.

2° alcohol + Lucas reagent → turbidity after 5 mins.

1° alcohol + Lucas reagent → No reaction.
Thus, the required alcohol is 2-methylpropan-2-ol, i.e.,

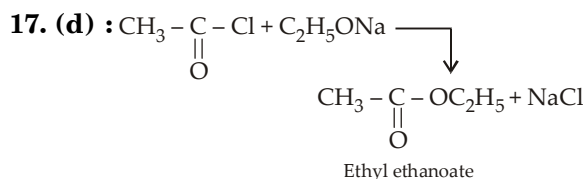
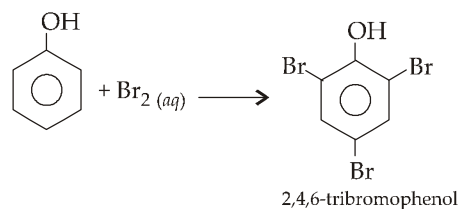


15. (b) :

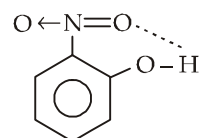


The preferential formation of this compound is due to conjugation in the compound.

16. (d) : $\text{KBr}_{(aq)} + \text{KBrO}_{3(aq)} \rightarrow \text{Br}_{2(aq)}$
This bromine reacts with phenol gives 2,4,6-tribromophenol.



18. (a) : *o*-Nitrophenol is stable due to intramolecular hydrogen bonding.



It is difficult to break the H-bonding when dissolved in water thus less soluble.

19. (c) : In Lucas test, turbidity appears immediately with tertiary alcohol by S_N1 mechanism.

20. (d) : Electron donating groups (—CH₃ and —OCH₃) decrease while electron withdrawing groups (—NO₂ and —Cl) increase the acidity. Since —OCH₃ is a stronger electron donating group than —CH₃ and —NO₂ is stronger electron withdrawing group than —Cl, therefore order of decreasing acidity is III > I > II > IV.

21. (a) : PCC is highly effective in oxidizing 1° alcohols to aldehydes.

