

Alcohols, Phenols and Ethers

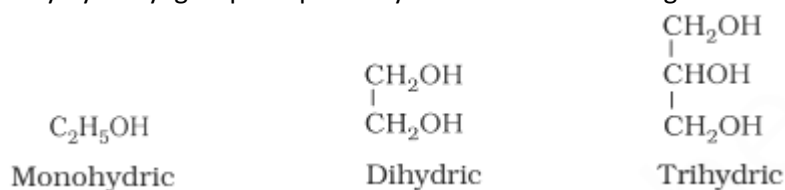
Alcohols, phenols and ethers are the basic compounds for the formation of detergents, antiseptics and fragrances, respectively.

Alcohols and phenols are formed when a hydrogen atom in a hydrocarbon, aliphatic and aromatic respectively, is replaced by -OH group. An alcohol contains one or more hydroxyl (OH) group(s) directly attached to carbon atom(s), of an aliphatic system (CH_3OH) while a phenol contains -OH group(s) directly attached to carbon atom(s) of an aromatic system ($\text{C}_6\text{H}_5\text{OH}$).

The substitution of a hydrogen atom in a hydrocarbon by an alkoxy or aryloxy group (R-O/Ar-O) yields another class of compounds known as 'ethers', for example, CH_3OCH_3 (dimethyl ether).

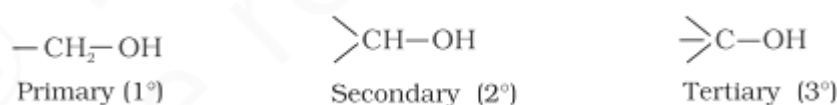
Classification:

Alcohols: Mono, Di, Tri or Polyhydric alcohols depending on whether they contain one, two, three or many hydroxyl groups respectively in their structures as given below:

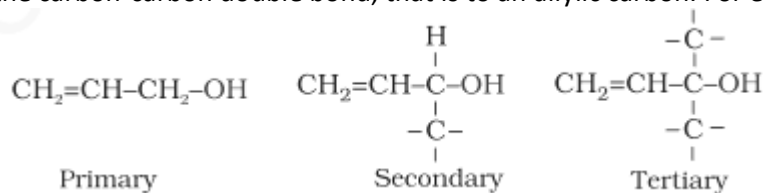


Monohydric alcohols may be further classified according to the hybridisation of the carbon atom to which the hydroxyl group is attached.

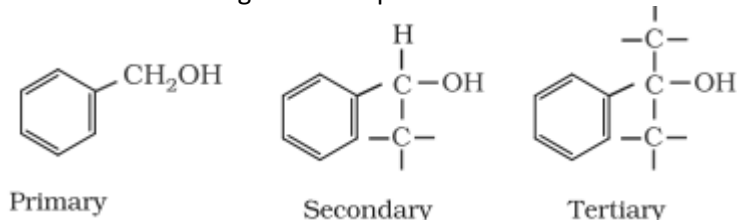
(i) Compounds containing $\text{C}_{\text{sp}^3} - \text{OH}$ bond: In this class of alcohols, the -OH group is attached to an sp^3 hybridised carbon atom of an alkyl group. They are further classified as follows: Primary, secondary and tertiary alcohols: In these three types of alcohols, the -OH group is attached to primary, secondary and tertiary carbon atom, respectively as depicted below:



Allylic alcohols: In these alcohols, the -OH group is attached to a sp^3 hybridised carbon adjacent to the carbon-carbon double bond, that is to an allylic carbon. For example



Benzylic alcohols: In these alcohols, the -OH group is attached to a sp^3 —hybridised carbon atom next to an aromatic ring. For example.

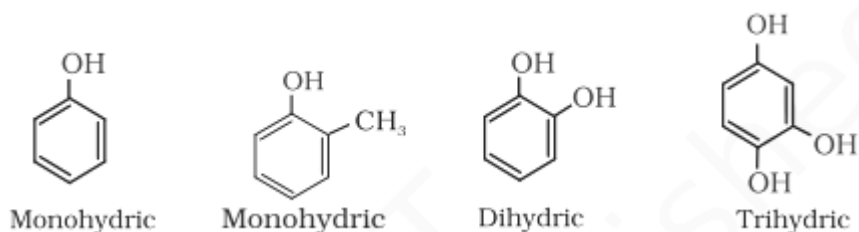


(ii) Compounds containing $\text{C}_{\text{sp}^2} - \text{OH}$ bond:

These alcohols contain -OH group bonded to a carbon-carbon double bond, i.e., to a vinylic carbon or to an aryl carbon. These alcohols are also known as vinylic alcohols.

Vinylic alcohol: $\text{CH}_2 = \text{CH} - \text{OH}$

Phenols— Mono, Di and Trihydric phenols:



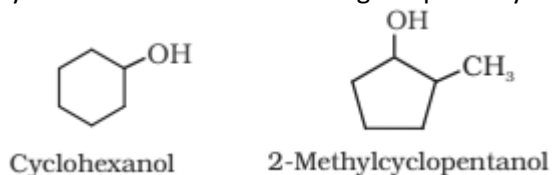
Ethers: Ethers are classified as simple or symmetrical, if the alkyl or aryl groups attached to the oxygen atom are the same, and mixed or unsymmetrical, if the two groups are different. Diethyl ether, $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$, is a symmetrical ether whereas $\text{C}_2\text{H}_5\text{OCH}_3$ and $\text{C}_2\text{H}_5\text{OC}_6\text{H}_5$ are unsymmetrical ethers.

Nomenclature:

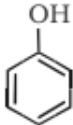
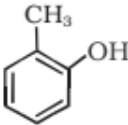
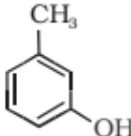
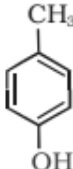
(a) Alcohols: The common name of an alcohol is derived from the common name of the alkyl group and adding the word alcohol to it. For example, CH_3OH is methyl alcohol. According to IUPAC system, the name of an alcohol is derived from the name of the alkane from which the alcohol is derived, by substituting 'e' of alkane with the suffix 'ol'.

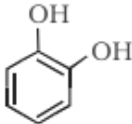
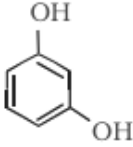
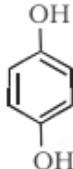
Compound	Common name	IUPAC name
$\text{CH}_3 - \text{OH}$	Methyl alcohol	Methanol
$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{OH}$	<i>n</i> -Propyl alcohol	Propan-1-ol
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_3 \\ \\ \text{OH} \end{array}$	Isopropyl alcohol	Propan-2-ol
$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{OH}$	<i>n</i> -Butyl alcohol	Butan-1-ol
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_3 \\ \\ \text{OH} \end{array}$	<i>sec</i> -Butyl alcohol	Butan-2-ol
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{OH} \\ \\ \text{CH}_3 \end{array}$	Isobutyl alcohol	2-Methylpropan-1-ol
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{OH} \\ \\ \text{CH}_3 \end{array}$	<i>tert</i> -Butyl alcohol	2-Methylpropan-2-ol
$\text{HO} - \text{H}_2\text{C} - \text{CH}_2 - \text{OH}$	Ethylene glycol	Ethane-1,2-diol
$\begin{array}{c} \text{CH}_2 - \text{CH} - \text{CH}_2 \\ \quad \quad \\ \text{OH} \quad \text{OH} \quad \text{OH} \end{array}$	Glycerol	Propane -1, 2, 3-triol

Cyclic alcohols are named using the prefix cyclo and considering the $-\text{OH}$ group attached to C-1.

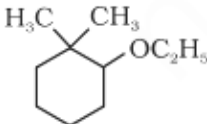


Phenols:

				
Common name	Phenol	<i>o</i> -Cresol	<i>m</i> -Cresol	<i>p</i> -Cresol
IUPAC name	Phenol	2-Methylphenol	3-Methylphenol	4-Methylphenol

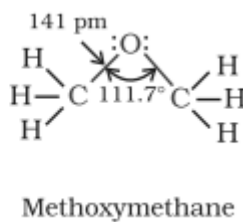
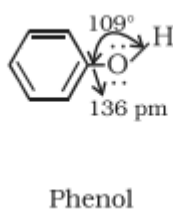
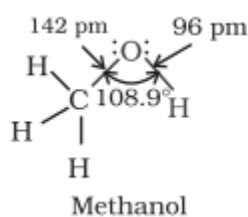
			
Common name	Catechol	Resorcinol	Hydroquinone or quinol
IUPAC name	Benzene-1,2-diol	Benzene-1,3-diol	Benzene-1,4-diol

(c) Ethers:

Compound	Common name	IUPAC name
CH_3OCH_3	Dimethyl ether	Methoxymethane
$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	Diethyl ether	Ethoxyethane
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3$	Methyl <i>n</i> -propyl ether	1-Methoxypropane
$\text{C}_6\text{H}_5\text{OCH}_3$	Methyl phenyl ether (Anisole)	Methoxybenzene (Anisole)
$\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_3$	Ethyl phenyl ether (Phenetole)	Ethoxybenzene
$\text{C}_6\text{H}_5\text{O}(\text{CH}_2)_6 - \text{CH}_3$	Heptyl phenyl ether	1-Phenoxyheptane
$\text{CH}_3\text{O}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$	Methyl isopropyl ether	2-Methoxypropane
$\text{C}_6\text{H}_5-\text{O}-\text{CH}_2-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$	Phenyl isopentyl ether	3- Methylbutoxybenzene
$\text{CH}_3-\text{O}-\text{CH}_2-\text{CH}_2-\text{OCH}_3$	—	1,2-Dimethoxyethane
	—	2-Ethoxy- -1,1-dimethylcyclohexane

Structures of Functional Groups:

In alcohols, the oxygen of the $-\text{OH}$ group is attached to carbon by a sigma (σ) bond formed by the overlap of a sp^3 hybridised orbital of carbon with a sp^3 hybridised orbital of oxygen.



The bond angle in alcohols is slightly less than the tetrahedral angle ($109^{\circ}-28'$). It is due to the repulsion between the unshared electron pairs of oxygen. In phenols, the $-\text{OH}$ group is attached to sp^2 hybridised carbon of an aromatic ring. The carbon–oxygen bond length (136 pm) in phenol is slightly less than that in methanol. This is due to

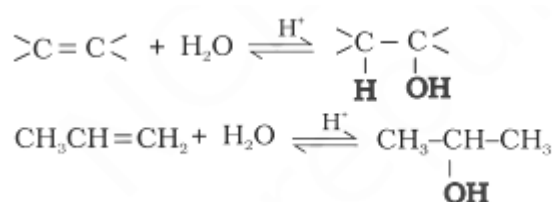
- (i) partial double bond character on account of the conjugation of unshared electron pair of oxygen with the aromatic ring and
- (ii) sp^2 hybridised state of carbon to which oxygen is attached.

In ethers, the four electron pairs, i.e., the two bond pairs and two lone pairs of electrons on oxygen are arranged approximately in a tetrahedral arrangement. The bond angle is slightly greater than the tetrahedral angle due to the repulsive interaction between the two bulky ($-\text{R}$) groups. The C–O bond length (141 pm) is almost the same as in alcohols.

Preparation of Alcohols:

1. From alkenes :

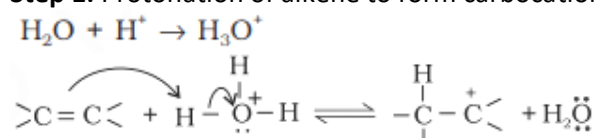
(i) By acid catalysed hydration: Alkenes react with water in the presence of acid as catalyst to form alcohols. In case of unsymmetrical alkenes, the addition reaction takes place in accordance with Markovnikov's rule.



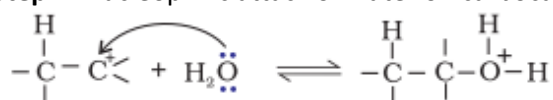
Mechanism

The mechanism of the reaction involves the following three steps:

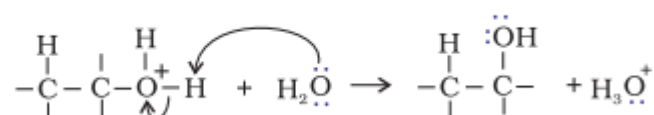
Step 1: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+ .



Step 2: Nucleophilic attack of water on carbocation.

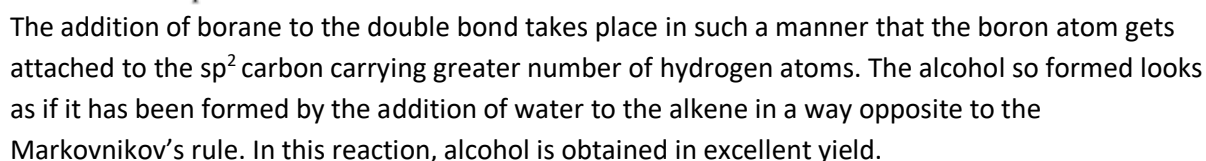


Step 3: Deprotonation to form an alcohol.

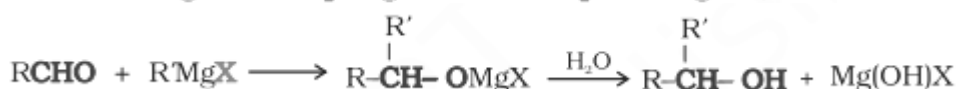
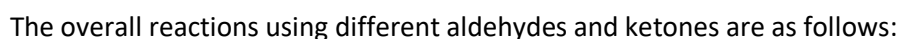
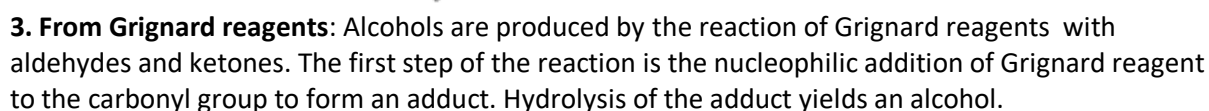
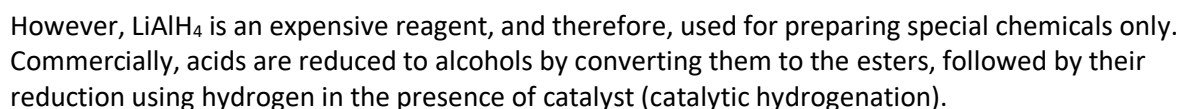
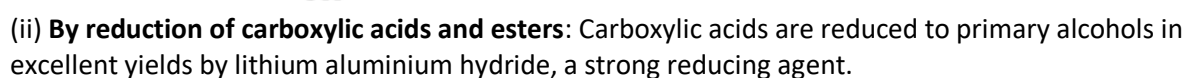


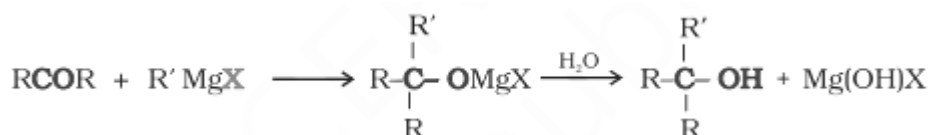
(ii) By hydroboration–oxidation:

Diborane (BH_3)₂ reacts with alkenes to give trialkyl boranes as addition product. This is oxidised to alcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide.



(i) **By reduction of aldehydes and ketones:** Aldehydes and ketones are reduced to the corresponding alcohols by addition of hydrogen in the presence of catalysts (catalytic hydrogenation). The usual catalyst is a finely divided metal such as platinum, palladium or nickel. It is also prepared by treating aldehydes and ketones with sodium borohydride (NaBH_4) or lithium aluminium hydride (LiAlH_4). Aldehydes yield primary alcohols whereas ketones give secondary alcohols.

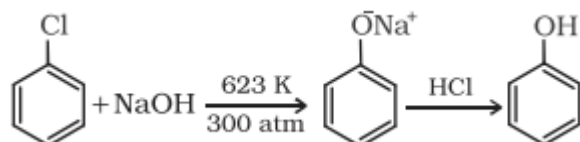




Preparation of Phenols:

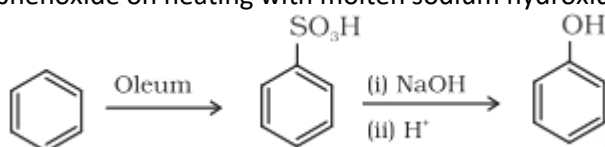
1. From haloarenes:

Chlorobenzene is fused with NaOH at 623K and 320 atmospheric pressure. Phenol is obtained by acidification of sodium phenoxide so produced



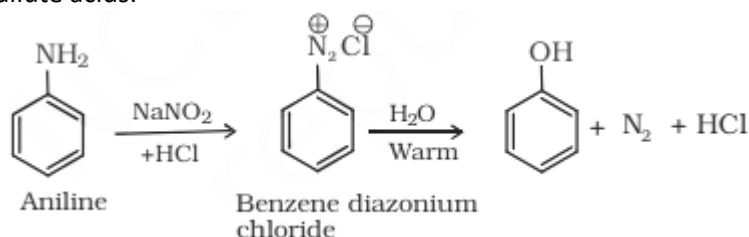
2. From benzenesulphonic acid:

Benzene is sulphonated with oleum and benzene sulphonic acid so formed is converted to sodium phenoxide on heating with molten sodium hydroxide. Acidification of the sodium salt gives phenol.



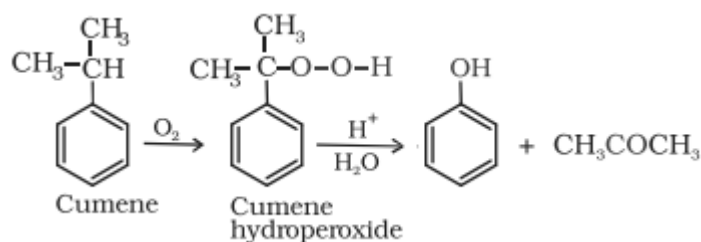
3. From diazonium salts:

A diazonium salt is formed by treating an aromatic primary amine with nitrous acid ($\text{NaNO}_2 + \text{HCl}$) at 273-278 K. Diazonium salts are hydrolysed to phenols by warming with water or by treating with dilute acids.



4. From cumene :

Phenol is manufactured from the hydrocarbon, cumene. Cumene (isopropylbenzene) is oxidised in the presence of air to cumene hydroperoxide. It is converted to phenol and acetone by treating it with dilute acid. Acetone, a by-product of this reaction, is also obtained in large quantities by this method.

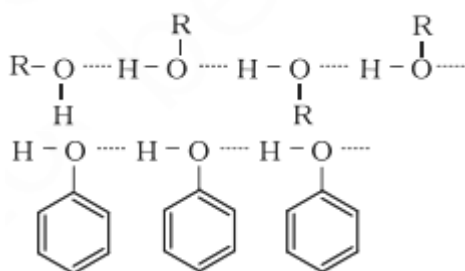


Physical Properties: Alcohols and phenols consist of two parts, an alkyl/aryl group and a hydroxyl group. The properties of alcohols and phenols are chiefly due to the hydroxyl group. The nature of alkyl and aryl groups simply modify these properties.

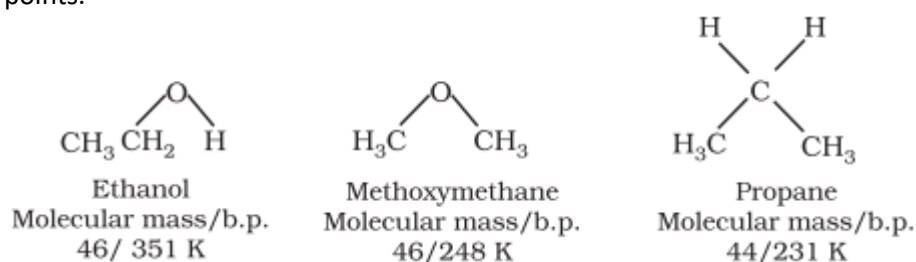
Boiling Points :

The boiling points of alcohols and phenols increase with increase in the number of carbon atoms (increase in van der Waals forces). In alcohols, the boiling points decrease with increase of branching in carbon chain (because of decrease in van der Waals forces with decrease in surface area).

The –OH group in alcohols and phenols is involved in intermolecular hydrogen bonding as shown below:



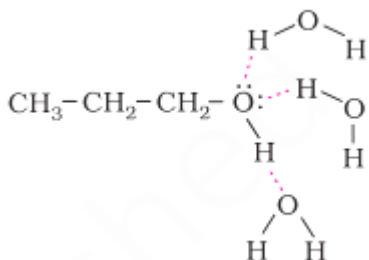
It is interesting to note that boiling points of alcohols and phenols are higher in comparison to other classes of compounds, namely hydrocarbons, ethers, haloalkanes and haloarenes of comparable molecular masses. For example, ethanol and propane have comparable molecular masses but their boiling points differ widely. The boiling point of methoxymethane is intermediate of the two boiling points.



The high boiling points of alcohols are mainly due to the presence of intermolecular hydrogen bonding in them which is lacking in ethers and hydrocarbons

Solubility:

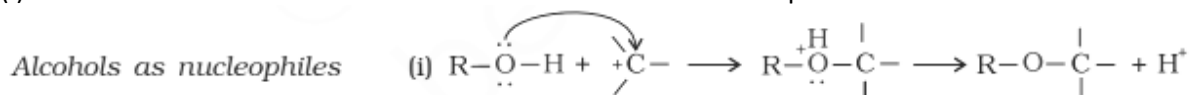
Solubility of alcohols and phenols in water is due to their ability to form hydrogen bonds with water molecules as shown. The solubility decreases with increase in size of alkyl/aryl (hydrophobic) groups. Several of the lower molecular mass alcohols are miscible with water in all proportions.



Chemical Reactions:

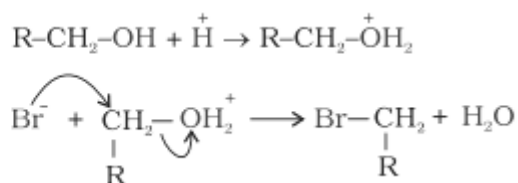
Alcohols are versatile compounds. They react both as nucleophiles and electrophiles.

(i) The bond between O–H is broken when alcohols react as nucleophiles.



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

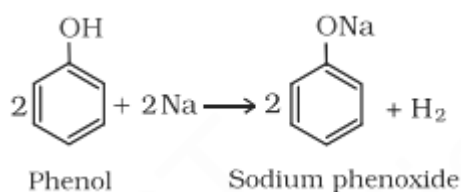
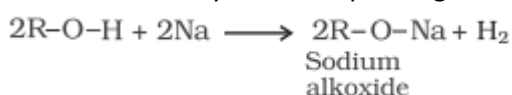
Protonated alcohols as electrophiles



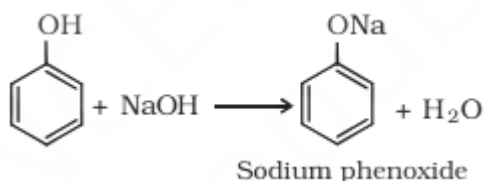
(a) Reactions involving cleavage of O–H bond:

1. Acidity of alcohols and phenols :

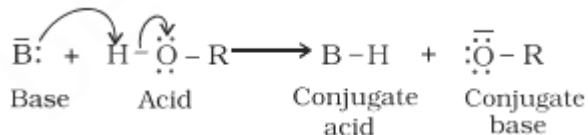
(i) **Reaction with metals:** Alcohols and phenols react with active metals such as sodium, potassium and aluminium to yield corresponding alkoxides/phenoxides and hydrogen.



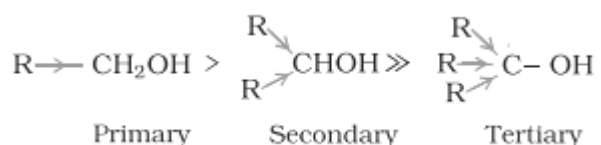
In addition to this, phenols react with aqueous sodium hydroxide to form sodium phenoxides.



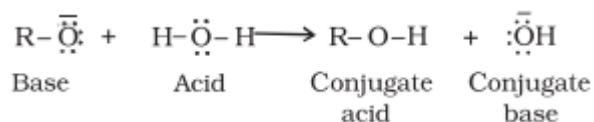
The above reactions show that alcohols and phenols are acidic in nature. In fact, alcohols and phenols are Brönsted acids i.e., they can donate a proton to a stronger base (B:).



(ii) **Acidity of alcohols:** The acidic character of alcohols is due to the polar nature of O–H bond. An electron-releasing group (–CH₃, –C₂H₅) increases electron density on oxygen tending to decrease the polarity of O–H bond. This decreases the acid strength. For this reason, the acid strength of alcohols decreases in the following order:



Alcohols are, however, weaker acids than water. This can be illustrated by the reaction of water with an alkoxide.

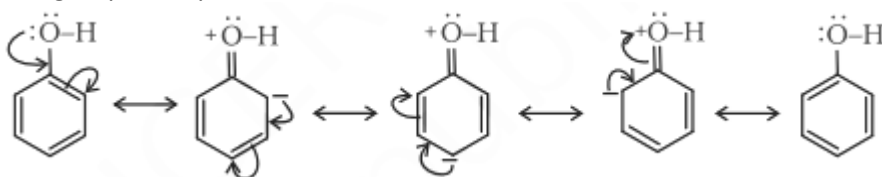


This reaction shows that water is a better proton donor (i.e., stronger acid) than alcohol. Also, in the above reaction, we note that an alkoxide ion is a better proton acceptor than hydroxide ion, which suggests that alkoxides are stronger bases (sodium ethoxide is a stronger base than sodium hydroxide).

Alcohols act as Brønsted bases as well. It is due to the presence of unshared electron pairs on oxygen, which makes them proton acceptors.

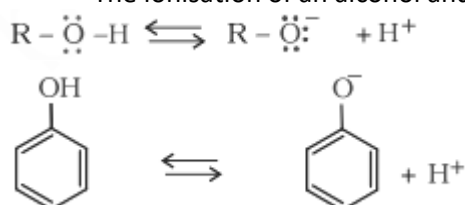
(iii) **Acidity of phenols:** The reactions of phenol with metals (e.g., sodium, aluminium) and sodium hydroxide indicate its acidic nature. The hydroxyl group, in phenol is directly attached to the sp²

hybridised carbon of benzene ring which acts as an electron withdrawing group. Due to this, the charge distribution in phenol molecule, as depicted in its resonance structures, causes the oxygen of –OH group to be positive.



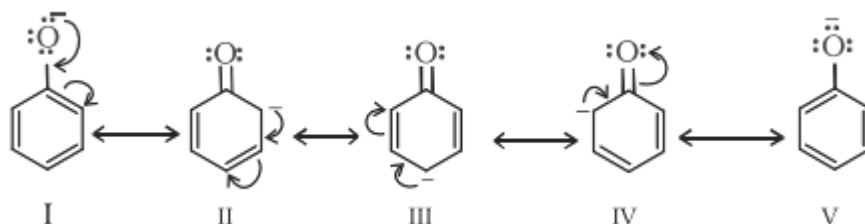
The reaction of phenol with aqueous sodium hydroxide indicates that phenols are stronger acids than alcohols and water. Let us examine how a compound in which hydroxyl group attached to an aromatic ring is more acidic than the one in which hydroxyl group is attached to an alkyl group.

The ionisation of an alcohol and a phenol takes place as follows:



Due to the higher electronegativity of sp^2 hybridised carbon of phenol to which –OH is attached, electron density decreases on oxygen. This increases the polarity of O–H bond and results in an increase in ionisation of phenols than that of alcohols.

Now let us examine the stabilities of alkoxide and phenoxide ions. In alkoxide ion, the negative charge is localised on oxygen while in phenoxide ion, the charge is delocalised. The delocalisation of negative charge (structures I-V) makes



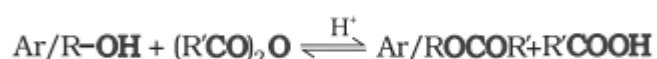
The delocalisation of negative charge (structures I-V) makes phenoxide ion more stable and favours the ionisation of phenol. Although there is also charge delocalisation in phenol, its resonance structures have charge separation due to which the phenol molecule is less stable than phenoxide ion.

In substituted phenols, the presence of electron withdrawing groups such as nitro group, enhances the acidic strength of phenol. This effect is more pronounced when such a group is present at ortho and para positions. It is due to the effective delocalisation of negative charge in phenoxide ion when substituent is at ortho or para position. On the other hand, electron releasing groups, such as alkyl groups, in general, do not favour the formation of phenoxide ion resulting in decrease in acid strength. Cresols, for example, are less acidic than phenol.

Compound	Formula	pK _a
<i>o</i> -Nitrophenol	<i>o</i> -O ₂ N-C ₆ H ₄ -OH	7.2
<i>m</i> -Nitrophenol	<i>m</i> -O ₂ N-C ₆ H ₄ -OH	8.3
<i>p</i> -Nitrophenol	<i>p</i> -O ₂ N-C ₆ H ₄ -OH	7.1
Phenol	C ₆ H ₅ -OH	10.0
<i>o</i> -Cresol	<i>o</i> -CH ₃ -C ₆ H ₄ -OH	10.2
<i>m</i> -Cresol	<i>m</i> -CH ₃ -C ₆ H ₄ -OH	10.1
<i>p</i> -Cresol	<i>p</i> -CH ₃ -C ₆ H ₄ -OH	10.2
Ethanol	C ₂ H ₅ OH	15.9

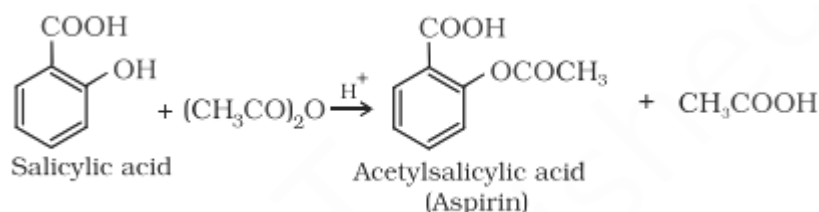
From the above data, you will note that phenol is million times more acidic than ethanol.

2. Esterification :Alcohols and phenols react with carboxylic acids, acid chlorides and acid anhydrides to form esters.



The reaction with carboxylic acid and acid anhydride is carried out in the presence of a small amount of concentrated sulphuric acid. The reaction is reversible, and therefore, water is removed as soon as it is formed. The reaction with acid chloride is carried out in the presence of a base (pyridine) so as to neutralise HCl which is formed during the reaction. It shifts the equilibrium to the right hand side. The introduction of acetyl (CH₃CO) group in alcohols or phenols is known as acetylation.

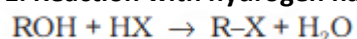
Acetylation of salicylic acid produces aspirin.



(b) Reactions involving cleavage of carbon – oxygen (C–O) bond in alcohols:

The reactions involving cleavage of C–O bond take place only in alcohols. Phenols show this type of reaction only with zinc.

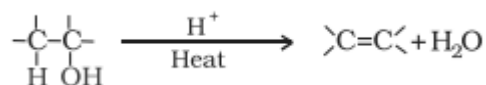
1. Reaction with hydrogen halides: Alcohols react with hydrogen halides to form alkyl halides.



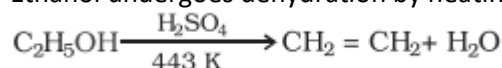
The difference in reactivity of three classes of alcohols with HCl distinguishes them from one another (Lucas test). Alcohols are soluble in Lucas reagent (conc. HCl and ZnCl₂) while their halides are immiscible and produce turbidity in solution. In case of tertiary alcohols, turbidity is produced immediately as they form the halides easily. Primary alcohols do not produce turbidity at room temperature.

2. Reaction with phosphorus trihalides: Alcohols are converted to alkyl bromides by reaction with phosphorus tribromide.

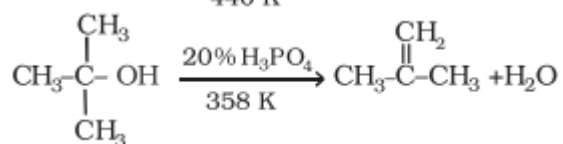
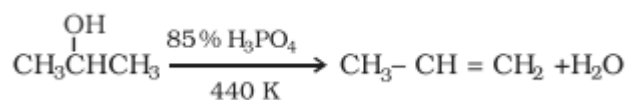
3. Dehydration: Alcohols undergo dehydration (removal of a molecule of water) to form alkenes on treating with a protic acid e.g., concentrated H_2SO_4 or H_3PO_4 , or catalysts such as anhydrous zinc chloride or alumina.



Ethanol undergoes dehydration by heating it with concentrated H_2SO_4 at 443 K.



Secondary and tertiary alcohols are dehydrated under milder conditions. For example

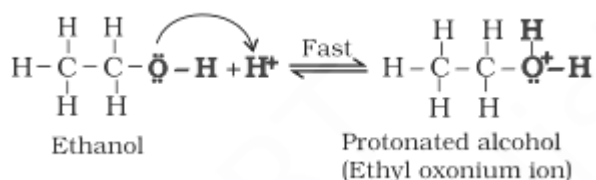


Thus, the relative ease of dehydration of alcohols follows the following order:

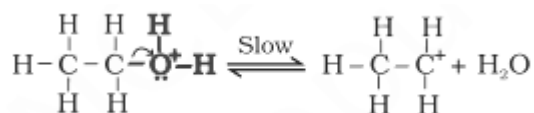
Tertiary > Secondary > Primary

The mechanism of dehydration of ethanol involves the following steps:

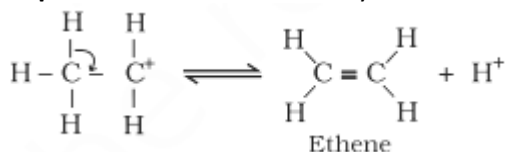
Step 1: Formation of protonated alcohol.



Step 2: Formation of carbocation: It is the slowest step and hence, the rate determining step of the reaction

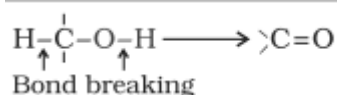


Step 3: Formation of ethene by elimination of a proton.

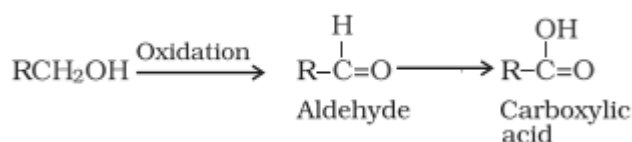


The acid used in step 1 is released in step 3. To drive the equilibrium to the right, ethene is removed as it is formed.

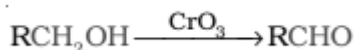
4. Oxidation: Oxidation of alcohols involves the formation of a carbon-oxygen double bond with cleavage of an O-H and C-H bonds.



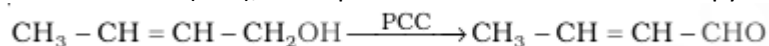
Such a cleavage and formation of bonds occur in oxidation reactions. These are also known as dehydrogenation reactions as these involve loss of dihydrogen from an alcohol molecule. Depending on the oxidising agent used, a primary alcohol is oxidised to an aldehyde which in turn is oxidised to a carboxylic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



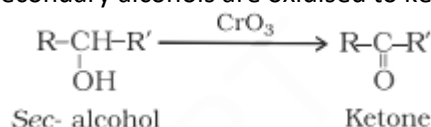
Strong oxidising agents such as acidified potassium permanganate are used for getting carboxylic acids from alcohols directly. CrO_3 in anhydrous medium is used as the oxidising agent for the isolation of aldehydes.



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

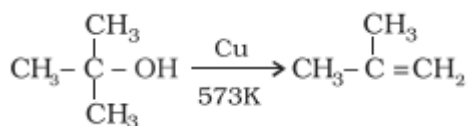
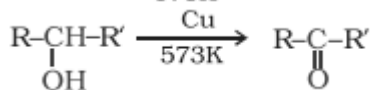
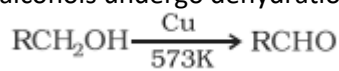


Secondary alcohols are oxidised to ketones by chromic anhydride (CrO_3).



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

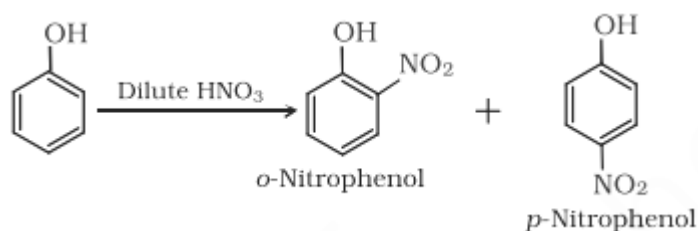
Dehydrogenation: When the vapours of a primary or a secondary alcohol are passed over heated copper at 573 K, dehydrogenation takes place and an aldehyde or a ketone is formed while tertiary alcohols undergo dehydration.



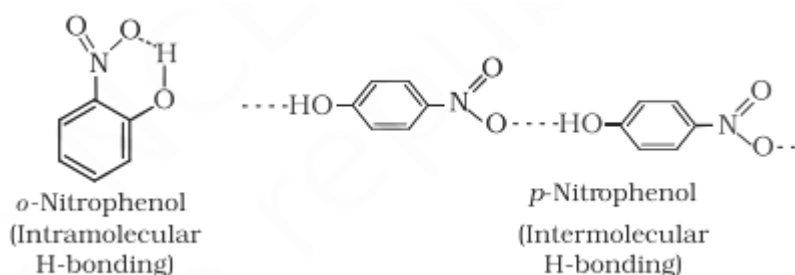
(c) Reactions of phenols:

1. Electrophilic aromatic substitution: In phenols, the reactions that take place on the aromatic ring are electrophilic substitution reactions. The $-\text{OH}$ group attached to the benzene ring activates it towards electrophilic substitution. Also, it directs the incoming group to ortho and para positions in the ring as these positions become electron rich due to the resonance effect caused by $-\text{OH}$ group.

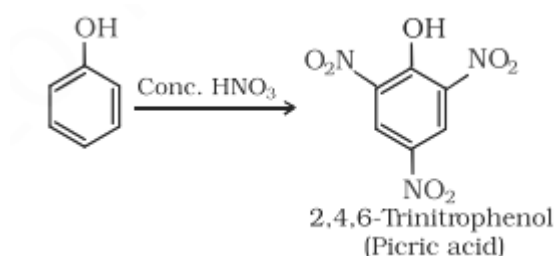
(i) Nitration: With dilute nitric acid at low temperature (298 K), phenol yields a mixture of ortho and para nitrophenols.



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

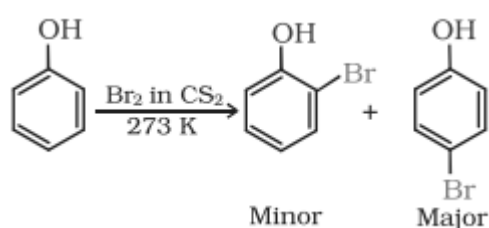


With concentrated nitric acid, phenol is converted to 2,4,6-trinitrophenol. The product is commonly known as picric acid. The yield of the reaction product is poor.



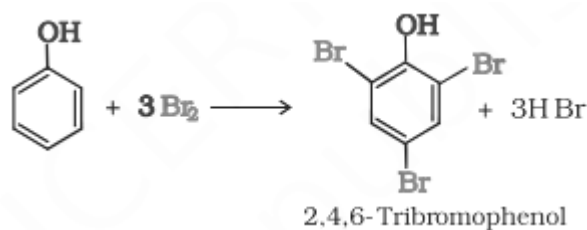
- Nowadays picric acid is prepared by treating phenol first with concentrated sulphuric acid which converts it to phenol-2,4-disulphonic acid, and then with concentrated nitric acid to get 2,4,6-trinitrophenol.

(ii) Halogenation: On treating phenol with bromine, different reaction products are formed under different experimental conditions. (a) When the reaction is carried out in solvents of low polarity such as CHCl_3 or CS_2 and at low temperature, monobromophenols are formed.

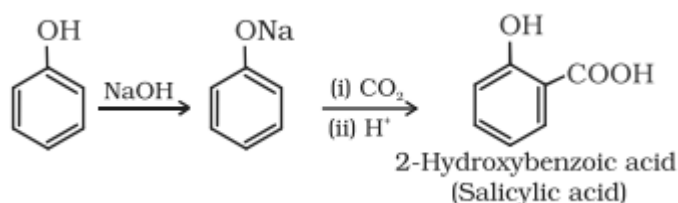


The usual halogenation of benzene takes place in the presence of a Lewis acid, such as FeBr_3 , which polarises the halogen molecule. In case of phenol, the polarisation of bromine molecule takes place even in the absence of Lewis acid. It is due to the highly activating effect of $-\text{OH}$ group attached to the benzene ring.

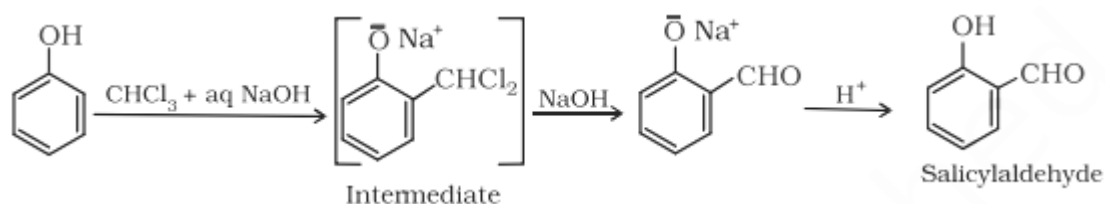
(b) When phenol is treated with bromine water, 2,4,6-tribromophenol is formed as white precipitate.



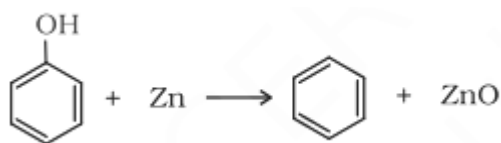
2. Kolbe's reaction: Phenoxide ion generated by treating phenol with sodium hydroxide is even more reactive than phenol towards electrophilic aromatic substitution. Hence, it undergoes electrophilic substitution with carbon dioxide, a weak electrophile. Ortho hydroxybenzoic acid is formed as the main reaction product.



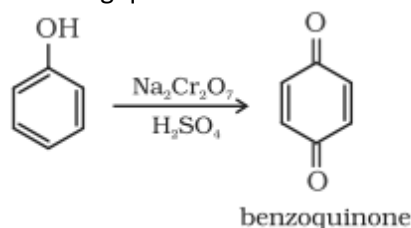
3. Reimer-Tiemann reaction : On treating phenol with chloroform in the presence of sodium hydroxide, a -CHO group is introduced at ortho position of benzene ring. This reaction is known as Reimer - Tiemann reaction. The intermediate substituted benzal chloride is hydrolysed in the presence of alkali to produce salicylaldehyde.



4. Reaction of phenol with zinc: dust Phenol is converted to benzene on heating with zinc dust.

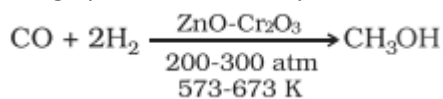


5. Oxidation: Oxidation of phenol with chromic acid produces a conjugated diketone known as benzoquinone. In the presence of air, phenols are slowly oxidised to dark coloured mixtures containing quinone.



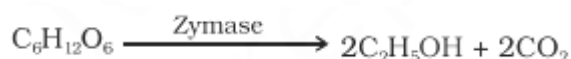
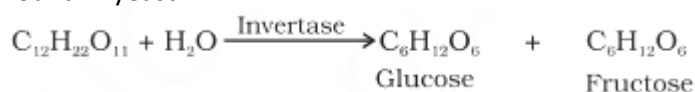
Some Commercially Important Alcohols

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



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

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



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

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

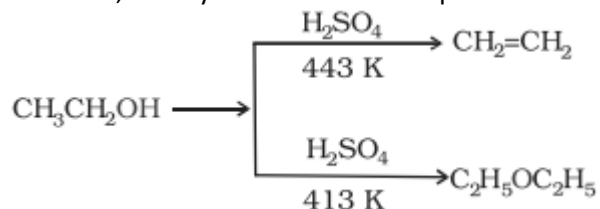
Ethanol is a colourless liquid with boiling point 351 K. It is used as a solvent in paint industry and in the preparation of a number of carbon compounds. The commercial alcohol is made unfit for drinking by mixing in it some copper sulphate (to give it a colour) and pyridine (a foul smelling liquid).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

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

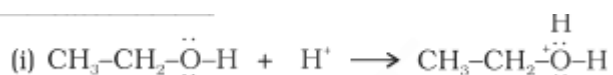
Ethers:

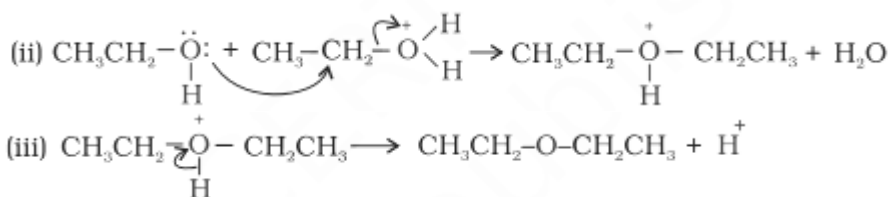
Preparation of Ethers:

1. By dehydration of alcohols: Alcohols undergo dehydration in the presence of protic acids (H_2SO_4 , H_3PO_4). The formation of the reaction product, alkene or ether depends on the reaction conditions. For example, ethanol is dehydrated to ethene in the presence of sulphuric acid at 443 K. At 413 K, ethoxyethane is the main product.



The formation of ether is a nucleophilic bimolecular reaction ($\text{S}_\text{N}2$) involving the attack of alcohol molecule on a protonated alcohol, as indicated below:



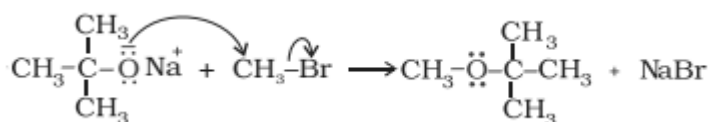


The method is suitable for the preparation of ethers having primary alkyl groups only. The alkyl group should be unhindered and the temperature be kept low. Otherwise the reaction favours the formation of alkene. The reaction follows $\text{S}_{\text{N}}1$ pathway when the alcohol is secondary or tertiary. However, the dehydration of secondary and tertiary alcohols to give corresponding ethers is unsuccessful as elimination competes over substitution and as a consequence, alkenes are easily formed.

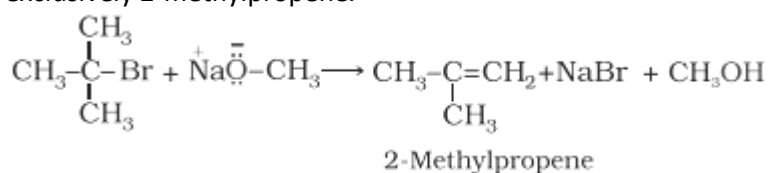
2. Williamson synthesis: It is an important laboratory method for the preparation of symmetrical and unsymmetrical ethers. In this method, an alkyl halide is allowed to react with sodium alkoxide.



Ethers containing substituted alkyl groups (secondary or tertiary) may also be prepared by this method. The reaction involves $\text{S}_{\text{N}}2$ attack of an alkoxide ion on primary alkyl halide.



Better results are obtained if the alkyl halide is primary. In case of secondary and tertiary alkyl halides, elimination competes over substitution. If a tertiary alkyl halide is used, an alkene is the only reaction product and no ether is formed. For example, the reaction of CH_3ONa with $(\text{CH}_3)_3\text{C}-\text{Br}$ gives exclusively 2-methylpropene.



It is because alkoxides are not only nucleophiles but strong bases as well. They react with alkyl halides leading to elimination reactions.

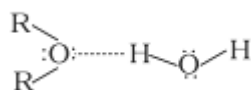
Physical Properties:

The C-O bonds in ethers are polar and thus, ethers have a net dipole moment. The weak polarity of ethers do not appreciably affect their boiling points which are comparable to those of the alkanes of comparable molecular masses but are much lower than the boiling points of alcohols as shown in the following cases:

Formula	$\text{CH}_3(\text{CH}_2)_3\text{CH}_3$ n-Pentane	$\text{C}_2\text{H}_5-\text{O}-\text{C}_2\text{H}_5$ Ethoxyethane	$\text{CH}_3(\text{CH}_2)_3-\text{OH}$ Butan-1-ol
b.p./K	309.1	307.6	390

The large difference in boiling points of alcohols and ethers is due to the presence of hydrogen bonding in alcohols.

The miscibility of ethers with water resembles those of alcohols of the same molecular mass. Both ethoxyethane and butan-1-ol are miscible to almost the same extent i.e., 7.5 and 9 g per 100 mL water, respectively while pentane is essentially immiscible with water. This is due to the fact that just like alcohols, oxygen of ether can also form hydrogen bonds with water molecule as shown.



Chemical Reactions:

1. Cleavage of C-O bond in ethers

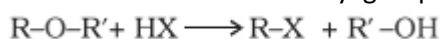
Ethers are the least reactive of the functional groups. The cleavage of C-O bond in ethers takes place under drastic conditions with excess of hydrogen halides. The reaction of dialkyl ether gives two alkyl halide molecules.



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



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

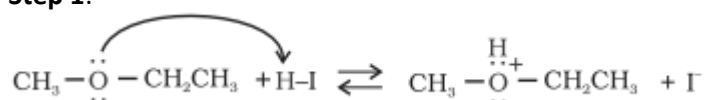


The order of reactivity of hydrogen halides is as follows: $HI > HBr > HCl$. The cleavage of ethers takes place with concentrated HI or HBr at high temperature.

Mechanism:

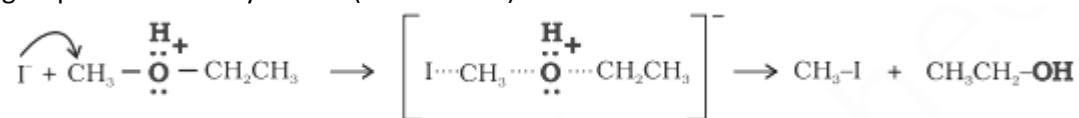
The reaction of an ether with concentrated HI starts with protonation of ether molecule.

Step 1:



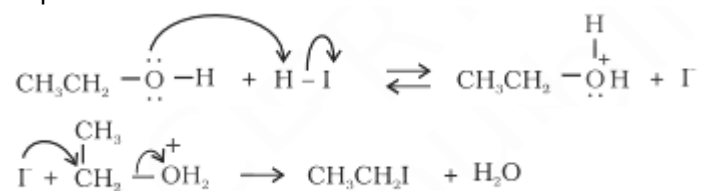
The reaction takes place with HBr or HI because these reagents are sufficiently acidic

Step 2: Iodide is a good nucleophile. It attacks the least substituted carbon of the oxonium ion formed in step 1 and displaces an alcohol molecule by S_N2 mechanism. Thus, in the cleavage of mixed ethers with two different alkyl groups, the alcohol and alkyl iodide formed, depend on the nature of alkyl groups. When primary or secondary alkyl groups are present, it is the lower alkyl group that forms alkyl iodide (S_N2 reaction).

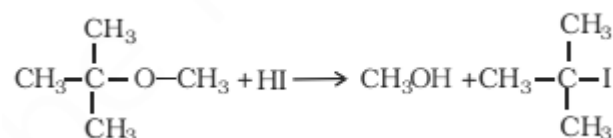


When HI is in excess and the reaction is carried out at high temperature, ethanol reacts with another molecule of HI and is converted to ethyl iodide.

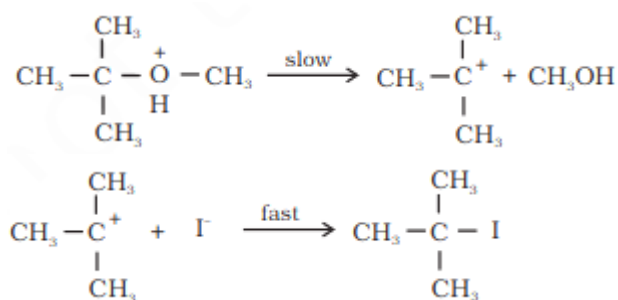
Step 3:



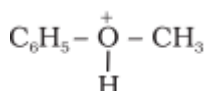
However, when one of the alkyl group is a tertiary group, the halide formed is a tertiary halide.



It is because in step- 2 of the reaction, the departure of leaving group ($HO-CH_3$) creates a more stable carbocation $[(CH_3)_3C^+]$, and the reaction follows S_N1 mechanism.



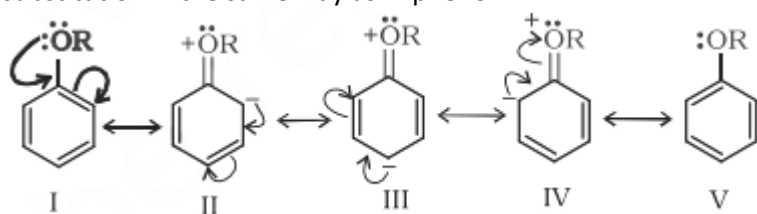
In case of anisole, methylphenyl oxonium ion, is formed by protonation of ether



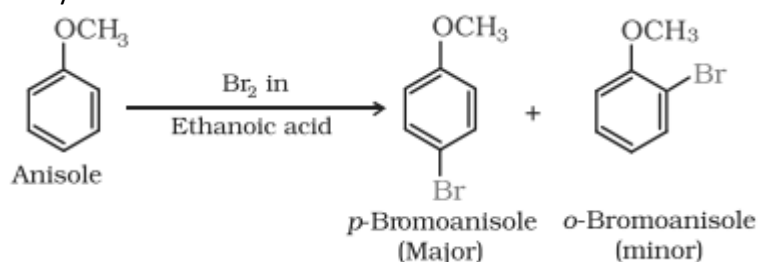
The bond between O-CH₃ is weaker than the bond between O-C₆H₅ because the carbon of phenyl group is sp² hybridised and there is a partial double bond character. Therefore the attack by I⁻ ion breaks O-CH₃ bond to form CH₃ I. Phenols do not react further to give halides because the sp² hybridised carbon of phenol cannot undergo nucleophilic substitution reaction needed for conversion to the halide.

2. Electrophilic substitution:

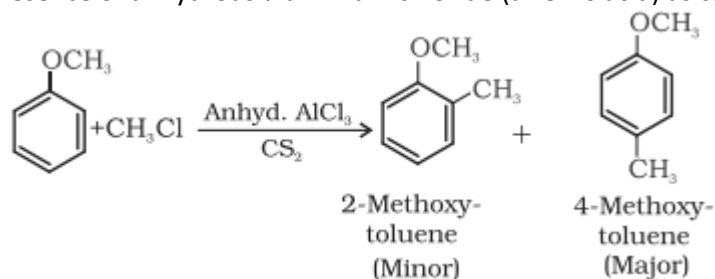
The alkoxy group (-OR) is ortho, para directing and activates the aromatic ring towards electrophilic substitution in the same way as in phenol.

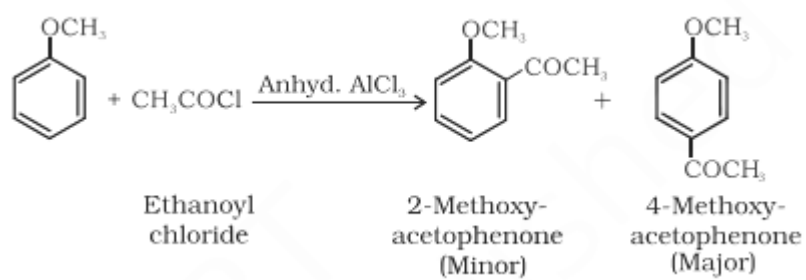


(i) Halogenation: Phenylalkyl ethers undergo usual halogenation in the benzene ring, e.g., anisole undergoes bromination with bromine in ethanoic acid even in the absence of iron (III) bromide catalyst. It is due to the activation of benzene ring by the methoxy group. Para isomer is obtained in 90% yield.



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





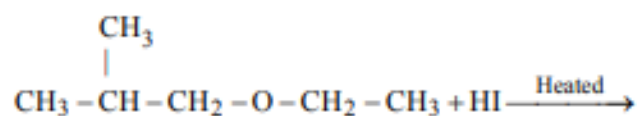
(iii) Nitration: Anisole reacts with a mixture of concentrated sulphuric and nitric acids to yield a mixture of ortho and para nitroanisole.



MCQ:

1. In the reaction:

[CBSE-PMT 2007]

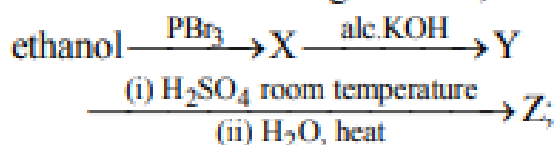


Which of the following compounds will be formed?

- (a) $\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_3 + \text{CH}_3\text{CH}_2\text{OH} \\ | \\ \text{CH}_3 \end{array}$
- (b) $\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2\text{OH} + \text{CH}_3\text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$
- (c) $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{CH} - \text{CH}_2\text{OH} + \text{CH}_3 - \text{CH}_2 - \text{I} \end{array}$
- (d) $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{I} + \text{CH}_3\text{CH}_2\text{OH} \end{array}$

2. Consider the following reaction,

[CBSE-PMT 2009]



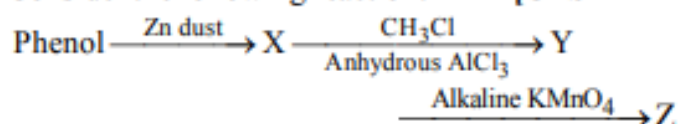
the product Z is:

- (a) $\text{CH}_3\text{CH}_2 - \text{O} - \text{CH}_2 - \text{CH}_3$
(b) $\text{CH}_3 - \text{CH}_2 - \text{O} - \text{SO}_3\text{H}$
(c) $\text{CH}_3\text{CH}_2\text{OH}$
(d) $\text{CH}_2 = \text{CH}_2$

3. $\text{H}_2\text{COH} \cdot \text{CH}_2\text{OH}$ on heating with periodic acid gives: [CBSE-PMT 2009]

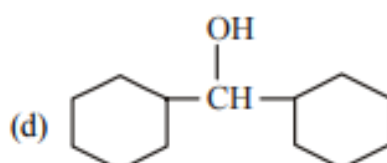
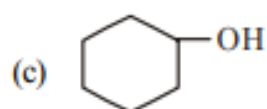
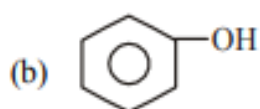
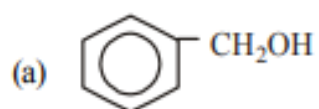
- (a) 2HCOOH (b) $\begin{array}{c} \text{CHO} \\ | \\ \text{CHO} \end{array}$
- (c) $2 \begin{array}{c} \text{H} \\ \diagdown \\ \text{C} = \text{O} \\ \diagup \\ \text{H} \end{array}$ (d) 2CO_2

4. Consider the following reaction: [CBSE-PMT 2009]



The product Z is:

- (a) benzaldehyde (b) benzoic acid
(c) benzene (d) toluene
5. Which one of the following compounds has the most acidic nature? [CBSE-PMT 2010]



6. Among the following four compounds [CBSE-PMT 2010]

- (i) phenol (ii) methylphenol
(iii) meta-nitrophenol (iv) para-nitrophenol

the acidity order is :

- (a) ii > i > iii > iv (b) iv > iii > i > ii
(c) iii > iv > i > ii (d) i > iv > iii > ii

7. When glycerol is treated with excess of HI, it produces:

[CBSE-PMT 2010]

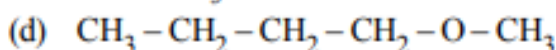
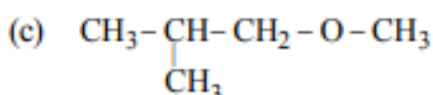
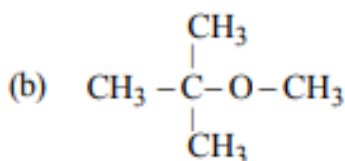
- (a) glycerol triiodide (b) 2-iodopropane
(c) allyl iodide (d) propene

8. Which of the following compounds can be used as antifreeze in automobile radiators ? [CBSE-PMT 2012]

- (a) Methyl alcohol (b) Glycol
(c) Nitrophenol (d) Ethyl alcohol

9. Among the following ethers, which one will produce methyl alcohol on treatment with hot concentrated HI?

- (a) $\text{CH}_3 - \text{CH}_2 - \underset{\text{CH}_3}{\text{CH}} - \text{O} - \text{CH}_3$ [NEET 2013]



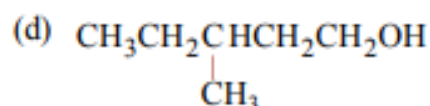
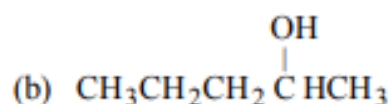
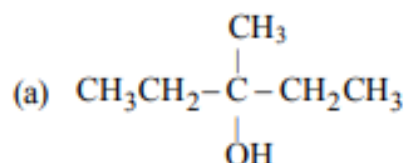
10. An ether is more volatile than an alcohol having the same molecular formula. This is due to [AIEEE 2003]

- (a) alcohols having resonance structures
(b) inter-molecular hydrogen bonding in ethers

(c) inter-molecular hydrogen bonding in alcohols

(d) dipolar character of ethers

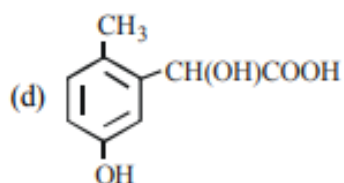
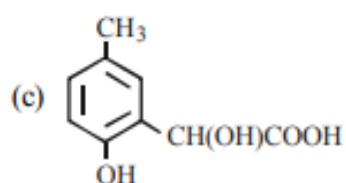
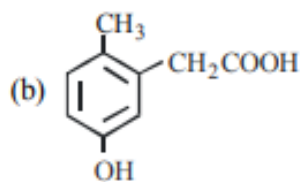
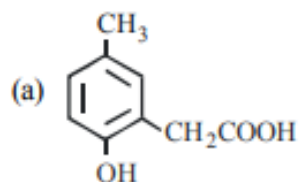
11. During dehydration of alcohols to alkenes by heating with conc. H_2SO_4 the initiation step is [AIEEE 2003]
- formation of carbocation
 - elimination of water
 - formation of an ester
 - protonation of alcohol molecule
12. Among the following compounds which can be dehydrated very easily is [AIEEE 2004]



13. The best reagent to convert pent-3-en-2-ol into pent-3-en-2-one is [AIEEE 2005]
- pyridinium chloro-chromate
 - chromic anhydride in glacial acetic acid
 - acidic dichromate
 - acidic permanganate

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

[AIEEE 2005]



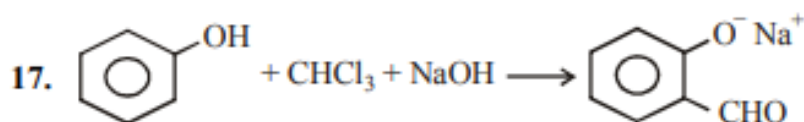
15. Phenyl magnesium bromide reacts with methanol to give

[AIEEE 2006]

- (a) a mixture of toluene and $\text{Mg}(\text{OH})\text{Br}$
- (b) a mixture of phenol and $\text{Mg}(\text{Me})\text{Br}$
- (c) a mixture of anisole and $\text{Mg}(\text{OH})\text{Br}$
- (d) a mixture of benzene and $\text{Mg}(\text{OMe})\text{Br}$

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

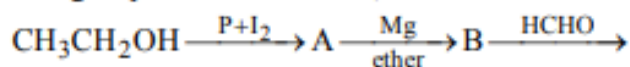
- (a) $\text{CH}_3 - \overset{\text{CH}_3}{\underset{|}{\text{CH}}} \text{CH}_2\text{OH}$
 (b) PhCHOHCH_3
 (c) $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$
 (d) $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{OH}$



The electrophile involved in the above reaction is

[AIEEE 2006]

- (a) trichloromethyl anion (CCl_3^-)
 (b) formyl cation (CHO^+)
 (c) dichloromethyl cation (CHCl_2^+)
 (d) dichlorocarbene ($:\text{CCl}_2$)
18. In the following sequence of reactions,



the compound D is

[AIEEE 2007]

- (a) propanal (b) butanal
 (c) *n*-butyl alcohol (d) *n*-propyl alcohol.
19. Phenol, when it first reacts with concentrated sulphuric acid and then with concentrated nitric acid, gives [AIEEE 2008]
- (a) 2, 4, 6-trinitrobenzene (b) *o*-nitrophenol
 (c) *p*-nitrophenol (d) nitrobenzene

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

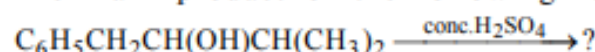
- (a) salicylaldehyde (b) salicylic acid
(c) phthalic acid (d) benzoic acid

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

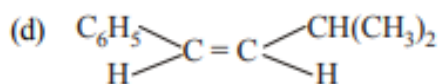
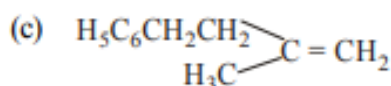
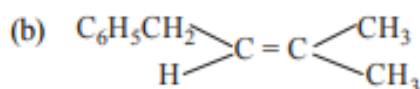
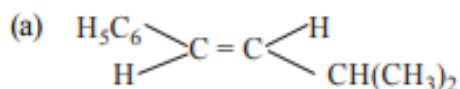
[AIEEE 2010]

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

22. The main product of the following reaction is



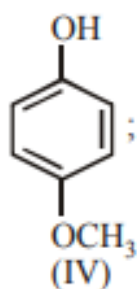
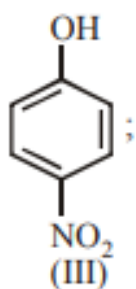
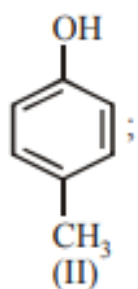
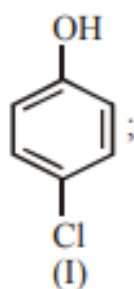
[AIEEE 2010]




23. The correct order of acid strength of the following compounds : [AIEEE 2011 RS]





- | | |
|---|---|
| (A) Phenol | (B) <i>p</i> -Cresol |
| (C) <i>m</i> -Nitrophenol | (D) <i>p</i> -Nitrophenol |
| (a) $\text{D} > \text{C} > \text{A} > \text{B}$ | (b) $\text{B} > \text{D} > \text{A} > \text{C}$ |
| (c) $\text{A} > \text{B} > \text{D} > \text{C}$ | (d) $\text{C} > \text{B} > \text{A} > \text{D}$ |

24. Consider the following reaction :
 $\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{SO}_4 \longrightarrow \text{Product}$
 Among the following, which one cannot be formed as a product under any conditions ? [AIEEE 2011 RS]
- (a) Ethylene
 (b) Acetylene
 (c) Diethyl ether
 (d) Ethyl-hydrogen sulphate
25. Phenol is heated with a solution of mixture of KBr and KBrO_3 . The major product obtained in the above reaction is : [AIEEE 2011]
- (a) 2-Bromophenol (b) 3-Bromophenol
 (c) 4-Bromophenol (d) 2, 4, 6-Tribromophenol
26. Which of the following reagents may be used to distinguish between phenol and benzoic acid? [AIEEE 2011]
- (a) Aqueous NaOH (b) Tollen's reagent
 (c) Molisch reagent (d) Neutral FeCl_3
27. Arrange the following compounds in order of decreasing acidity : [JEE M 2013]

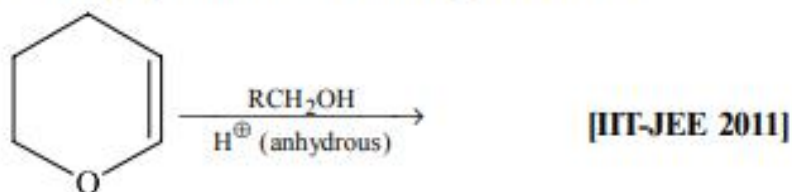


- (a) $\text{II} > \text{IV} > \text{I} > \text{III}$ (b) $\text{I} > \text{II} > \text{III} > \text{IV}$
 (c) $\text{III} > \text{I} > \text{II} > \text{IV}$ (d) $\text{IV} > \text{III} > \text{I} > \text{II}$

28. In the reaction  $\xrightarrow{\text{HBr}}$ the products are

- (a)  OCH_3 and H_2 [IIT-JEE 2010]
(b)  Br and CH_3Br
(c)  Br and CH_3OH
(d)  OH and CH_3Br

29. The major product of the following reaction is



- (a) a hemiacetal (b) an acetal
(c) an ether (d) an ester

