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CHAPTER

alcohols, phenols and ethers

- **Alcohols** are compounds of the general formula ROH where R is any alkyl or substituted alkyl group.
- An alcohol is classified as primary, secondary or tertiary according to the kind of carbon that bears the **OH group**.
- Aliphatic hydroxy compounds in which the hydroxyl group is linked to an aliphatic carbon chain are called **aliphatic alcohols**.
- Aromatic hydroxy compounds in which the hydroxyl group is linked to the side chain of an aromatic hydrocarbon are called **aromatic alcohols**.
- An alcohol molecule is dipolar in nature with the oxygen carrying a partial negative charge (δ^-) and carbon and hydrogen each carrying a partial positive charge (δ^+).
- Alcohols are further classified as **monohydric**, **dihydric**, **trihydric** and **polyhydric** according as their molecules contain one, two or three or many hydroxyl groups respectively.
- Characteristic or functional groups of primary, secondary and tertiary alcohols are – CH_2OH, > CHOH and $\geq C - OH$ respectively.
- The general formula of monohydric alcohols is $\mathbf{C_nH_{2n+1}OH}$ where $n = 1, 2, 3$ ... etc. or ROH where R is any alkyl group.
- According to common system of nomenclature, monohydric alcohols are called **alkyl alcohols**.
- According to IUPAC system, the parent structure with the longest continuous carbon chain that contains the OH group is selected.
- The carbon atom carrying the OH group gets the smallest number. The positions of other groups attached to the parent chain are indicated by suitable numbers.
- The general formula of dihydric alcohols is $(CH_2)_n(OH)_2$ where $n = 2, 3, 4,$ ... etc.
- Dihydric alcohols are also known as **glycols** because of their sweet taste.
- In the IUPAC system, glycols are named as diols and their class name is **alkane diols**.
- In IUPAC system, trihydric alcohols are called **alkane triols**.
- Alcohols show increase in boiling point with increasing carbon number and decrease in boiling point with branching. [Reason: Alcohols like water are associated liquid and their abnormally high boiling points are due to the greater energy needed to break the hydrogen bonds that holds the molecules together].
- At ordinary temperature, lower members of alcohols are colourless liquids with distinct smell.

- Higher members of alcohols are colourless, odourless, waxy solids.
- Amongst isomeric alcohols, the boiling points decrease with branching due to corresponding decrease in surface area. *i.e.* boiling points decrease in the order primary > secondary > tertiary.
- The lower alcohols are highly soluble in water due to the formation of hydrogen bonds between alcohol and water molecules.
- The solubility of alcohols decreases with the increase in molecular mass of the alcohol.
- Amongst isomeric alcohol, the solubility increases with branching. This is due to the reason that as the branching increases, the surface area of the non-polar hydrocarbon part decreases and the solubility increases.
- Lower alcohols form solid derivatives with metallic salts in which alcohol molecules show **solvation phenomenon**.
- Alcohols containing four or more carbon atoms exhibit chain isomerism due to difference in the nature of the carbon chain attached to the hydroxyl group.
- Alcohols containing three or more carbon atoms show position isomerism due to difference in the position of the hydroxyl group.
- Monohydric alcohols containing two or more carbon atoms show functional isomerism with ethers.
- Monohydric alcohols containing chiral carbon atoms exhibit enantiomers.
- Ethanol and methoxy methane are **functional isomers**.
- Alcohols are produced when haloalkanes (alkyl halides) are heated with aqueous sodium or potassium hydroxide or moist silver oxide.
- Reactive alkenes directly add to a molecule of water in the presence of mineral acid as a catalyst to form alcohols. The addition of water takes place in accordance with the Markownikoff's rule.
- In **hydroboration-oxidation** reaction, alkene is treated with diborane followed by treatment with water in the presence of H_2O_2 when alcohols is formed.
- Alkenes react with mercuric acetate, $(CH_3COO)_2Hg$ to form adducts which upon reduction with $NaBH_4$ in basic medium give alcohols. This two-step process is called oxymercuration-reduction or oxymercuration-demercuration and gives alcohols corresponding to Markownikoff's addition of water to alkenes.
- The reduction of aldehydes, ketones and esters with sodium and alcohol is commonly known as **Bouveault-Blanc reduction**.
- Grignard reagents react with aldehydes, ketones and esters to form addition products which upon decomposition with water or preferably with dilute HCl or dilute H_2SO_4 give alcohols.
- The process of breaking down large molecules into simpler ones in the presence of enzymes is called **fermentation**.
- Alcohols on heating with conc. H_2SO_4 at 435-445 K or phosphoric acid at 495-500 K are converted into alkenes on dehydration.
- The acidic character of alcohols is due to the electronegative oxygen atom which withdraws the electrons of the O – H bond towards itself.

- Alcohols are weak acids ($K_a = 1 \times 10^{-16} - 10^{-18}$) even weaker than water ($K_w = 1 \times 10^{-14}$).
- Electron releasing inductive effect of the alkyl group makes the alcohols weaker acids than water.
- The acidic strength of alcohols follows the order : primary > secondary > tertiary.
- In esterification reaction, the order of reactivity of alcohols follows the order $CH_3OH > CH_3CH_2OH > (CH_3)_2CHOH > (CH_3)_3COH$ and that of carboxylic acid follows the order $HCOOH > CH_3COOH > (CH_3)_2CHCOOH > (CH_3)_3CCOOH$.
- Both alcohols and phenols react with Grignard reagents to form hydrocarbons. This reaction is called **Zerewitinoff's active hydrogen determination**.
- Strong bases like metal hydrides and metal amides react with alcohol to give H_2 and NH_3 respectively.
- The order of reactivity of alcohols towards HX is 3° > 2° > 1°.
- The order of reactivity of alcohols in the reactions involving the cleavage of C – OH bond follows the sequence : tertiary > secondary > primary.
- The order of reactivity of halogen acids with alcohols follows the sequence :

  HI > HBr > HCl.

  [I^- is a better nucleophile than Br^- which in turn is better than Cl^- ion].
- The order of reactivity of alcohols differ widely in ease of dehydration. Ease of dehydration of alcohols - 3° > 2° > 1°.
- Medically ethanol is classified as a hypnotic (sleep producer), it is less toxic than other alcohols.
- Nearly all the ethanol used is a mixture of 95% alcohol and 5% water.
- The least reactive of the hydrogen halides, HCl requires the presence of anhydrous zinc chloride for reaction with primary and secondary alcohols.
- No catalyst is needed in the reactions of HCl with tertiary alcohols.
- The dehydration of 2° and 3° alcohols occur in accordance with the **Saytzeff rule** *i.e.* the more highly substituted alkene is always the major product.
- If the major product obtained due to the dehydration of alcohols in accordance with Saytzeff's rule is capable of showing *cis-trans* isomerism, then it is always the *trans*-product which predominates.
- The oxidation of an alcohol involves the loss of one or more hydrogens (α-hydrogens) from the carbon bearing the – OH group.
- A primary alcohol contains two α-hydrogens and can either lose one of them to form an aldehyde or both of them to form a carboxylic acid.
- A secondary alcohol can lose its only α-hydrogen to form a ketone.
- A tertiary alcohol contains no α-hydrogen and is not oxidised.
- One of the best and most convenient reagent used for the conversion of primary alcohols to aldehydes is **pyridinium chlorochromate ($C_5H_5NH^+CrO_3Cl^-$)**.

- **Victor Meyer** test is based on the different behaviour of primary, secondary and tertiary nitroalkanes towards nitrous acid.
  (a) Primary alcohols produce a blood red colour.
  (b) Secondary alcohols produce blue colour.
  (c) Tertiary alcohols produce no colour.

Primary	**Secondary**	**Tertiary**
RCH_2OH $P/I_2 \Big\downarrow HI$ RCH_2I $\Big\downarrow AgNO_2$ RCH_2NO_2 $\Big\downarrow HONO$ $\begin{matrix}R-C-NO_2\\ \Vert \\ NOH\end{matrix}$ Nitrolic acid $\Big\downarrow NaOH$ Blood red colour	$\begin{matrix}R\\R\end{matrix}\!\!>CHOH$ $P/I_2 \Big\downarrow HI$ $\begin{matrix}R\\R\end{matrix}\!\!>CHI$ $\Big\downarrow AgNO_2$ $\begin{matrix}R\\R\end{matrix}\!\!>CHNO_2$ $\Big\downarrow HONO$ $\begin{matrix}R\\R\end{matrix}\!\!>\begin{matrix}C-NO_2\\ \vert \\ NO\end{matrix}$ Pseudo nitrol $\Big\downarrow NaOH$ Blue colour	$\begin{matrix}R\\R\\R\end{matrix}\!\!>C-OH$ $\Big\downarrow HI$ $\begin{matrix}R\\R\\R\end{matrix}\!\!>C-I$ $\Big\downarrow AgNO_2$ $\begin{matrix}R\\R\\R\end{matrix}\!\!>C-NO_2$ $\Big\downarrow HONO$ no reaction $\Big\downarrow NaOH$ Colourless

- **Dichromate test :**

Primary alcohol	**Secondary alcohol**	**Tertiary alcohol**
$R-CH_2OH$ $[O]\Big\downarrow \begin{matrix}Na_2Cr_2O_7\\ H_2SO_4\end{matrix}$ $\begin{matrix}O\\ \Vert \\ R-C-H\end{matrix}$ aldehyde $[O]\Big\downarrow \begin{matrix}Na_2Cr_2O_7\\ H_2SO_4\end{matrix}$ $\begin{matrix}O\\ \Vert \\ R-C-OH\end{matrix}$ Acid (orange solution becomes green)	$\begin{matrix}R\\ \vert \\ R-C-OH\\ \vert \\ H\end{matrix}$ $[O]\Big\downarrow \begin{matrix}Na_2Cr_2O_7\\ H_2SO_4\end{matrix}$ $\begin{matrix}R\\ \vert \\ R-C=O\end{matrix}$ Ketone (orange solution becomes green)	$\begin{matrix}R\\ \vert \\ R-C-OH\\ \vert \\ R\end{matrix}$ $[O]\Big\downarrow \begin{matrix}Na_2Cr_2O_7\\ H_2SO_4\end{matrix}$ No reaction (solution remains orange)

- Lucas reagent is a solution of HCl with $ZnCl_2$. With Lucas reagent
  Primary alcohol – no cloudiness
  Secondary alcohol – cloudiness in 5 minutes
  Tertiary alcohol – cloudiness immediately

- **Methanol** is also called wood spirit since originally it was obtained by the destructive distillation of wood.
- Drinking of methyl alcohol causes blindness.
- Denatured alcohol is commonly known as **methylated spirit**.
- **Methanol** is used as an antifreeze for automobile radiators.
- **Ethanol** is used as power alcohol- a mixture of 20% absolute alcohol and 80% petrol (gasoline) with benzene or tetralin as cosolvent.
- **Methanol** is used for the manufacture of formaldehyde which is used in the manufacture of formaldehyde resins such as manufacture of bakelite, melamine-formaldehyde, urea-formaldehyde.
- Hydroxylation of a double bond can 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 glycols in quantitative yield.
- Conversion of ethylene into ethylene glycol by the action of cold dilute alkaline $KMnO_4$ is called **hydroxylation**.
- When vapours of alcohols are passed over heated copper at 573 K, 1° alcohols give aldehydes, 2° alcohols give ketones and 3° alcohols give alkenes.
- Methylated spirit or denatured alcohol is obtained by adding methyl alcohol, acetone and pyridine to alcohol to make it unfit for drinking purposes.
- A cold dilute alkaline $KMnO_4$ solution is called **Baeyer's reagent**.
- **Rectified spirit** contains 96.5% alcohol and 4.4% water and is obtained by fermentation of carbohydrates.
- Ketones are reduced to secondary alcohols by aluminium isopropoxide in isopropyl alcohol. The reduction by this method is known as **Meerwein-Ponndorf-Verley (MPV) reduction** and is considered as an important method for fermentation of secondary alcohols.
- Cycloalkanols in presence of 50% HNO_3 at 55°C undergo cleavage forming dioic acids.
- Ethane-1,2-diol undergoes extensive intermolecular hydrogen bonding because of the presence of two – OH groups in its molecule.
- Due to extensive intermolecular hydrogen bonding, the boiling point of ethane –1,2-diol is quite high (470 K).
- With aldehydes and ketones in presence of *p*-toluenesulphonic acid (PTS) as catalyst, ethylene glycol gives cyclic acetals and cyclic ketals (1,3-dioxolanes) respectively.
- Ethylene glycol on oxidation with conc. HNO_3 mainly gives glycolic acid and oxalic acid.
- When ethylene glycol is treated with HIO_4 or lead tetra-acetate, carbon-carbon bond fission occurs to give formaldehyde.
- The per-iodic acid cleavage of 1,2-glycols is sometimes called as **Malaprade reaction**.
- **Ethylene glycol** is used for preparing 1,4-dioxane and polyethylene glycols which are used as industrial solvents.

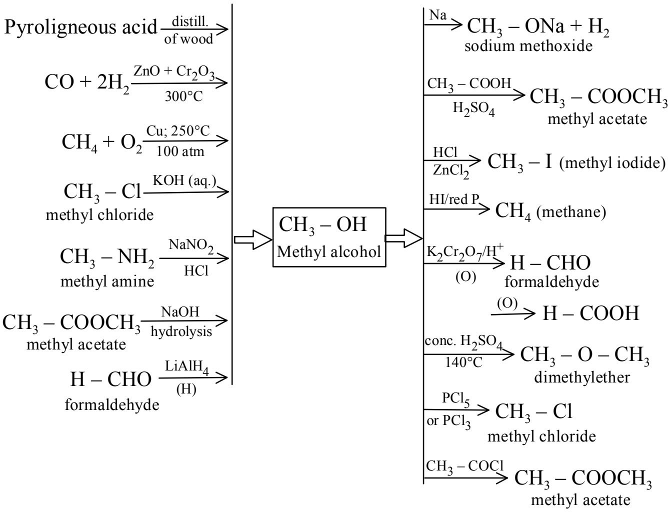
- **Glycerol** or glycerine occurs in almost all vegetable and animals oils and fats which are the triesters of glycerol with long chain fatty acids.
- Glycerol undergoes extensive intermolecular H-bonding because of the presence of three – OH groups.
- Due to extensive intermolecular hydrogen bonding, the boiling point of glycerol is quite high (563 K) even higher than that of ethylene glycol.
- Glycerol is miscible with water and alcohol in all proportions.
- A mixture of glyceryl trinitrate and glyceryl dinitrate absorbed on Kieselguhr is called **dynamite**.
- When glycerol is treated with a small amount of HI or PI_3, allyl iodide is formed.
- The smokeless powder cordite is a mixture of nitroglycerine, gun cotton and vaselin.
- Nitration of glycerol with a mixture of conc. HNO_3 + conc. H_2SO_4 gives **nitroglycerine**.
- When heated with acidified $KMnO_4$ solution, glycerol gets oxidised to oxalic acid, carbon dioxide and water.
- **Glycerol** is used as an antifreeze in automobile radiators.
- Ethanol is the only primary alcohol that gives iodoform test.
- **Isopropyl iodide** is obtained when glycerol is heated with excess PI_3.
- Haloform reaction does not take place with methanol.
- Acid catalysed dehydration of *t*-butanol is faster than *n*-butanol since *t*-butyl carbocation is more stable than *n*-butyl carbocation.
- **Phenols** are compounds of the general formula ArOH, where Ar is phenyl, substituted phenyl or some other aryl group (*e.g.* naphthyl).
- Phenol has a smaller dipole moment (1.54 D) than methanol because 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 methyl group.
- The simplest phenols are liquids or low-melting solids.
- Phenols have quite high boiling points because of intermolecular hydrogen bonding.
- Phenol is soluble in water (9 g per 100 g) because of hydrogen bonding with water.
- *o*-Nitrophenol has a lower boiling point and it is steam volatile than the *m*- and *p*-isomers because *o*-nitrophenol exists as discrete molecules and cannot form H-bonds with water.
- Most phenols have K_a values in the neighbourhood of 10^{-10} and are thus considerably weaker acids than the carboxylic acids (K_a values about 10^{-5}).
- Phenols are produced when sodium salts of aromatic sulphonic acids are fused with NaOH at 300-350°C followed by acidification.
- In **Dow's process**, phenol is obtained when chlorobenzene is heated with 6-8% NaOH solution at 623 K under 300 atmospheric pressure.
- Phenols turn reddish brown due to atmospheric oxidation.
- Phenols are stronger acids than alcohol because the phenoxide ion left after the release of a proton is stabilised by resonance but the alkoxide ion is not.
- *o*-Nitrophenol is less acidic than *p*-nitrophenol due to intramolecular H-bonding which makes loss of a proton difficult.

- Greater the number of electron withdrawing groups at the *o*- and *p*- positions more acidic is the phenol.
- Acidity of nitrophenols with respect to phenol decreases in the order : 2,4,6-trinitrophenol > 2,4-dinitrophenol > 4-nitrophenol or 2-nitrophenol > phenol.
- Electron donating group donates electrons, intensifies the negative charge, destabilizes the phenoxide ion with respect to phenol and thus decreases the acid strength.
- Acidic strength of cresols (alkyl phenols) decreases in the order :
  m-cresol > *p*-cresol > *o*-cresol.
- Due to –I effect of the halogen, all halophenols are more acidic than phenol.
- Acidity of all the *o*-halophenols decreases in the order:
  o-chlorophenol > *o*-bromophenol > *o*-iodophenol > *o*-fluorophenol.
- In *p*-fluorophenol, +R effect and –I effect of F almost balance each other and hence it is acidic as phenol itself.
- Phenols are soluble in aqueous solutions of NaOH or KOH since phenols react with alkalis (NaOH or KOH) to form salt and water.
- Electron-attracting substituents tend to disperse the negative charge of the phenoxide ion whereas electron-releasing substituents tend to intensify the charge.
- When esters of phenols are heated with aluminium chloride, the acyl group migrates from the phenolic oxygen to an *ortho* and *para* position of the ring thus yielding a ketone. This reaction is called **Fries rearrangement**.
- Treatment of phenol with chloroform and aqueous hydroxide introduces an aldehyde group – CHO, onto the aromatic ring generally *ortho* to the – OH. This reaction is known as the **Reimer-Tiemann reaction**.
- Phenol reacts with Grignard reagent to form hydrocarbons.
- Benzoylation of phenols in the presence of aq. NaOH is known as **Schotten Baumann reaction**.
- In **Kolbe's Schmidt reaction**, sodium phenoxide is heated with CO_2 at 390-410 K and at a pressure of 4-7 atmospheres sodium salicylate is formed as the major product.
- Sodium phenoxide when heated with CO_2 at 400 K under a pressure of 4-7 atmospheres followed by acidification gives salicylic acid. This reaction is known as **Kolbe's reaction**.
- Salicylic acid reacts with phenol in presence of $POCl_3$ to form **phenyl salicylate** (salol) which is used as an internal antiseptic.
- Phenol condenses with pthalic anhydride in presence of conc. H_2SO_4 to form phenolphthalein which is widely used as an indicator in acid-alkali titrations.
- Salicylic acid on acetylation with acetic anhydride in presence of CH_3COONa or a few drops of conc. H_2SO_4 gives **aspirin** which is used as an internal antiseptic.
- Phenol as such or its trichloroderivative i.e. **trichlorophenol** or TCP is used as a preservative for ink and other water-based colours.
- Phenol is used in the manufacture of drugs like salicylic acid, phenacetin, aspirin, salol etc.
- Ethers are compounds having general formula $R – O – R'$, $Ar – O – R$ or $Ar – O – Ar$. [Ar is phenyl or some other aromatic group].

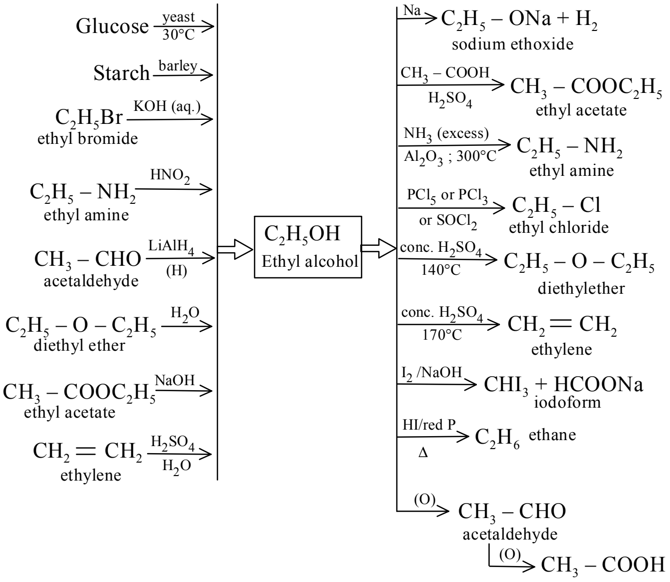
- Ethers in which the groups R and R′ are same are called simple or symmetrical ethers while those in which the groups R and R′ are different are called **mixed** or **unsymmetrical ethers**.
- Ethers like water have a tetrahedral geometry *i.e.* oxygen is sp^3-hybridised.
- The C – O – C angle in ethers has been found to 110°.
- Methyl phenyl ether is called **anisole** and ethyl phenyl ether is called **phenetole**.
- Ethers having the same alkyl groups on either side of the oxygen atom but different arrangement of the carbon chain within the alkyl groups are called **chain isomers**.
- Ethers having the same molecular formulae but different alkyl groups on either side of the oxygen atom are called **metamers**.
- **Williamson's synthesis** of ethers involves the treatment of an alkyl halide with a suitable sodium alkoxide.
- Williamson's synthesis involves the nucleophilic displacement of the halide ion from the alkyl halide by the alkoxide ion by S_N2 mechanism.
- Ethers may be prepared by dehydration of alcohols either in the presence of acids or heated alumina.
- Dehydration of *tert*-butyl alcohol with conc. H_2SO_4 at 415 K yields only isobutylene.
- Due to the bent structure of ethers and polarity of C – O bond, ethers have a net dipole moment. i.e. ethers are polar in nature.
- Ethers have lower boiling points as compared to isomeric alcohols because of the fact that ethers do not form hydrogen bonds.
- Order of dehydration of alcohols leading to the formation of ethers is :
  primary > secondary > tertiary.
- The solubility of lower ethers in water is due to the formation of hydrogen bonds between water and ether molecules.
- All ethers are lighter than water.
- Ethers are inert compounds due to the reason that the functional group of ethers (– O –) does not contain any active site in their molecule.
- Ethers behave as Lewis bases on account of the presence of two lone pairs of electrons on the oxygen atom.
- Being Lewis base, ethers form coordinate complexes known as etherates with Lewis acids such as BF_3, $AlCl_3$, $FeCl_3$, Grignard reagent etc.
- Ethers dissolves in cold concentrated inorganic acids to form stable oxonium salts.
- Ethers are cleaved at C – O bond by hydroiodic acid or conc. hydrobromic acid when heated to 370 K. The reaction of hydroiodic acid with ethers forms the basis of **Zeisel's method** for the estimation of alkoxy groups such as methoxy, ethoxy etc.
- When exposed to air and light for a long time, ethers are oxidised to form peroxides.
- **Dimethyl ether** is used as a refrigerent and as a solvent at low temperature.
- Diethyl ether is used as an anaesthetic in surgery.
- A sample of diethyl ether free of all traces of water and alcohol is called absolute ether.
- Order of reactivity of halogen acids towards ether is HI > HBr > HCl

- On heating with dilute H_2SO_4 under pressure ethers are hydrolysed to alcohols.
- When heated with conc. H_2SO_4, ethers form alcohols and alkyl hydrogen sulphates.
- Acid chlorides react with ethers when heated in the presence of anhydrous $ZnCl_2$ or $AlCl_3$ to form alkyl halides and esters.
- Ethers are used as a reaction medium for carrying out lithium aluminium hydride reduction and also for the preparation of Grignard and other organometallic reagents.

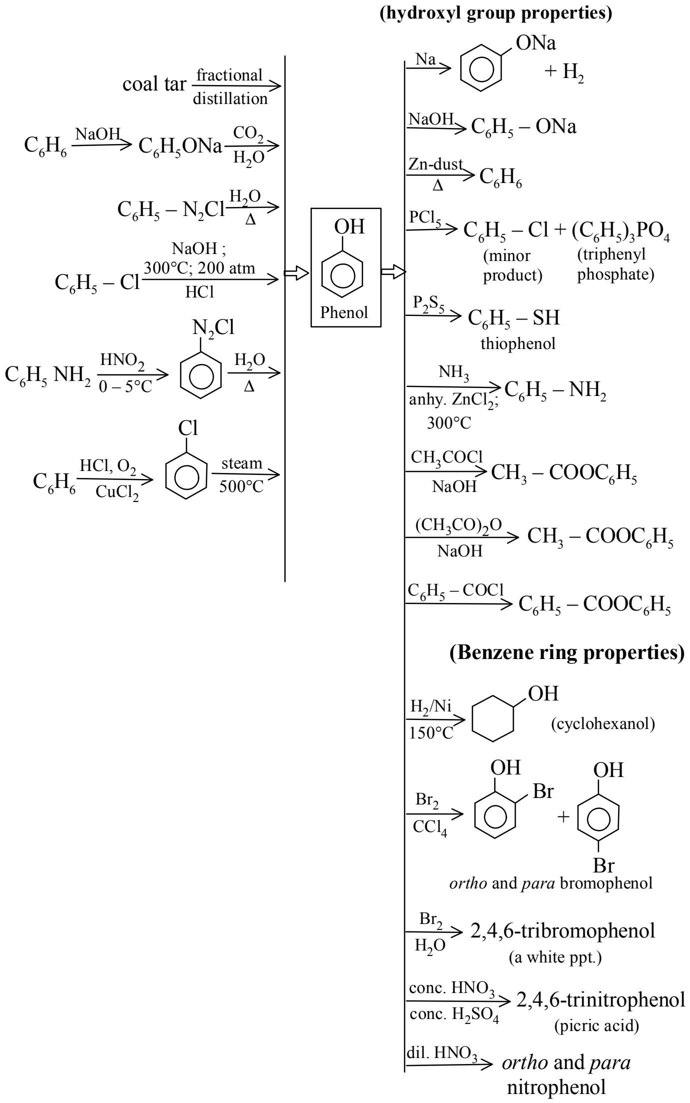
Flow chart for Methyl alcohol



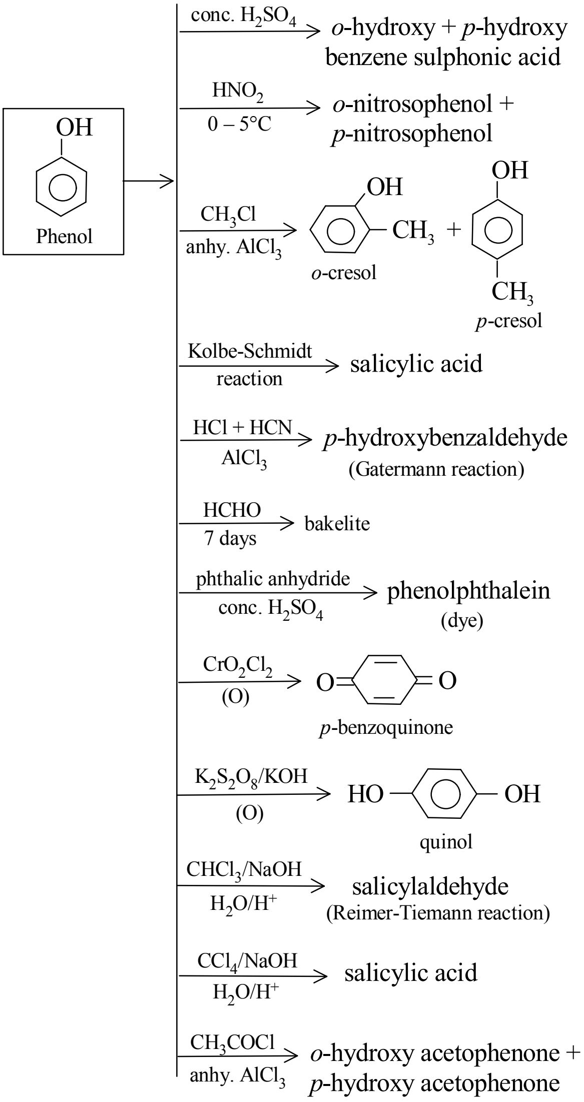
Flow chart for Ethyl alcohol



Flow chart for Phenol



Properties of Phenol



Flow chart for Diethyl ether