

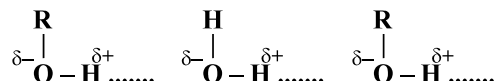
Alcohols, Ethers and Phenols

ALCOHOLS, ETHERS AND PHENOLS

Alcohols :

C1A Physical Properties :

The lower alcohols are completely soluble in water but as the number of carbon atoms increases, solubility decreases. This solubility in water is due to intermolecular H-bonding between water and alcohols molecules due to their polar character.

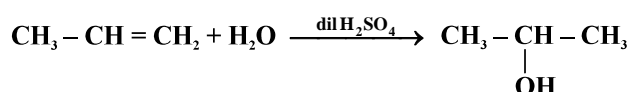


Increase in C-chain increases organic part hence solubility in water decreases.

Isomeric 1^o, 2^o, 3^o alcohols have solubility in order : 1^o > 2^o > 3^o.

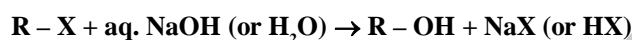
C1B Method of preparation of Alcohols :

(i) Hydration of Alkenes :



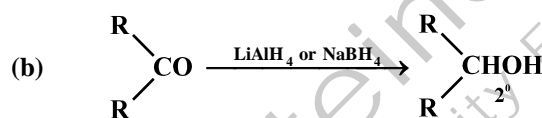
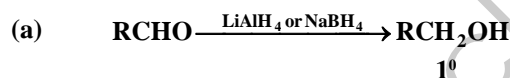
Intermediate is carbonium ion that can change to more stable carbanion ion by hydride shift, alkyl or phenyl shift.

(ii) Hydrolysis of Alkyl Halides :



Reaction can be S_N¹ or S_N² .

(iii) Reduction of Carbonyl Compounds (including acid derivative) :



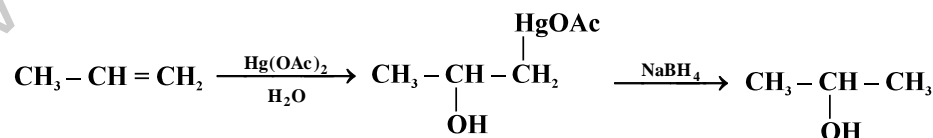
(c) Acid, acid halide, ester and anhydride are reduced to 1^o alcohol.

(iv) Hydroboration and oxidation :



The hydroboration-oxidation (HBO) process gives product corresponding to anti-Markownikoff addition of H₂O to the carbon-carbon double bond.

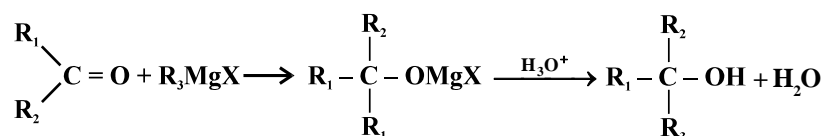
(v) Oxymercuration-Demercuration :



The alcohol obtained corresponds to Markownikov's addition of water to an Alkene.

(vi) (a) Through Grignard Reagent :

Addition of Grignard Reagent on carbonyl compounds followed by hydrolysis yields alcohols nature of which depends upon types of carbonyl compounds used.



R_1, R_2 can be H, alkyl or aryl but R_3 is not H.

- (b) Grignard reagent with epoxide and after hydrolysis gives 1° alcohol for e.g.,

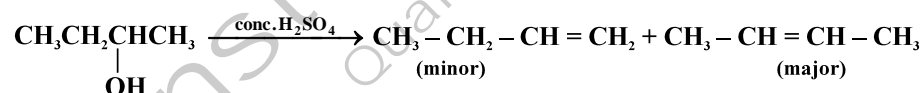


Practice Problems :

- Propene, $CH_3 - CH = CH_2$ can be converted into 1-propanol, Which of the reagent among the following is ideal to affect the conversion :
 - alkaline $KMnO_4$
 - B_2H_6 and alkaline H_2O_2
 - O_3/Zn
 - OsO_4/CH_2Cl_2
 - Glycol may be obtained :
 - by the oxidation of ethylene with cold, dilute, alkaline permanganate solution
 - by the hydrolysis of ethylene bromide under reflux with aqueous sodium carbonate solution
 - by the hydrolysis of ethylene chlorohydrin on boiling with aqueous sodium bicarbonate
 - by any of the above methods
 - Which of the following are the starting materials for the Grignard's synthesis of tert. butyl alcohol
 - $CH_3MgI + CH_3COCH_3$
 - $CH_3MgI + CH_3CHOHCH_3$
 - $CH_3CH_2MgBr + CH_3COCH_3$
 - $CH_3CH_2MgBr + CH_3CHO$
- [Answers : (1) b (2) d (3) a]

C2 Chemical Properties :

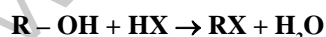
- (i) Dehydration of Alcohol :



Alcohols leading to conjugated alkenes are more easily dehydrated than those of alcohols leading to non-conjugated alkenes.

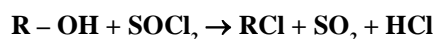
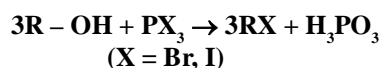
Dehydration of alcohol is in the order $3^\circ > 2^\circ > 1^\circ$ as intermediate is carbocation.

- (ii) Reaction with Halogen Acids :

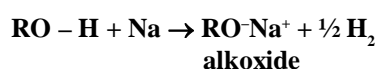


Intermediate is carbonium ion. The order of reactivity of HX : $HI > HBr > HCl$ for a given alcohol.

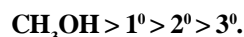
- (iii) Reaction with Phosphorous Halides and Thionyl Chloride :



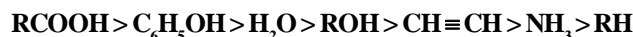
- (iv) Acidic Character of Alcohol :



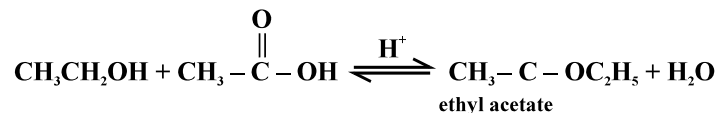
The order of acidic character of alcohol with metal is :



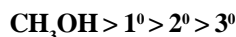
The relative acidities is as follows :



(v) Ester Formation (alcohol can act as a nucleophile also).



Thus reactivity of alcohols for given acid is in order :

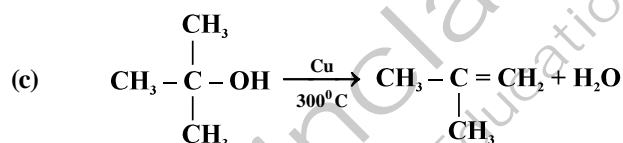
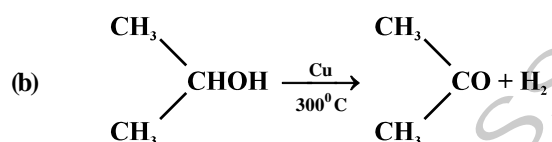
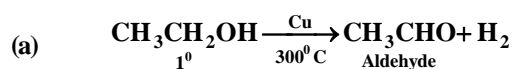


and those of acids for given alcohol is in order :

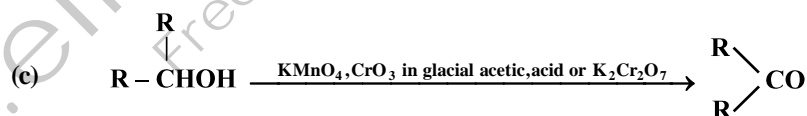
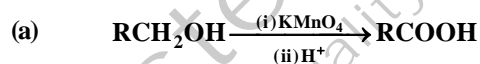


(vi) Oxidation of Alcohol :

1. Using Cu



2. Oxidation using $\text{KMnO}_4/\text{K}_2\text{Cr}_2\text{O}_7$



3. Other reagents used for oxidation :

(a) PCC (pyridinium chlorochromate) to oxidise 1° alcohols to aldehydes.

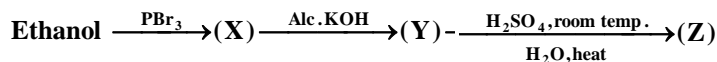
(b) MnO_2 selectively oxidises the OH group of allylic and benzylic 1° and 2° alcohols to give aldehydes and ketones respectively.

C3 Test to distinguish 1° , 2° and 3° Acohols :

- Lucas Reagent (anhydrous $\text{ZnCl}_2/\text{conc. HCl}$)
- Oxidation
- Victor Meyer Test

Practice Problems :

1. Identify (Z) in the following reactions series :

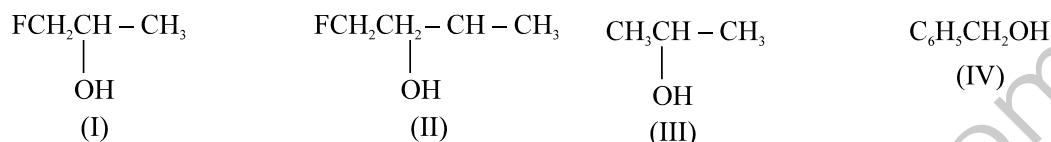


- (a)
- $\text{CH}_2 = \text{CH}_2$
- (b)
- $\text{CH}_3\text{CH}_2\text{OH}$
- (c)
- $\text{CH}_3\text{CH}_2\text{OSO}_3\text{H}$
- (d)
- $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$

2. An organic compound gives hydrogen on reacting with sodium metal. It also gives iodoform test and forms an aldehyde of molecular formula
- $\text{C}_2\text{H}_4\text{O}$
- on oxidation with acidified dichromate. The compound is :

- (a)
- CH_3OH
- (b)
- CH_3COOH
- (c)
- CH_3CHO
- (d)
- $\text{C}_2\text{H}_5\text{OH}$

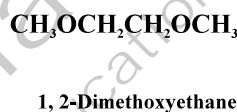
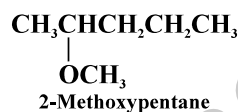
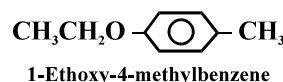
3. The order of reactivity of the following alcohols,



towards conc. HCl is

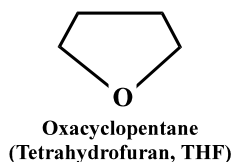
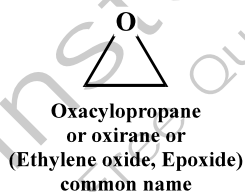
- (a)
- $\text{I} > \text{II} > \text{III} > \text{IV}$
- (b)
- $\text{I} > \text{III} > \text{II} > \text{IV}$
-
- (c)
- $\text{IV} > \text{III} > \text{II} > \text{I}$
- (d)
- $\text{IV} > \text{III} > \text{I} > \text{II}$

[Answers : (1) b (2) d (3) c]

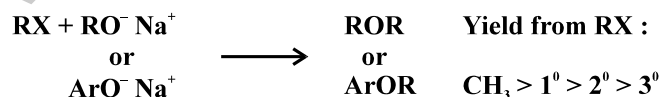
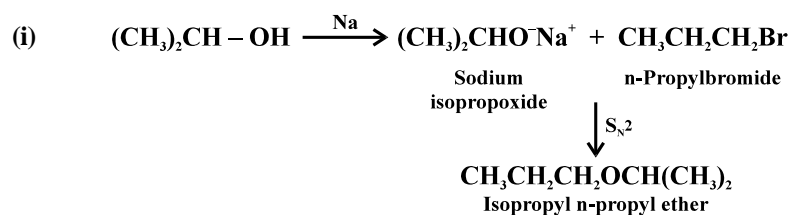
C4 Ethers**Nomenclature of Ethers :**

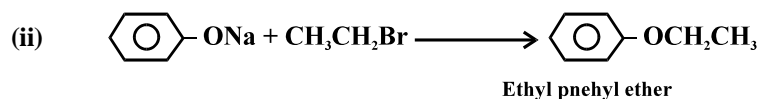
Cyclic ethers can be named in several ways :

In another system, a cyclic three membered ether is named as oxirane and a four membered ether is called oxetane.

**C5 Methods of Preparation of Ether :**

- (a)
- Williamson Synthesis :**

**Example :**

**Discussion : Phenol in Williamson's synthesis :**

Because phenols are stronger acids than alcohols they can react with NaOH to change into sodium phenoxide ion. But alcohols can be converted into sodium alkoxide ion by reaction with sodium metal only.

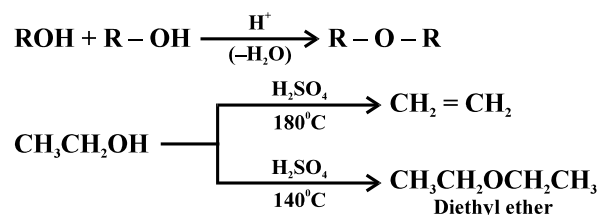
[Alkyl halide used here can not be aryl halide as it does not undergo nucleophilic substitution easily]

R – X → can be X = –Cl, –Br, I, –OSO₃CH₃ etc.

(b) Ethers by Intermolecular Dehydration of Alcohols :

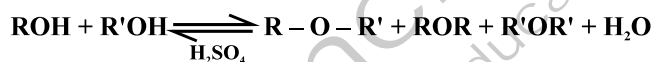
Alcohols can dehydrate to form alkenes.

1° Alcohols can also dehydrate to form ethers.

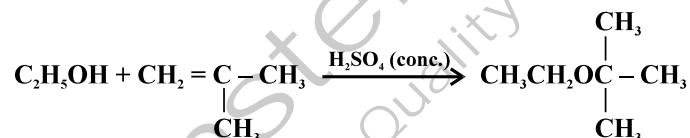


The formation of ether takes place by S_N2 mechanism mainly, with one molecule acting as the nucleophile and with another protonated molecules of the alcohol acting as the substrate.

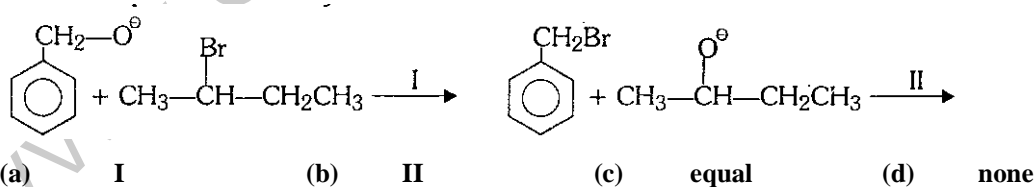
Finally this method is not useful for the preparation of ether with 3° alcohol because they form alkene too easily. This method is not useful for the preparation of unsymmetrical ethers from primary alcohols because the reaction leads to a mixture of products.



(c) Ethers may be prepared by the addition of alcohols to alkenes in the presence of acid e.g.

**Practice Problems :**

1. Which route provides a better synthesis of ether :



[Answers : (1) b]

C6 Reactions of Ethers :

(a) Ethers are comparatively unreactive compounds. The ether linkage are quite stable towards bases, oxidizing agent, reducing agents. Ether can undergo just one kind of reaction, cleavage by acids :

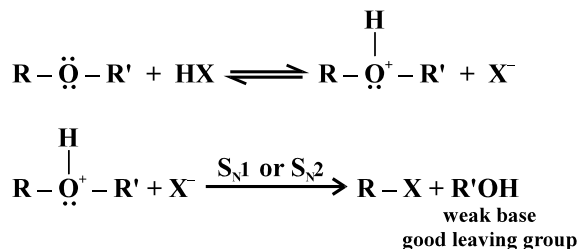


Reactivity of HX : HI > HBr > HCl

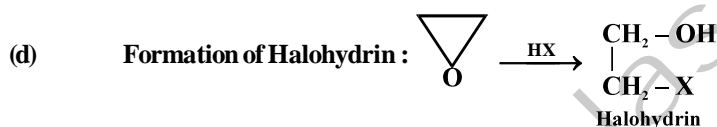
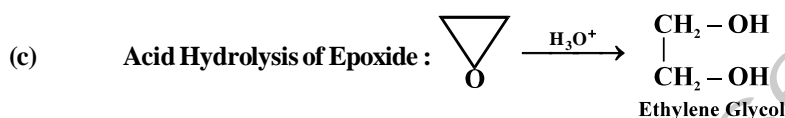
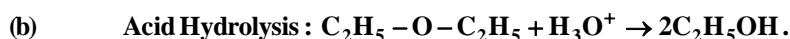
Cleavage takes place only under quite vigorous conditions : concentrated acids (usually HI or HBr) and high temperature.

Oxygen of the ether is basic, like the oxygen of alcohol. The initial reaction between an ether and an acid is undoubtedly formation of the protonated ether.

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



As we might expect primary alkyl group tend to undergo S_N2 and 3^0 tend to undergo S_N1 .



Practice Problems :

1. Ethoxy ethane does not react with

- (a) HI (b) conc. H_2SO_4 (c) PCl_5 (d) Na

2. An ether, (A) having molecular formula, $C_6H_{14}O$, when treated with excess of HI produced two alkyl iodides which on hydrolysis yield compounds (B) and (C). Oxidation of (B) gives an acid (D), whereas oxidation of (C) results in the formation of a mixed ketone, (E). Thus structures of (A) is

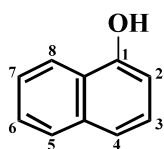
- (a) $H_3C-\overset{H_3C}{\underset{|}{CH}}-CH_2OCH_2-CH_3$ (b) $CH_3CH_2CH_2CH_2OCH_2CH_3$
- (c) $CH_3CH_2\overset{CH_3}{\underset{|}{CHO}}CH_2CH_3$ (d) $CH_3\overset{CH_3}{\underset{|}{CHO}}CH_2CH_2CH_3$

[Answers : (1) d (2) c]

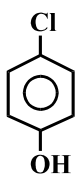
PHENOLS**C7A Structure and Nomenclature of Phenols :**

Compounds that have a hydroxyl group directly attached to benzene ring are called phenols. Thus phenol is specific name of hydroxy benzene

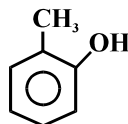
Compounds that have a hydroxyl group attached to a polycyclic benenoid ring are chemically similar to phenols, but they are called naphthols and phenanthrols, e.g.



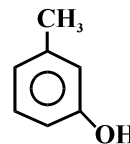
1-Naphthol
(α -Naphthol)



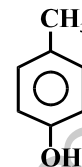
4-Chlorophenol



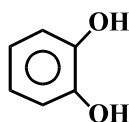
2-Methylphenol
(o-Cresol)



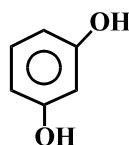
3-Methylphenol
(m-Cresol)



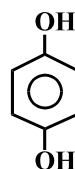
4-Methylphenol
(p-Cresol)



1, 2-Benzenediol
(Catechol)



1, 3-Benzenediol
(Resorcinol)



1, 4-Benzenediol
(Hydroquinone)

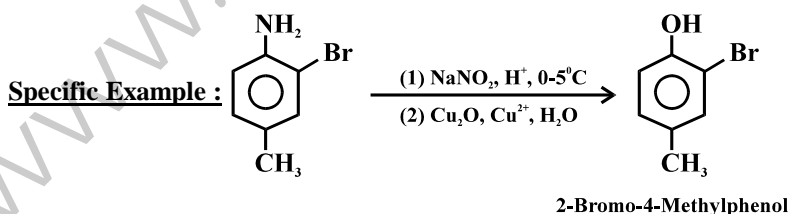
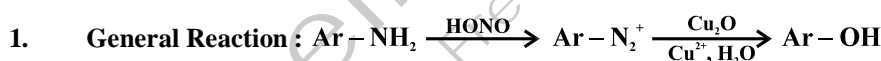
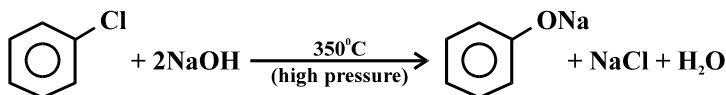
C7B Physical Properties of Phenols : The presence of hydroxy groups in the molecules of phenols means that phenols are like alcohols in being able to form strong intermolecular hydrogen bonds.

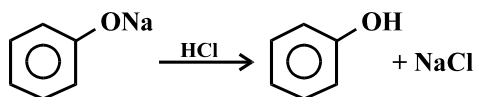
This hydrogen bonding causes phenols to be associated and therefore to have higher boiling points than hydrocarbons of the same molecular weight.

C8A Synthesis of Phenols :

Laboratory Synthesis : The most important laboratory synthesis of phenols is by hydrolysis of arenediazonium salts.

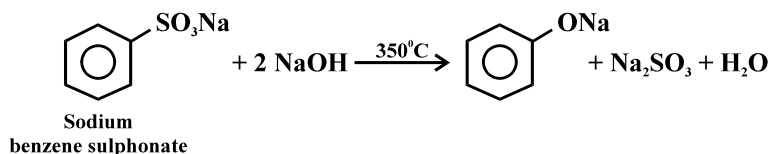
This method is highly versatile and the conditions required for the diazotisation step and the hydrolysis step are mild.

**Industrial Synthesis :****2. Hydrolysis of Chlorobenzene (Dow Process) :**

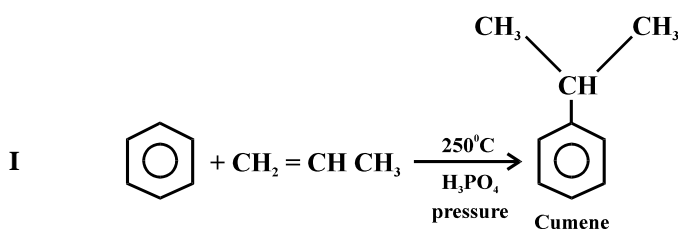


(The mechanism for the reaction probably involves benzyne intermediate)

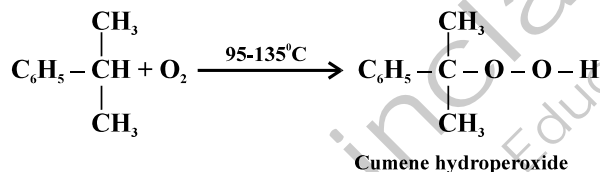
3. **Alkali Fusion of Sodium benzene sulfonate :** Sodium benzene sulfonate is melted (fused) with sodium hydroxide at 350°C to produce sodium phenoxide acidification then yields phenol.



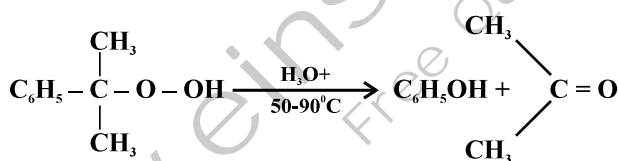
4. **From Cumene Hydroperoxide :**



- II This cumene is oxidized to cumene hydroperoxide



Finally, when treated with 10% sulfuric acid, cumene hydroperoxide undergoes a hydrolytic rearrangement that yields phenol and acetone.

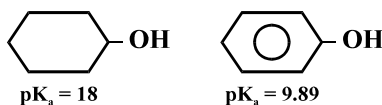


C8B Chemical Properties of Phenol :

1. **Reaction of Phenol as Acid : Strength of phenols as acids :**

Although phenols are structurally similar to alcohols, they are much stronger acids. The pK_a values of most alcohols are of the order of 18. However the pK_a values of phenols are smaller than 11.

Let us compare two superficially similar compounds cyclohexanol and phenol.



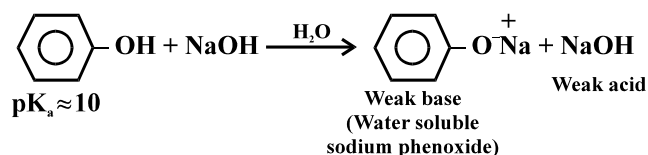
Although phenol is weak acid when compared with carboxylic acid such as acetic acid (pK_a = 4.75) phenol is much stronger than cyclohexanol by a factor of 8.

Phenols are more acidic than cyclohexanol because of following reasons :

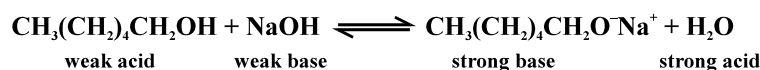
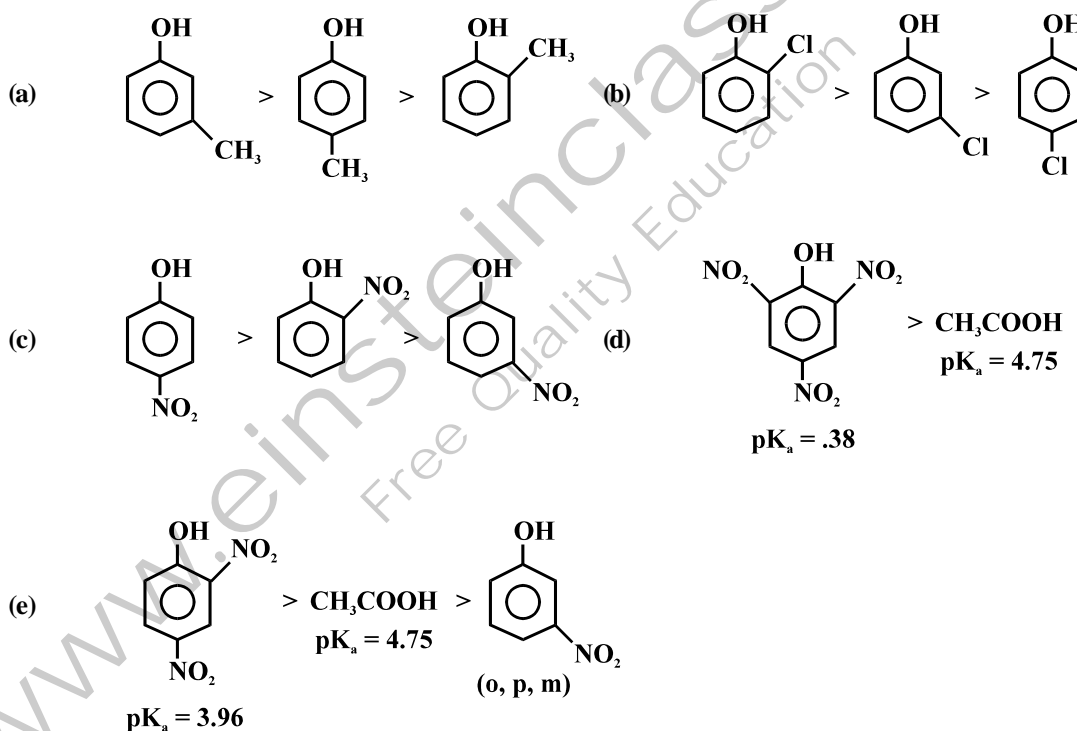
Phenoxide ion is more resonance stabilized than phenol. Resonance structures of phenoxide ion do not involve charge separation. No resonance structure can be written for cyclohexanol and its anion of course. The benzene ring of phenol acts as if it were as electron withdrawing group when we compare it with cyclohexanol. That causes –OH oxygen to be more positive.

Reason : Carbon atom that bears hydroxyl group in phenol is sp^2 hybridized, whereas in cyclohexanol sp^3 hybridised. Greater the S-character more electronegative the carbon. Thus carbon of benzene is more electronegative than cyclohexanol.

Because phenols are more acidic than water, the following reaction goes almost completion.



The reaction between cyclohexanol and NaOH does not occur to significant extent as H_2O is stronger acid than 1-cyclohexanol.

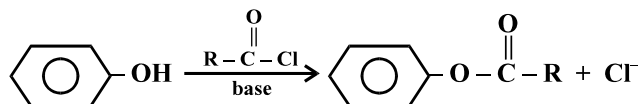
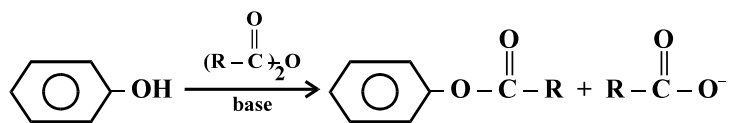
Acidity order of Phenols :Distinguishing and separating phenols from alcohols and carboxylic acids :

1. Phenols dissolve in aqueous sodium hydroxide whereas most alcohols with six carbon atoms or more do not. Thus we can distinguish them.
2. Alcohols with five carbon atoms are more or less soluble in NaOH but do not form appreciable amount of sodium alkoxide.
3. Most phenols are not soluble in aqueous sodium bicarbonate, but carboxylic acids are soluble.

C9 Other reactions of the O – H Group of Phenols :

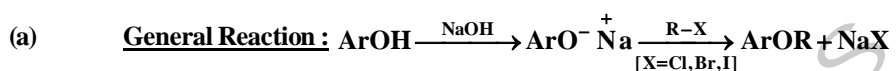
1. Phenols react with carboxylic acid anhydrides and acid chlorides to form esters.

These reactions are similar to alcoholic as we have already discussed in alcohols.

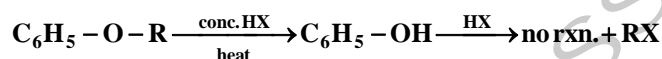


2. Phenols in the Williamson Synthesis :

Because phenols are more acidic than alcohols they can be converted to sodium phenoxide through the use of sodium hydroxide (rather than use of sodium metal, the reagent that convert alcohols to alkoxide ion).

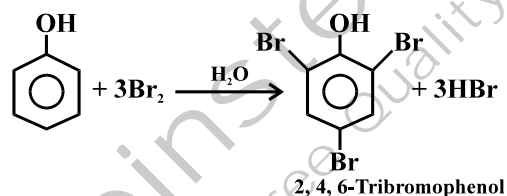


(b) Cleavage of Alkyl-Aryl Ether :

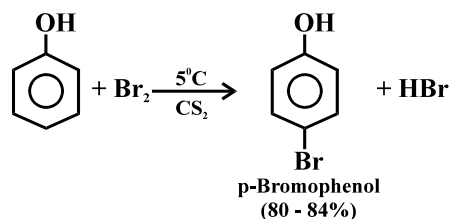


3. Reactions of the Benzene ring of Phenol :

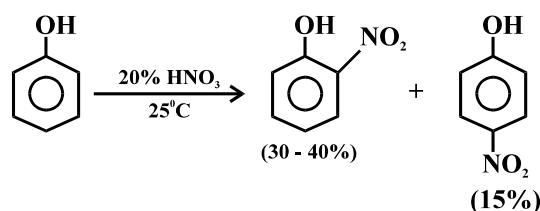
(a) Bromination : The hydroxyl group is a powerful activating group and an ortho-para director in electrophilic substitution. Phenol itself react with Br_2 in aqueous solution to yield 2, 4, 6-tribromophenol. Note that a Lewis acid is not required for the bromination of this highly activated ring.



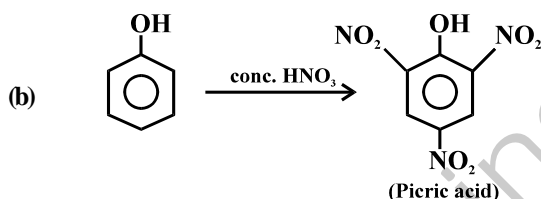
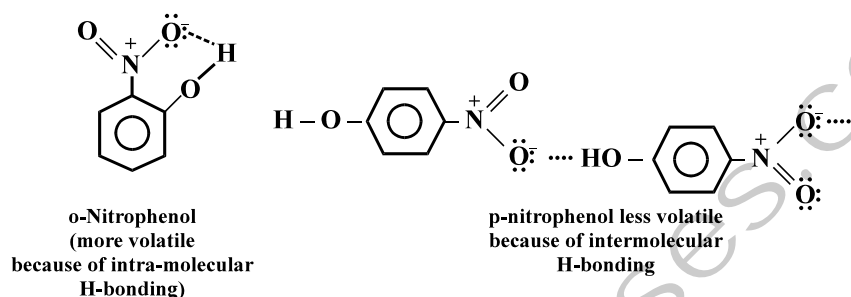
(b) Monobromination of phenol can be achieved by carrying out the reaction in carbon disulfide (CS_2) at low temperature. Conditions that reduce the electrophilic activity of bromine. The major product is the para isomer.



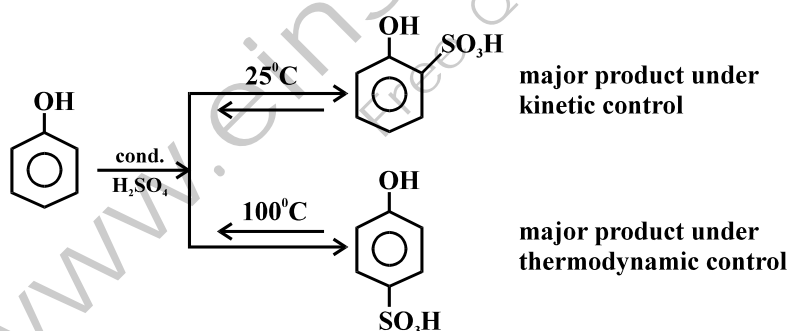
4. (a) **Nitration** : Phenol react with dilute nitric acid to yield a mixture o- and p-nitrophenol



Although the yield is relatively low (because of oxidation of ring). The ortho and para isomers can be separated by steam distillation. o-Nitrophenol is more volatile isomer because its intramolecular hydrogen bonding. p-Nitrophenol is less volatile because intermolecular H-bonding causing association among molecules. Thus o-nitrophenol passes over steam and p-Nitrophenol remain in the distillation flask.



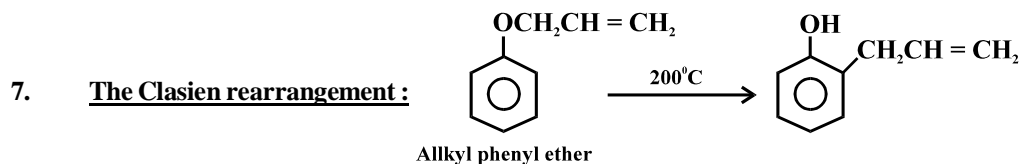
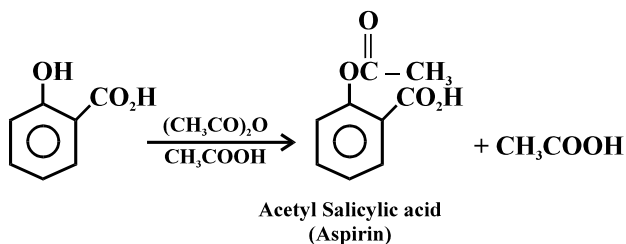
5. **Sulfonation** : Phenol reacts with concentrated sulfuric acid to yield mainly o-sulphonated product if the reaction is carried out at 25°C and mainly the para substituted product if the reaction is at 100°C.



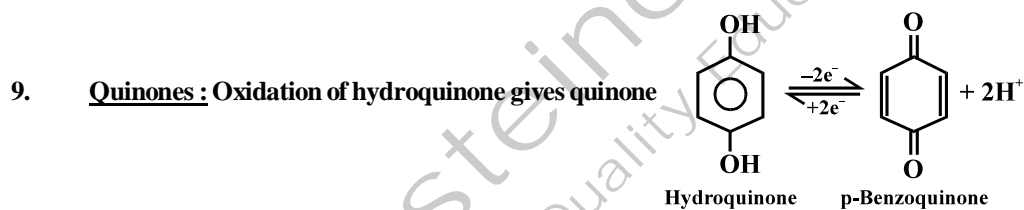
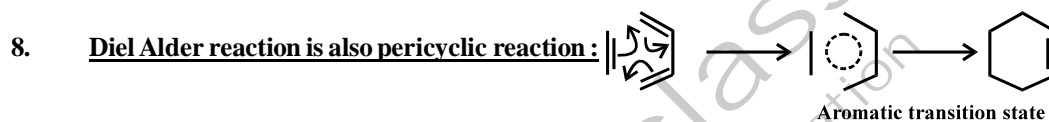
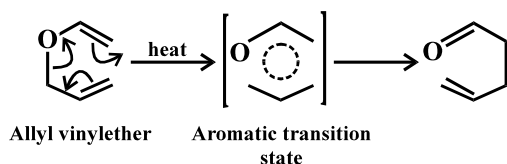
6. **Kolbe's Reaction** : The phenoxide ion is even more susceptible to electrophilic aromatic substitution, than phenol itself.

High reactivity of phenoxide ion is used in a reaction called as kolbe reaction. In kolbe reaction carbon dioxide act as the electrophile.

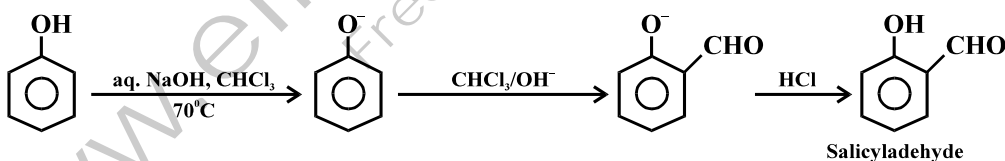
Reaction of salicylic acid with acetic anhydride yields widely used pain reliver aspirin.



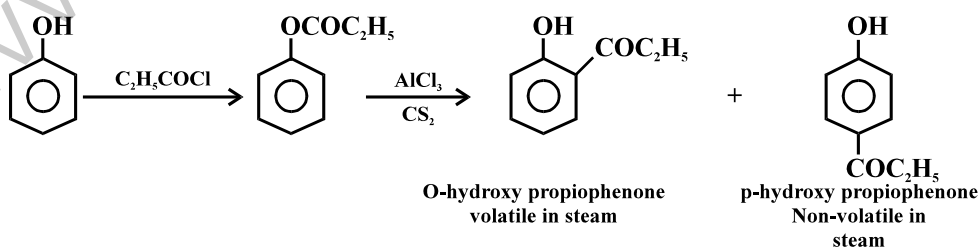
Claisen rearrangement can also take place when allyl vinyl ether are present



10. **Reimer-Tiemann Reaction :**



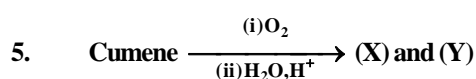
11. **Fries rearrangement :**



Rearrangement involves RCO^+ , which then attacks the ring.

Practice Problems :

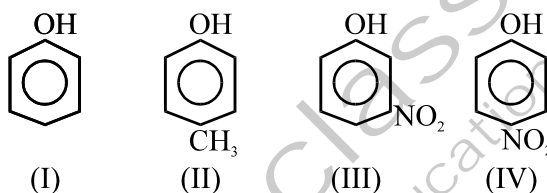
- When phenol is distilled with zinc dust, the main product is
 - biphenyl
 - benzene
 - benzaldehyde
 - phenolphthalein
- When sodium benzene sulphonate is fused with sodium hydroxide (solid), the product formed is
 - benzene
 - phenol
 - benzene triphenol
 - none of these
- Which of the following acids is strongest
 - $C_6H_5SO_3H$
 - CH_3COOH
 - C_6H_5COOH
 - $(COOH)_2$
- Phenol is less acidic than
 - p-nitrophenol
 - ethanol
 - cresol
 - benzyl alcohol



(X) and (Y) respectively are

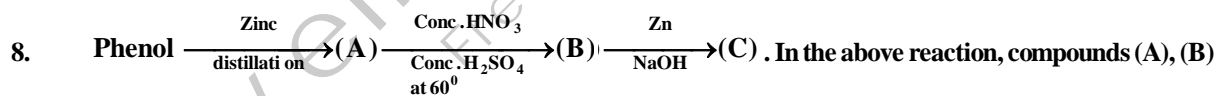
- toluene, propene
- toluene, propylchloride
- phenol, acetone
- phenol, acetaldehyde

6. In the following compounds



the order of acidity is

- III > IV > I > II
 - I > IV > III > II
 - II > I > III > IV
 - IV > III > I > II
7. When phenol reacts with benzene diazonium chloride, the product obtained as
- phenyl hydrazine
 - p-amino azobenzene
 - phenol hydroxylamine
 - p-hydroxy azobenzene



and (C) are

- benzene, nitrobenzene and aniline
- benzene, dinitrobenzene and m-nitroaniline
- toluene, nitrobenzene and m-toluidine
- benzene, nitrobenzene and hydrazobenzene

[Answers : (1) b (2) b (3) a (4) a (5) c (6) d (7) d (8) d]