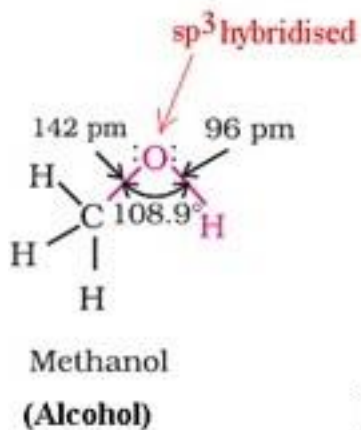


Alcohols, Phenols and Ethers

- **Structure of alcohols:**



- **Preparation of alcohols:**

- a) From alkene

Acid catalysed hydration
(H_2O, H^+)

Mark, Addition

Or

Hydroboration - oxidation

$B_2H_6, H_2O_2 / OH^-$

Mark, addition

Product is anti mark

Alkene $\xrightarrow{\text{Product is anti mark}}$ *Alcohol*

- b) From esters

Esters $\xrightarrow{H_2 \text{ catalyst}}$ *Alcohol*

- c) From aldehydes and ketones

H_2 / Pd or

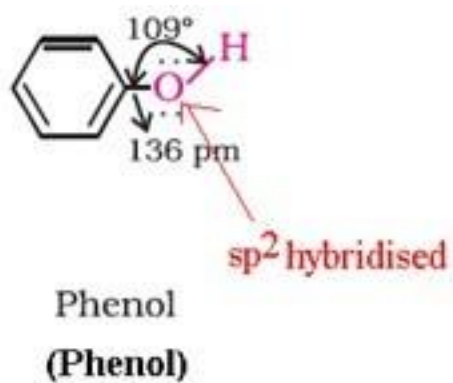
Alcohol $\xleftarrow{NaBH_4 \text{ Or } LiAlH_4 \text{ Or Grignard's reagent}}$ *Aldehyde and ketone*

- d) From carboxylic acids

Alcohol $\xleftarrow{LiAlH_4, H_2O}$ *Carboxylic acids*

-

- Structure of phenols:



- Preparation of phenols:

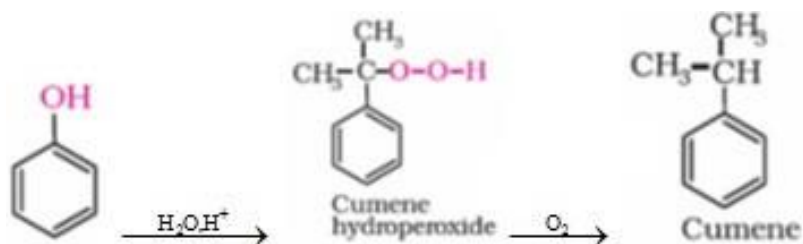
a) From benzene



b) From chlorobenzene



c) From cumene

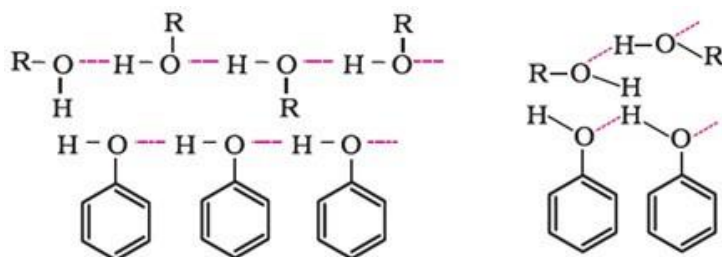


d) From aniline



- **Physical properties of alcohols and phenols:**

a) Boiling points: Boiling points of alcohols and phenols are higher in comparison to other classes of compounds. This is because the –OH group in alcohols and phenols is involved in intermolecular hydrogen bonding.



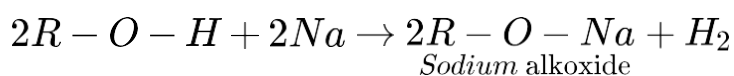
The boiling points of alcohols and phenols increase with increase in the number of carbon atoms. This is because of increase in van der Waals forces with increase in surface area. In alcohols, the boiling points decrease with increase of branching in carbon chain. This is because of decrease in van der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

b) Solubility: Solubility of alcohols and phenols are soluble in water due to their ability to form hydrogen bonds with water molecules. The solubility of alcohols decreases with increase in size of alkyl/aryl (hydrophobic) groups.

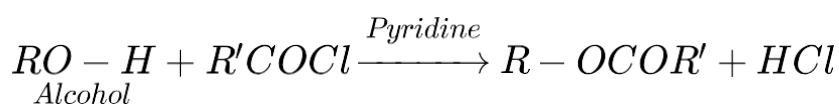
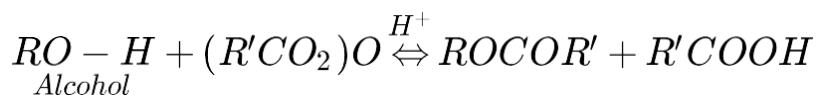
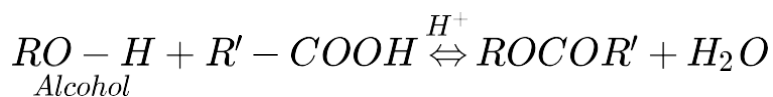
- **Chemical properties of alcohols:**

I. Reactions involving cleavage of O–H bond: Alcohols react as nucleophiles:

a) Reaction with metals

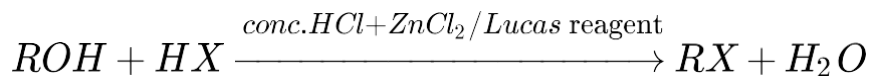


b) Esterification reaction

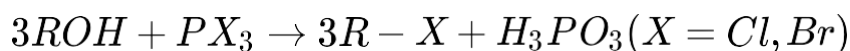


II. Reactions of alcohols involving cleavage of carbon – oxygen (C–O) bond:

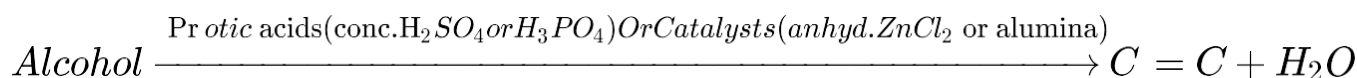
a) Reaction with hydrogen halides



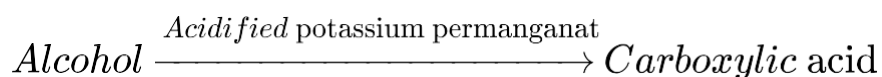
b) Reaction with phosphorus trihalides



c) Dehydration reaction



d). Oxidation reaction



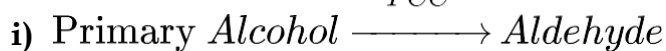
CU, 573k

Or

CrO₃

Or

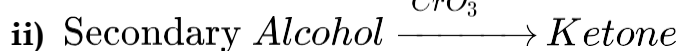
PCC



CU, 573k

Or

CrO₃



CU, 573k

Or

KMnO₄



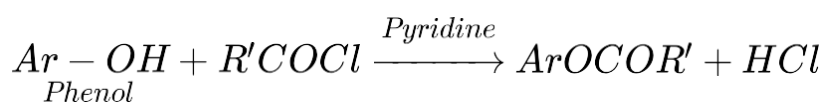
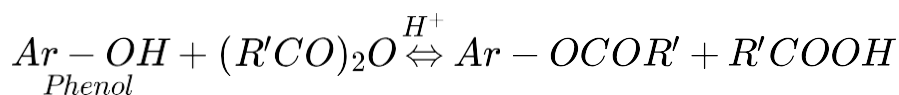
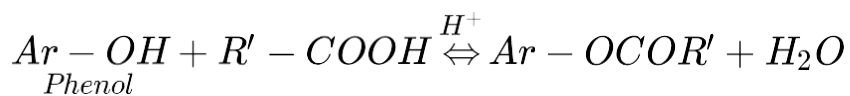
- Chemical properties of phenols:

I. Reactions involving cleavage of O–H bond: Alcohols react as nucleophiles:

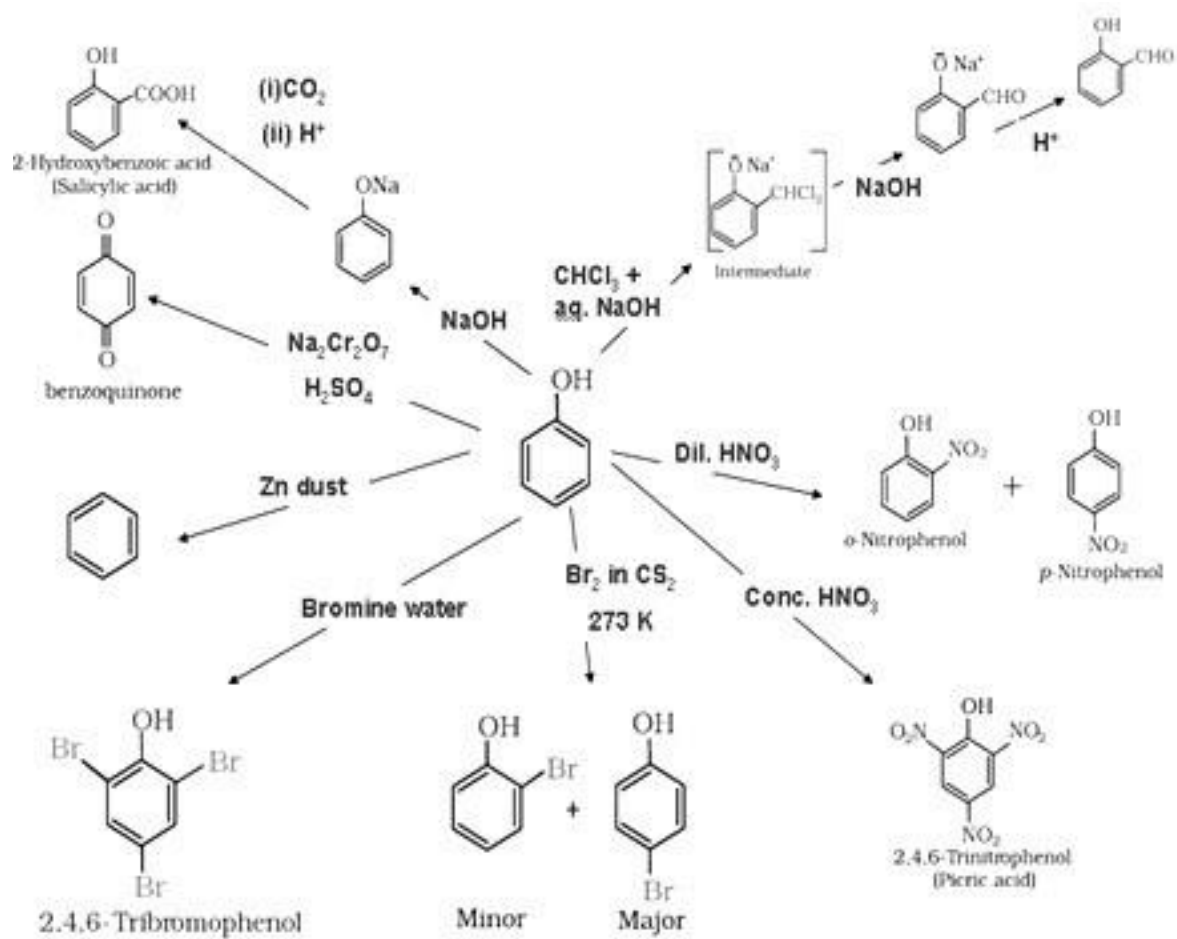
a) Reaction with metals



b) Esterification reaction



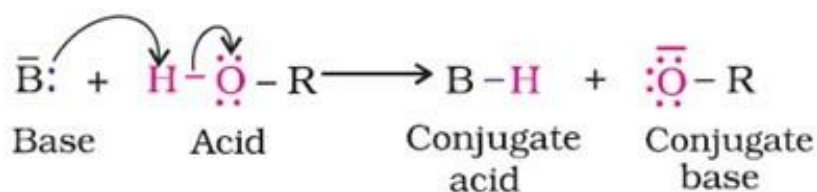
II. Other chemical reactions of phenols:



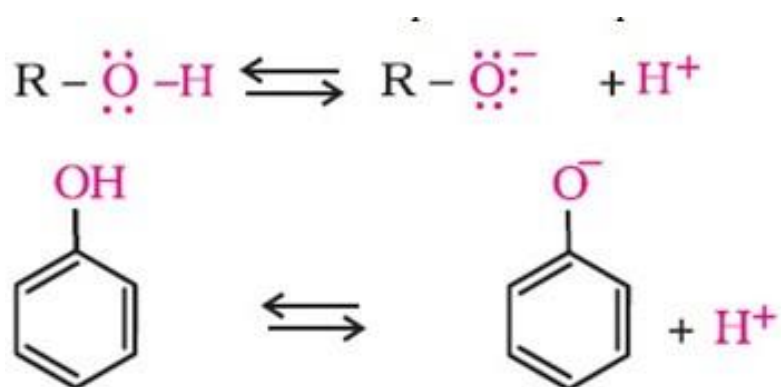
III. Acidic nature of phenol and alcohol:

a). Phenol > H₂O > Primary alcohol > Secondary alcohol > Tertiary alcohol.

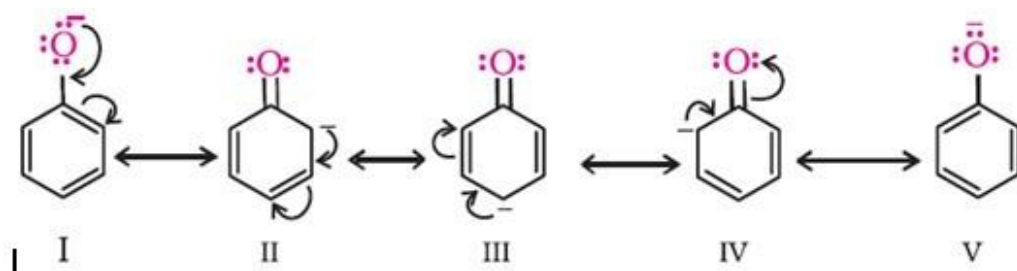
The acidic character of alcohols is due to the polar nature of O–H bond. Alkyl group is an electron-releasing group (–CH₃, –C₂H₅) or it has electron releasing inductive effect (+I effect). Due to +I effect of alkyl groups, the electron density on oxygen increases. This decreases the polarity of O–H bond. And hence the acid strength decreases.



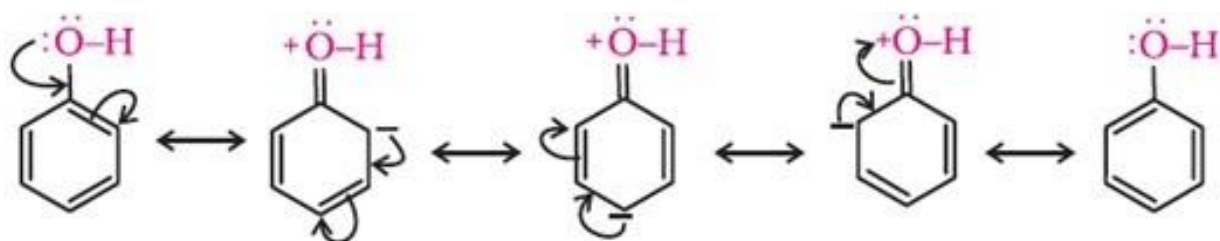
b) Phenol is more acidic than alcohol: In phenol, the hydroxyl group is directly attached to the *sp*² hybridised carbon of benzene ring which acts as an electron withdrawing group whereas in alcohols, the hydroxyl group is attached to the alkyl group which have electron releasing inductive effect. In phenol, the hydroxyl group is directly attached to the *sp*² hybridised carbon of benzene ring whereas in alcohols, the hydroxyl group is attached to the *sp*³ hybridised carbon of the alkyl group. The *sp*² hybridised carbon has higher electronegativity than *sp*³ hybridised carbon. Thus, the polarity of O–H bond of phenols is higher than those of alcohols. Hence, the ionisation of phenols is higher than that of alcohols. The ionisation of an alcohol and a phenol takes place as follows:



In alkoxide ion, the negative charge is localised on oxygen while in phenoxide ion, the charge is delocalised.



The delocalisation of negative charge 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.

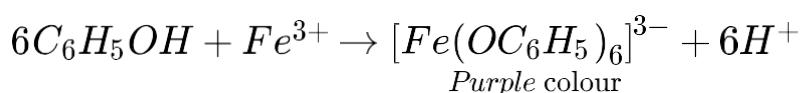


c) In substituted phenols, the presence of electron withdrawing groups such as nitro group enhances the acidic strength of phenol. On the other hand, electron releasing groups, such as alkyl groups, in general, decreases the acid strength. It is because electron withdrawing groups lead to effective delocalisation of negative charge in phenoxide ion.

- **Differentiate between organic compounds:**

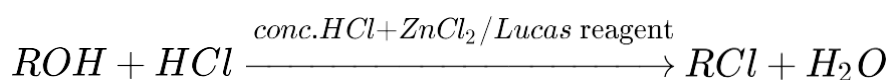
a) Alcohols and phenols

Phenol on reaction with neutral FeCl_3 gives purple colour whereas alcohols do not give purple colour.



b) Primary, secondary and tertiary alcohols

Lucas reagent test:



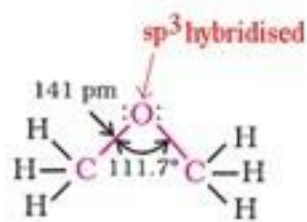
If it is a primary alcohol, no turbidity appears at room temperature. Turbidity appears only on heating. If it is a secondary alcohol, turbidity appears in 5 minutes. If it is a tertiary alcohol, turbidity appears immediately.

c) Methanol and ethanol

Iodoform test: Ethanol when reacted with (I₂ and NaOH) or NaOI gives yellow ppt of iodoform since it has the presence of CH₃-CH (OH)- group.



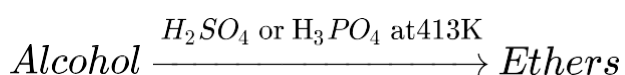
- **Structure of ethers:**



Methoxymethane
(Ether)

- **Preparation of ethers:**

a) From alcohols



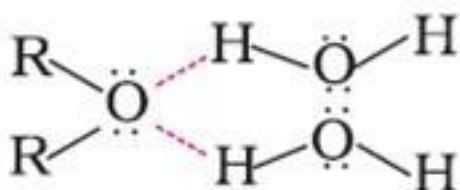
b) From alkyl halide and sodium alkoxide



Here, the alkyl halide should be primary and alkoxide should be tertiary. In case of aromatic ether, the aromatic part should be with phenoxide ion.

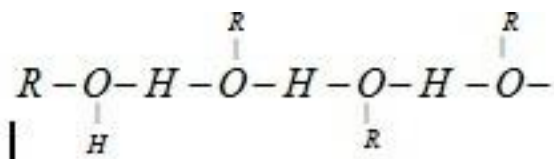
- **Physical properties of ethers:**

a) Miscibility: Miscibility of ethers with water resembles those of alcohols of the same molecular mass. This is due to the fact that just like alcohols, oxygen of ether can also form hydrogen bonds with water molecule.



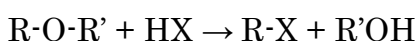
b) Boiling points:

Ethers have much lower boiling points than alcohols. This is due to the presence of hydrogen bonding in alcohols. Hydrogen bonding is absent in ethers.



• Chemical properties of ethers:

a) Cleavage of C-O bond in ethers:

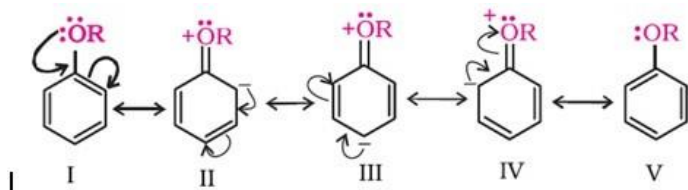


Excess

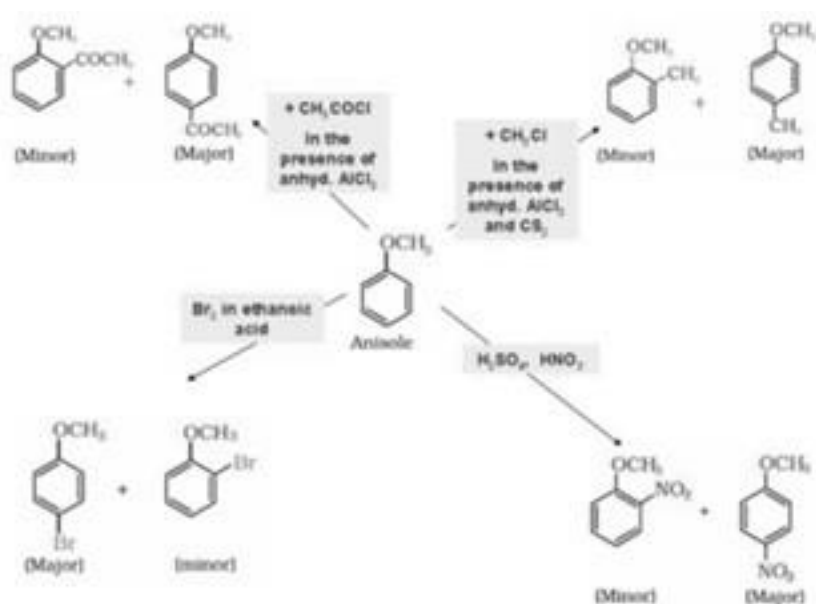
The order of reactivity of hydrogen halides is as follows: $HI > HBr > HCl$

Alkyl halide formed is always the lower alkyl group. But if a tertiary alkyl group is present, the alkyl halide is always tertiary. In case of phenolic ethers, the cleavage occurs with the formation of phenol and alkyl halide.

b) Electrophilic substitution reaction in aromatic ethers:

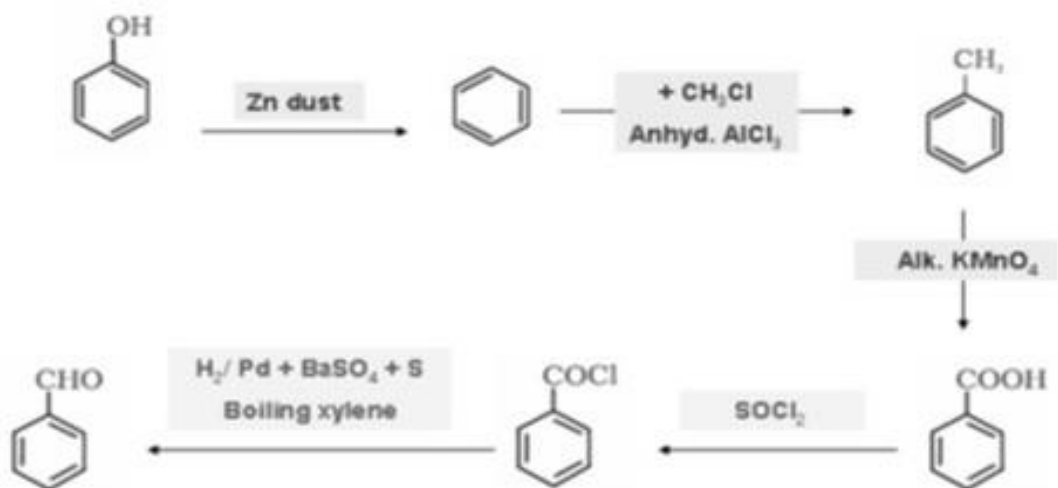


The electrophilic substitution reaction of aromatic ether involves the following reaction:



- Other conversion reactions:

a) Phenol to salicylaldehyde



b) Phenol to benzene diazonium chloride

