

CHEMISTRY STUDY MATERIALS FOR CLASS 12

(NCERT Based Key Points of Chapter - 11)

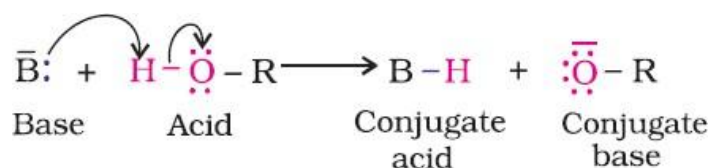
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DATE:- 25/09/2021

Alcohols, Phenols and Ethers

1. Acidic nature:

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



The acidic character of alcohols is due to the polar nature of O–H bond.

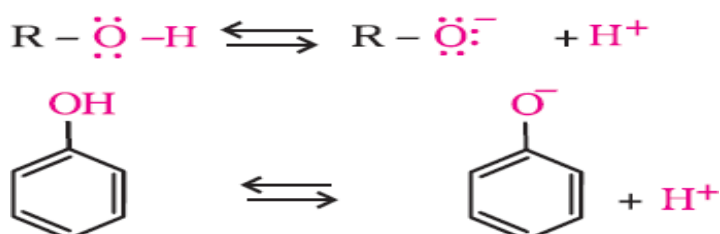
Alkyl group is an electron-releasing group (–CH₃, –C₂H₅) or it has electron releasing inductive effect (+I effect).

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.

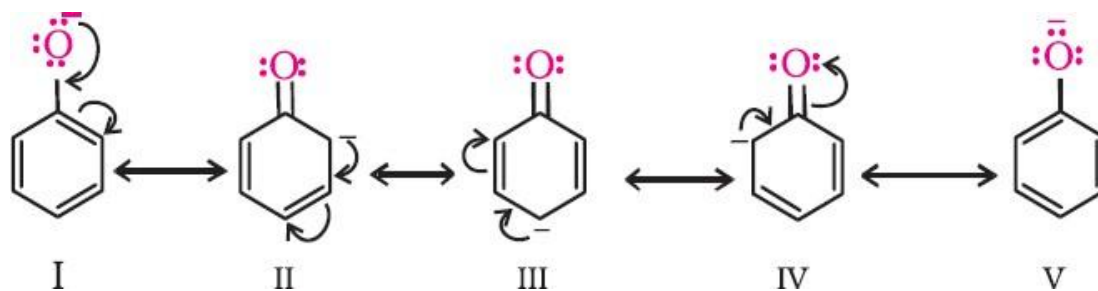
b. Phenol is more acidic than alcohol because:

- 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.

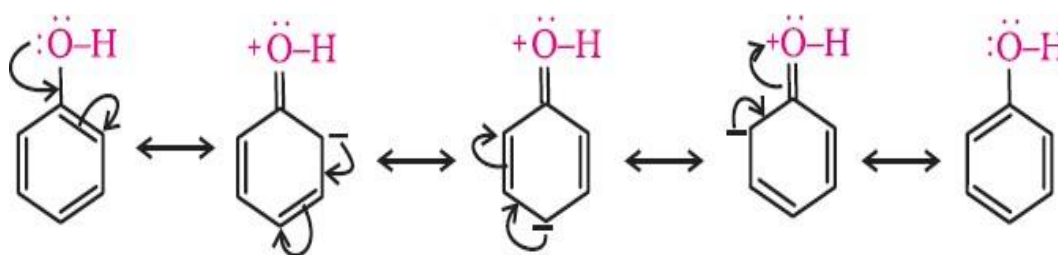


- The ionisation of an alcohol and a phenol takes place as follows: 2

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.



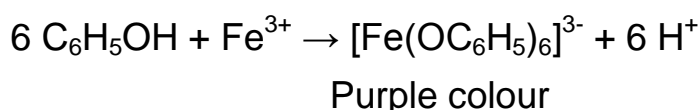
- c.** In substituted phenols, the presence of electron withdrawing groups such as nitro group enhances the acidic strength of phenol. On the other hand, electron releasing groups, such as alkyl groups, in general, decreases the acid strength.

It is because electron withdrawing groups lead to effective delocalisation of negative charge in phenoxide ion.

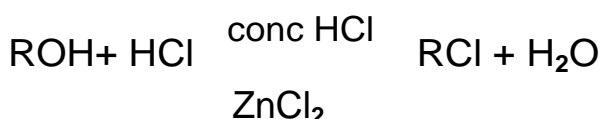
2. How to distinguish between some important pair of organic compounds:

a. Phenol and alcohol:

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



b. Primary, secondary and tertiary alcohol: (Lucas reagent test:)



If it is a primary alcohol, no turbidity appears at room temperature. Turbidity appears only on heating.

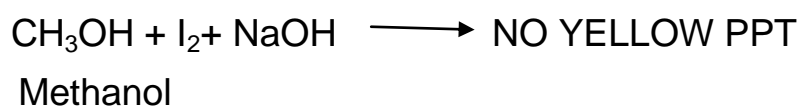
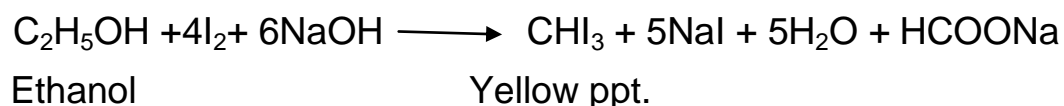
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If it is a secondary alcohol, turbidity appears in 5 minutes.

If it is a tertiary alcohol, turbidity appears immediately.

c. Methanol and ethanol: (Iodoform test)

Ethanol when reacted with (I_2 and NaOH) or NaOI gives yellow ppt of iodoform since it has the presence of $CH_3-CH(OH)-$ group.



3. Preparation of ethers:

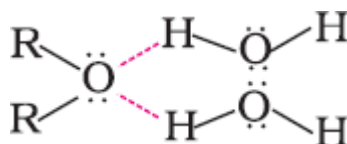


Important:

- Alkyl halide should be primary
- Alkoxide should be tertiary
- If aromatic ether has to form, the aromatic part should be with phenoxide ion

4. Physical properties of ethers:

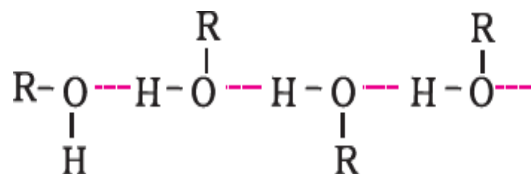
a. Miscibility:



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.

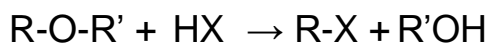
b. Boiling points:

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.



5. Chemical properties of ethers:

a. Cleavage of C–O bond in ethers:



Excess

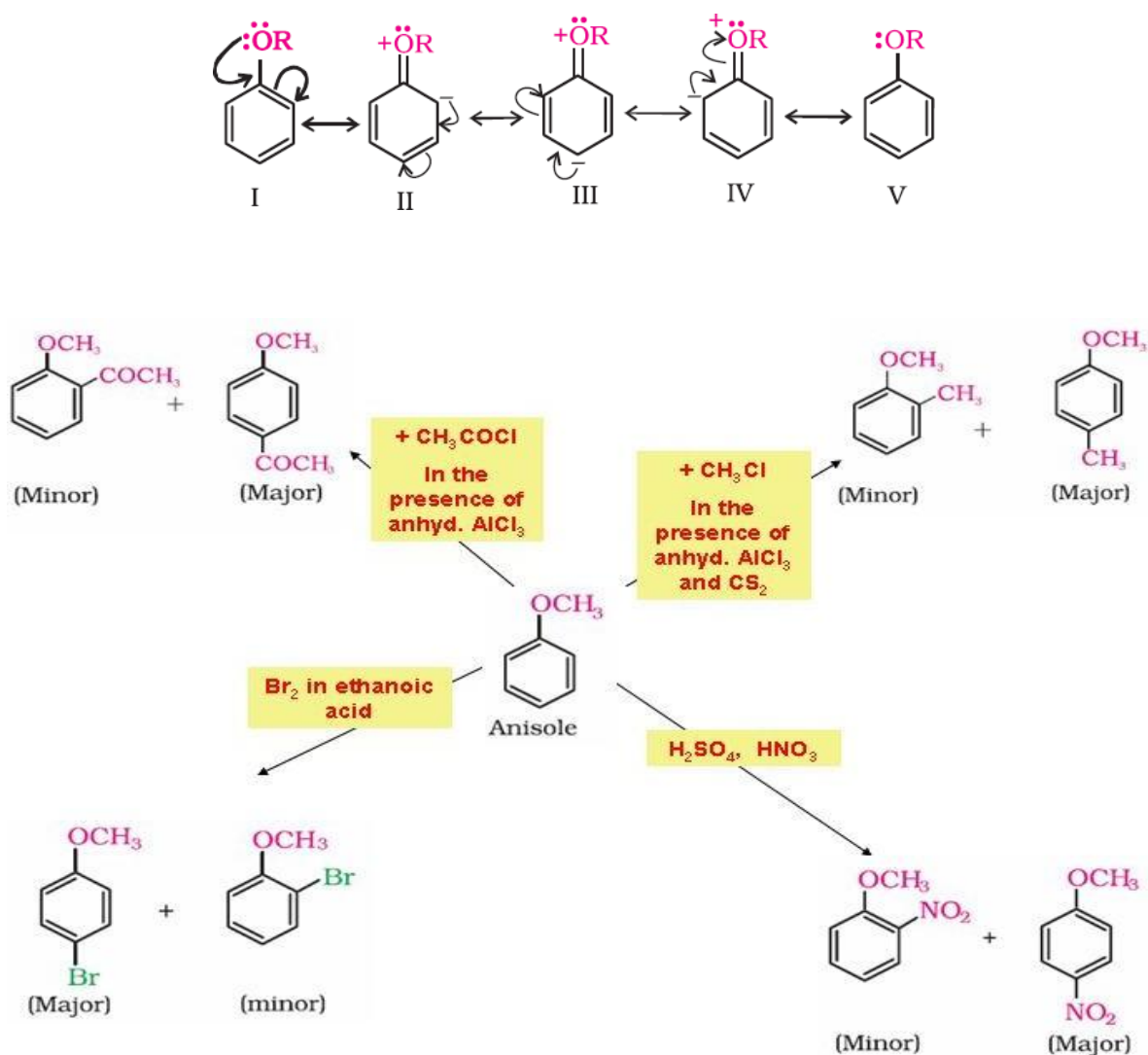
The order of reactivity of hydrogen halides is as follows: $\text{HI} > \text{HBr} > \text{HCl}$

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.

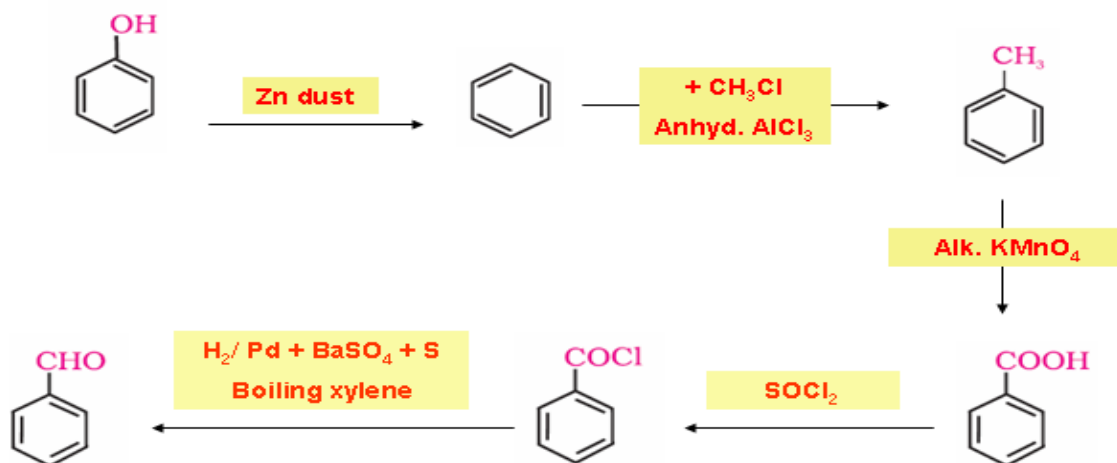
b. Electrophilic substitution reaction in aromatic ethers:



6. Some important reactions for conversions:

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a. Conversion 1:



b. Conversion 2:

