ALCOHOLS, PHENOLS AND ETHERS

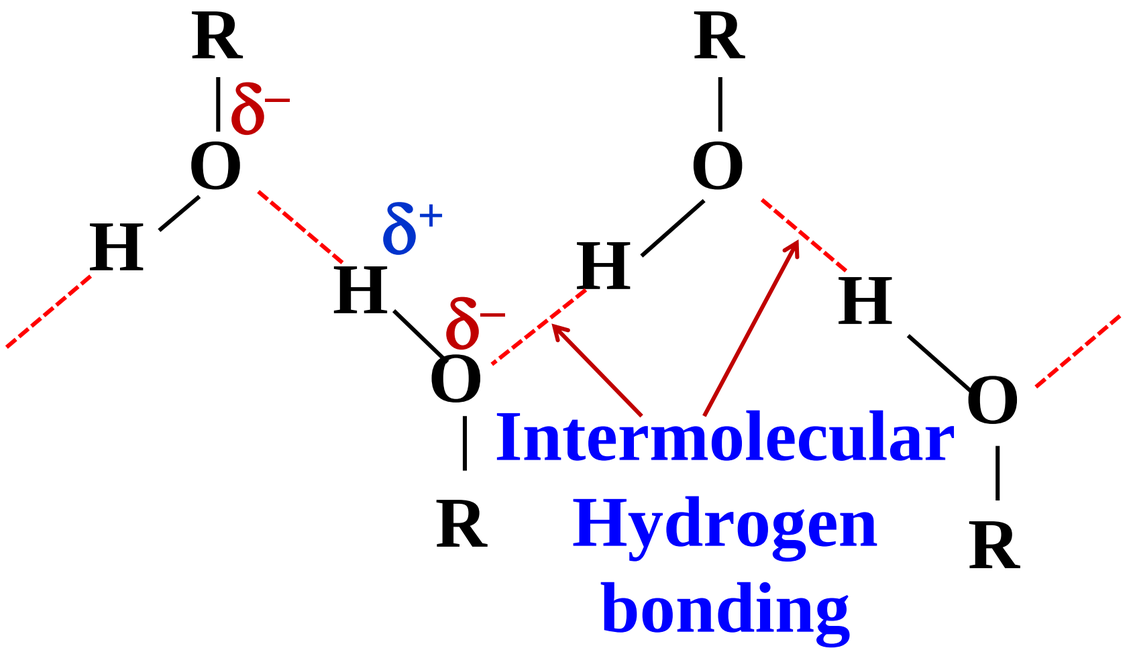
PROPERTIES OF ALCOHOLS

Physical properties of alcohols

- **Lower members are colourless liquids and have distinctive smell.**
- **Higher members are solids and almost colourless.**
- **Lower members of alcohols are soluble in water, solubility decreases with increase in their molecular weight.**

Physical properties of alcohols

- **Alcohols have high boiling points than that of corresponding alkanes, alkyl halides, aldehydes, ketones, ethers etc. due to the presence of intermolecular hydrogen bonding.**



Physical properties of alcohols

- Such hydrogen bonding is absent in alkyl halide, aldehydes, ketones, etc. and we require more energy to break this hydrogen bonding in case of alcohol, therefore, Alcohols have more boiling points than that of corresponding alkanes, alkyl halides, aldehydes, ketones, etc.

- Boiling point of alcohols increases with increase in their molecular weights.

Note :

- **Branched chain alcohols have low boiling points due to weak *Vander Waals forces.***
- **Alcohols are neutral to litmus.**
- **Alcohols are acting as Bronsted acids as well as lewis bases, therefore they are reactive.**

Chemical Properties of Alcohols (R – O – H)

Reactions involving breaking of O – H bond

(Reactivity of alcohols $1^0 > 2^0 > 3^0$)

Reactions involving breaking of R – O i.e. C – O bond

(Reactivity of alcohols $3^0 > 2^0 > 1^0$)

Chemical Properties of Alcohols

Reactions involving breaking of O – H bond

$$6H_5C_2 - OH + 2Al \rightarrow 2\,(H_5C_2O)_3\,Al + 3H_2\uparrow$$

Action of Metals

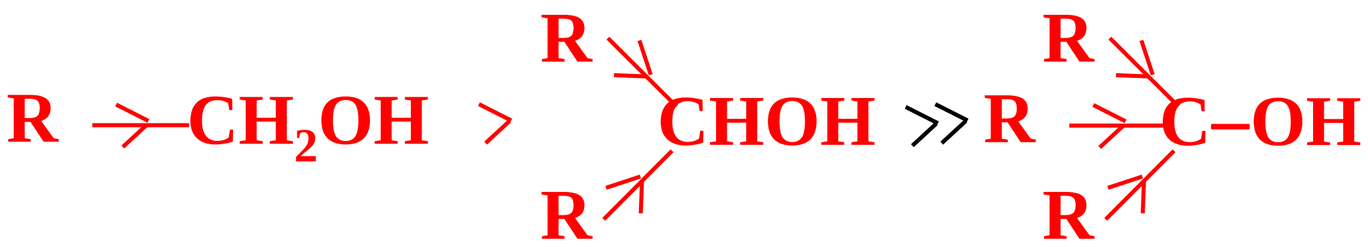
$$2R - OH + 2\,Na \rightarrow 2\,R - O\,Na + H_2\uparrow$$

$$2H_3C - OH + 2Na \rightarrow 2\,H_3C - ONa + H_2\uparrow$$

(sodium methoxide)

Acidity of alcohols:

Electron-releasing group ($-CH_3$, $-C_2H_5$) $\propto$ $\frac{1}{\text{Acid strength}}$



Primary **Secondary** **Tertiary**

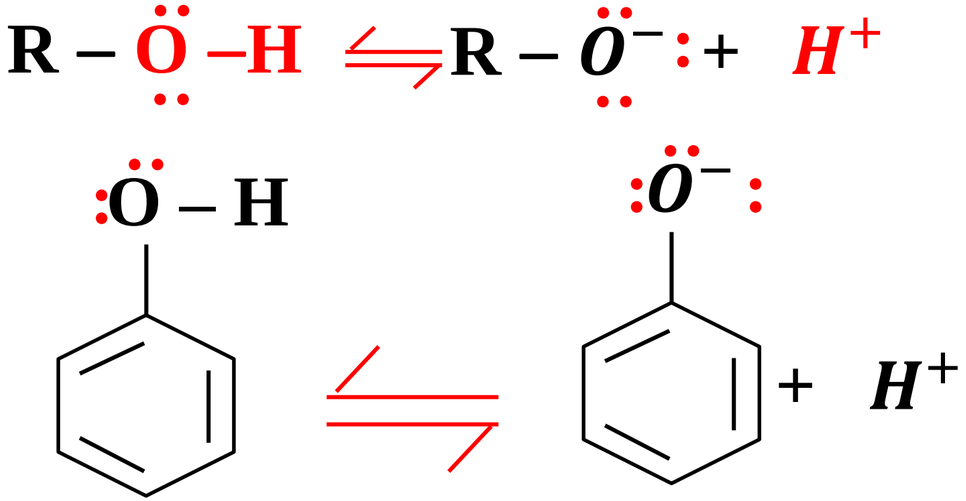
Alcohol can act as Brönsted acid as well as a Lewis base due to donation of proton and presence of unpaired electron on oxygen respectively.

- **Ethers do not have H-bond, so they have boiling points similar to hydrocarbons.**
- **Ethers are only slightly soluble in water and are highly flammable.**

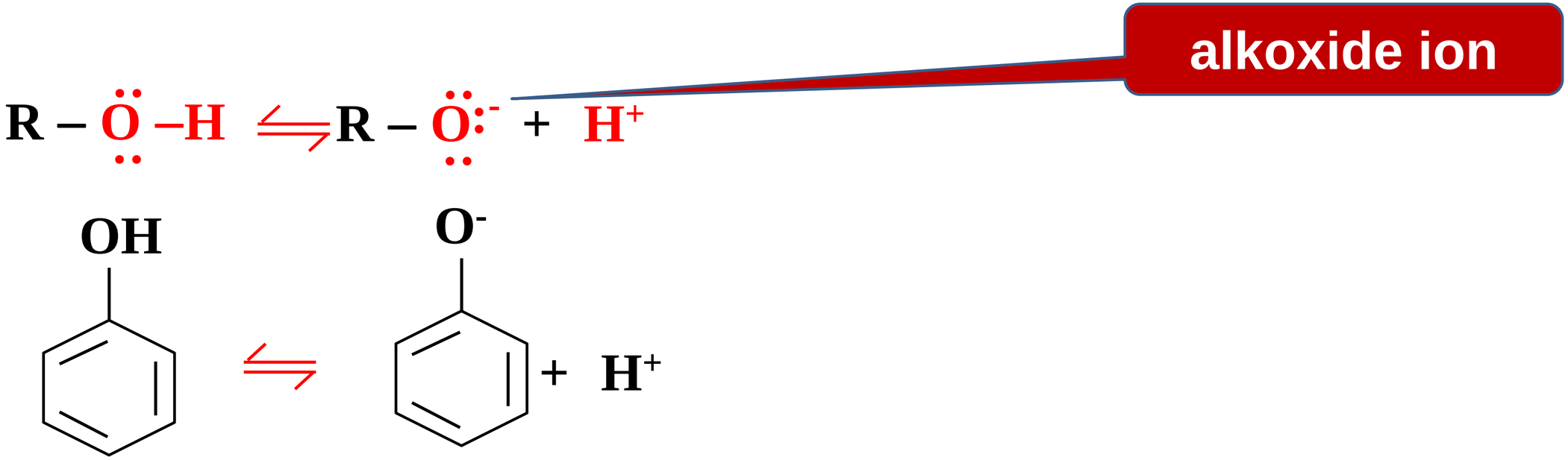
Acidity of phenols:

- **The reaction of phenol with metals like sodium, aluminum and sodium hydroxide indicate its acidic nature.**

This is because OH group directly attached to benzene ring of sp^2 hybridized carbon in phenol experiences electron withdrawing effect by benzene ring resulting in ionization of O-H more readily.



Comparity of acidic nature of phenols and aliphatic alcohols



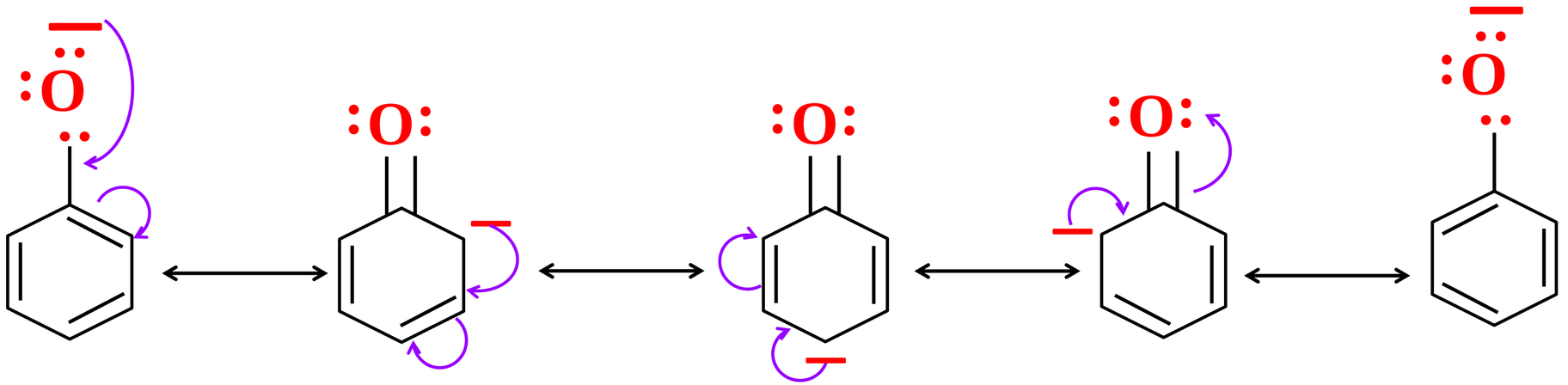
Phenoxide ion

- **The delocalization of negative charge makes phenoxide ion more stable and favours the acidic nature to the phenol (Resonance).**

- **Where as in alkoxide ion the negative charge is localized on oxygen. Hence the acidic nature of phenol is more than alcohol.**

- **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 phenoxide ion more stable and favours the ionisation of phenol.**



Reactions involving breaking of O – H bond

Esterification

Ethanol Acetic acid

i) $H_5C_2 - O\,H + H_3C - C(=O) - OH$

Dil. H_2SO_4 ⇌ Conc. H_2SO_4

$H_3C - C(=O) - O - C_2H_5 + H_2O$

Ethyl acetate

or

Ethylethanoate

Conc. H_2SO_4 is acting as a dehydrating agent

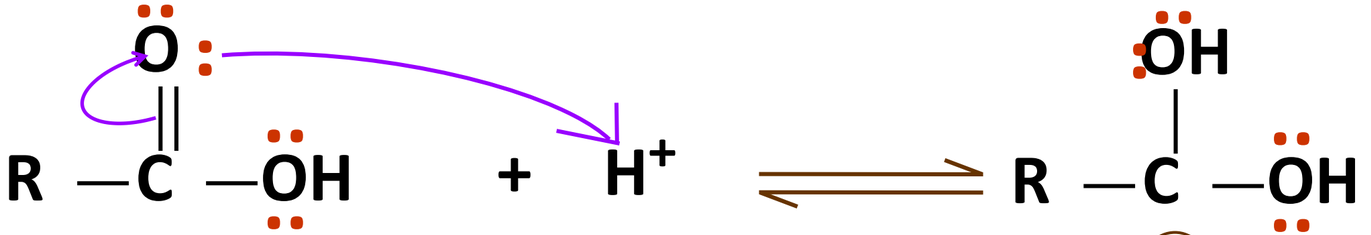
Note :

1) Hydrolysis of an ester is a reversible reaction of Esterification.

2) This reaction involves breaking of acyl – oxygen linkage.

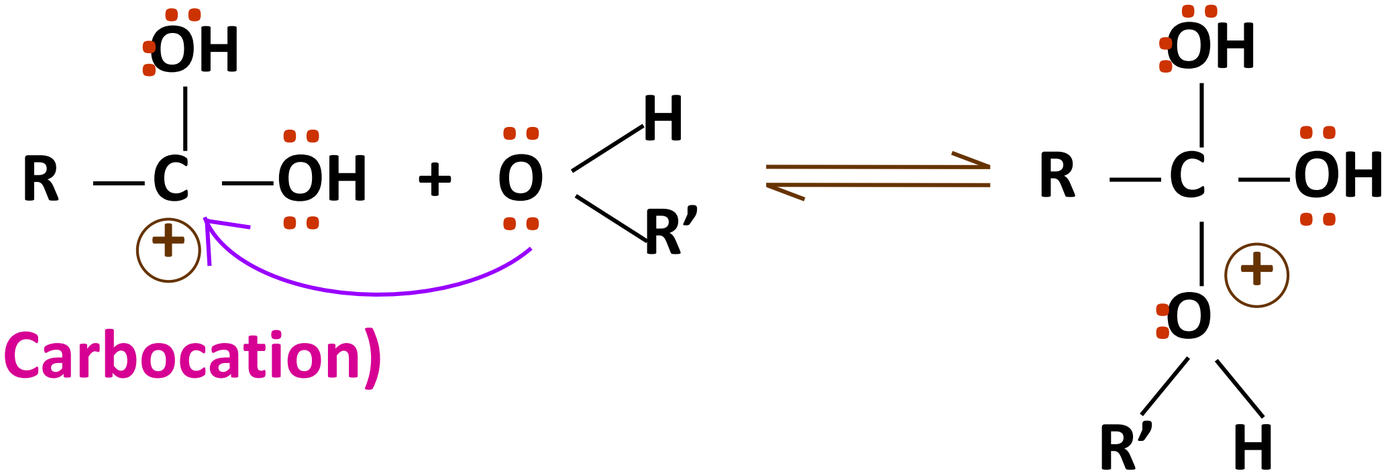
Mechanism : It involves following 3 steps :

Step I : Protonation of the carbonyl group:



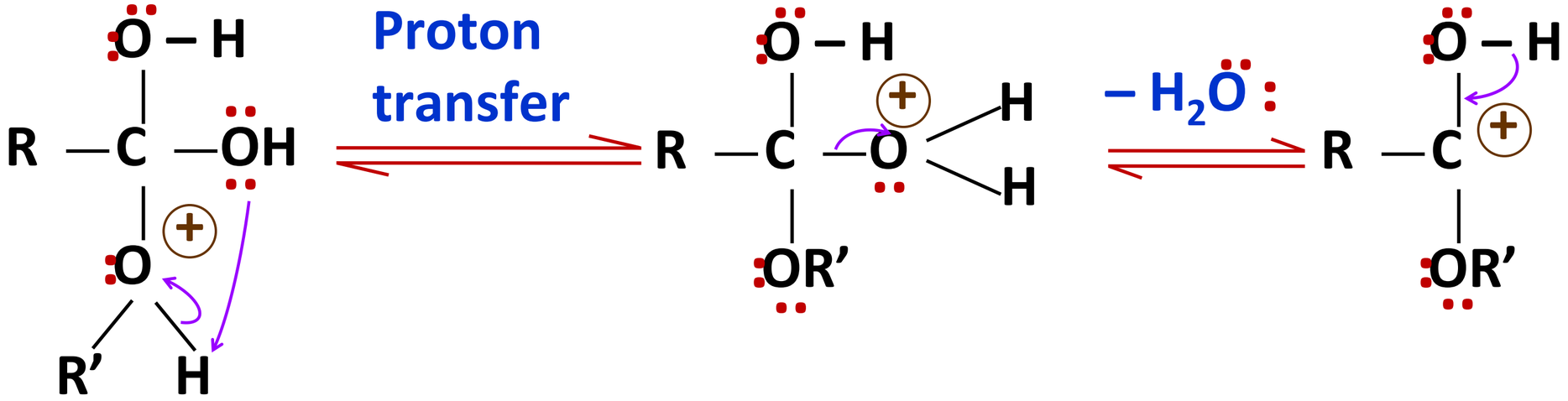
(Carbocation)

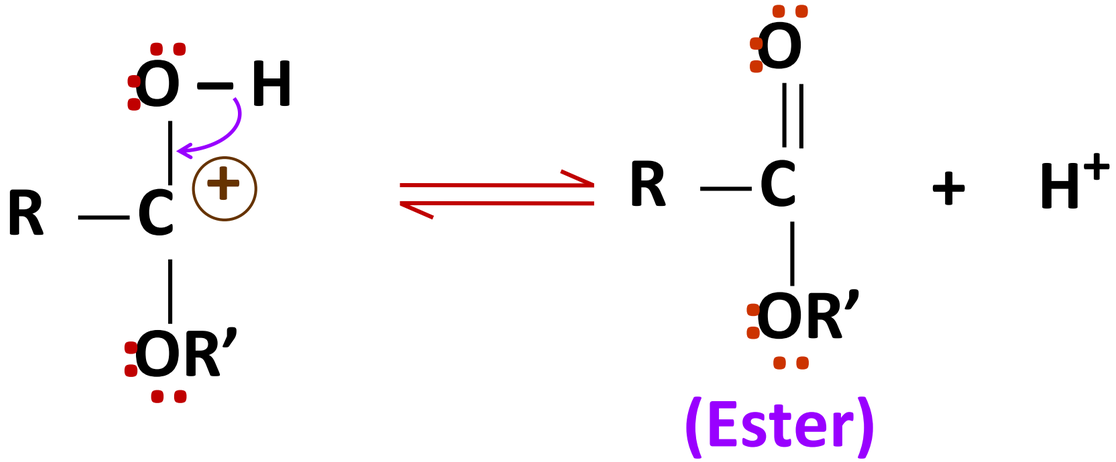
Step II :Nucleophilic attack by the alcohol molecule:



(Carbocation)

Step III : Loss of water molecule and a proton transfer :

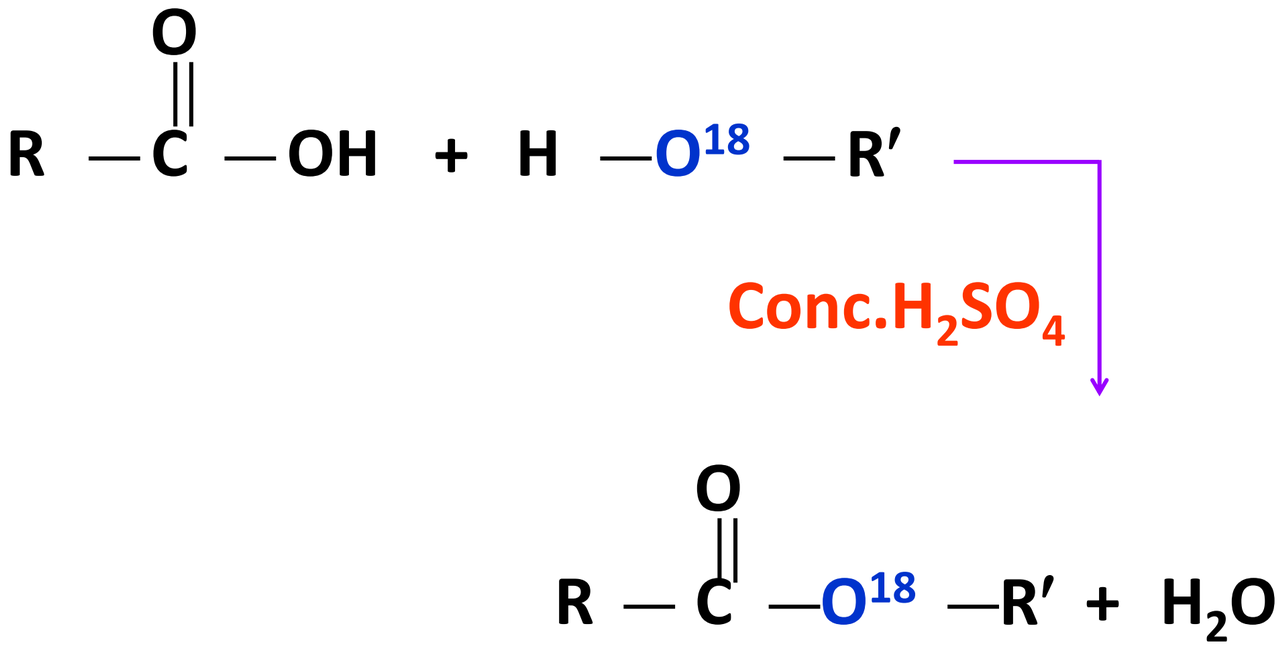




Note

It is observed from the experiments of **tracer technique** that,

1) If an esterification is carried out by using an alcohol containing radio – isotopic oxygen, O^{18} is found in *ester*.



MCQs

1. **Reactivity of alcohols towards reactions involving breaking of O – H bond…**

   a) $1^0 > 3^0 > 2^0$

   b) $1^0 > 2^0 > 3^0$ ✓

   c) $3^0 > 1^0 > 2^0$

   d) $2^0 > 1^0 > 3^0$

2. Esterification is … process

a) Irreversible

b) reversible

c) discontinuous

d) None of these

3. Ester is obtained when alcohols react with…

a) Carboxylic acids ✓

b) metals

c) Aldehydes

d) Ketones

4. Alcohols when react with metals, gives corresponding…

a) alkane

b) alkoxides 

c) ester

d) Metal oxides

ACTION OF HALOACID
LUCAS TEST

Reactions involving breaking of C – O bond

Action of Haloacid

Conc. HCl + Anhydrous $ZnCl_2$ = Lucas reagent

R – OH + Lucas reagent = The reaction is called Groove's process.

This is called Lucas test for alcohols.

(R – Cl is prepared)

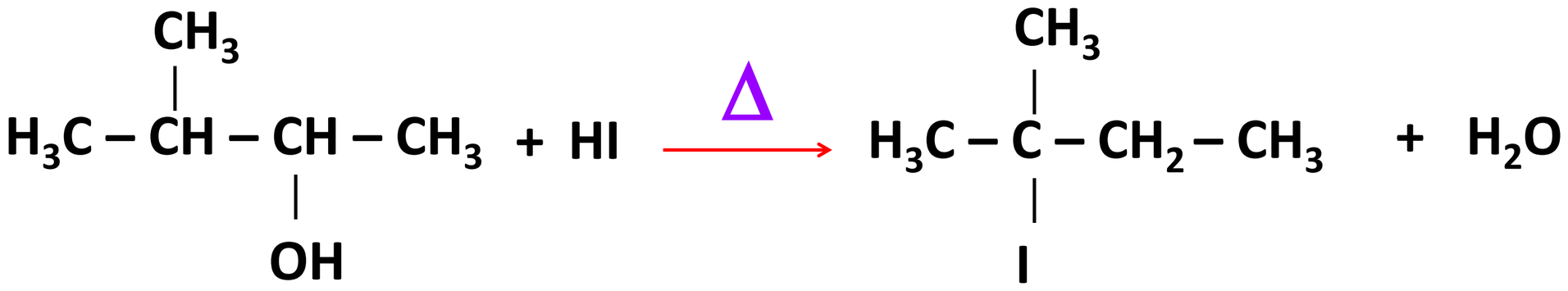
Note : Distinguishable reaction between 1^0, 2^0 and 3^0 alcohol

⇒ 3^0 alcohol —(Lucas reagent)→ Immediate appearance of turbidity.

⇒ 2^0 alcohol —(Lucas reagent)→ Turbidity within 5 min.

⇒ 1^0 alcohol —(Lucas reagent)→ Do not produce turbidity at room temp.

Note :

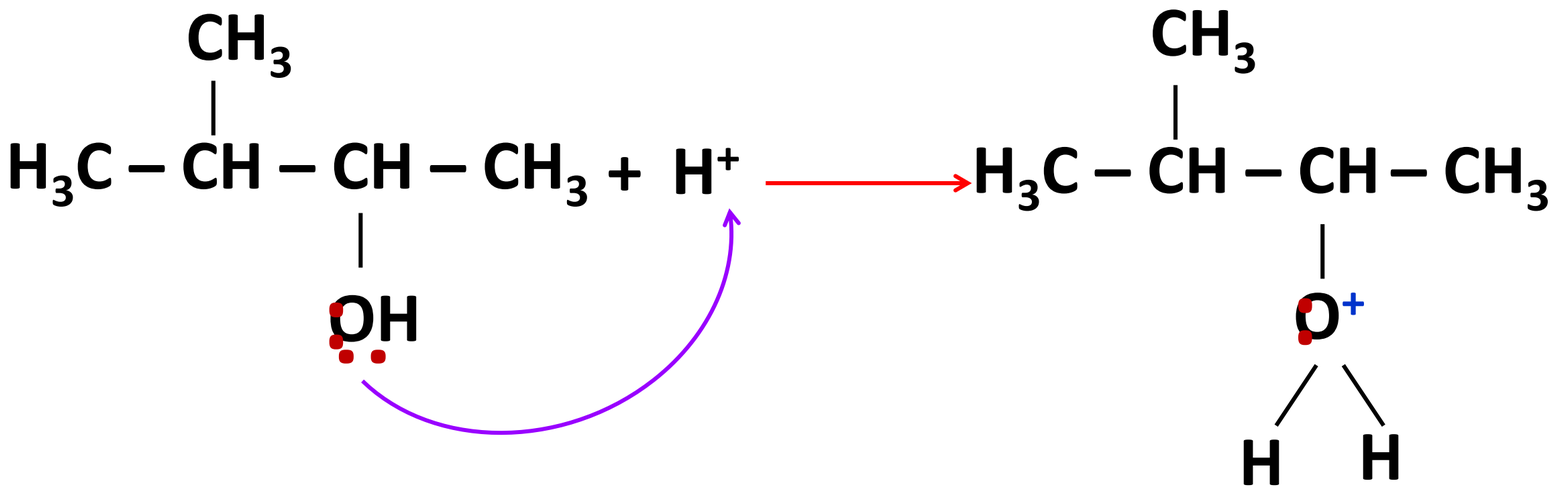


(2^0 alcohol)

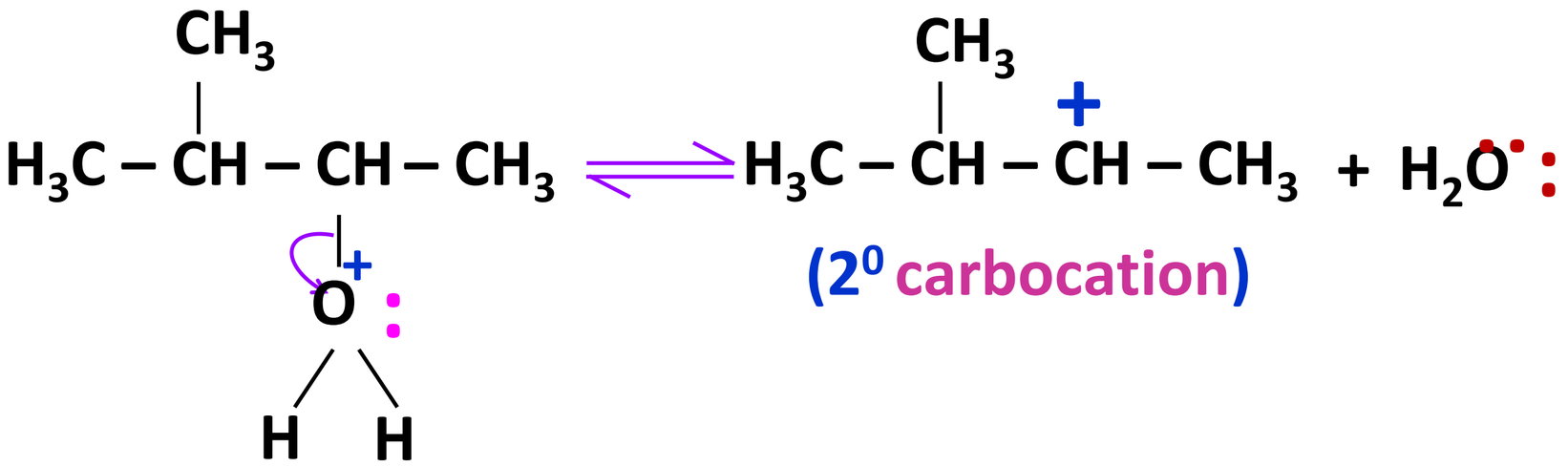
(ter-pentyliodide) (3^0)

Mechanism :

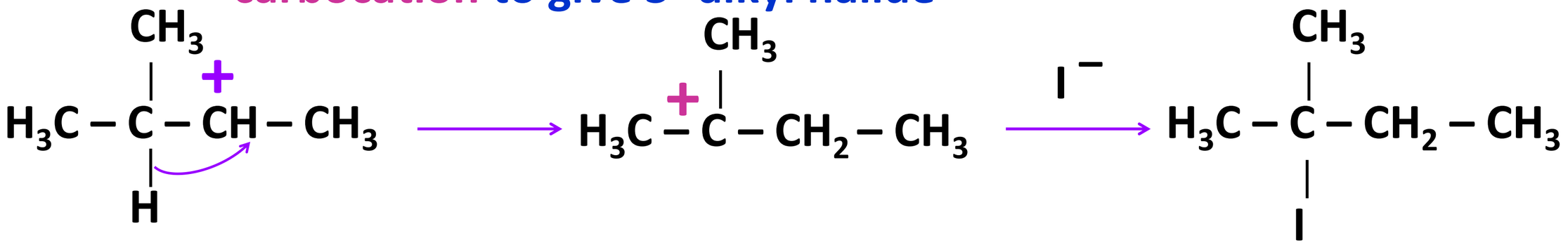
Step I : The alcohol is protonated by an acid :



Step II : Formation of carbocation :



Step III : Hydride shift followed by formation of stable 3^0 carbocation to give 3^0 alkyl halide



(2^0 carbocation) (3^0 carbocation) (3^0)

(more stable)

MCQs

1. Primary, secondary and tertiary alcohols are distinguished by…

a) Oxidation method

b) Lucas test

c) Victor Meyer’s method

d) All the above ✓

2. **Which alcohol is most reactive towards HCl in the presence of anhydrous $ZnCl_2$?**

a) primary

b) secondary

c) tertiary 

d) All are equal

3. Lucas reagent is…

a) Conc. HNO_3 + anhydrous $MgCl_2$

b) dil. HCl + anhydrous $ZnCl_2$

c) Conc. HNO_3 + anhydrous $ZnCl_2$

d) Conc. HCl + anhydrous $ZnCl_2$ 

REACTIONS INVOLVING BREAKING OF C – O BOND

Reactions involving breaking of C – O bond

- With PX_3

$$3\ R-OH + PX_3 \rightarrow 3\ R-X + H_3PO_3$$

- With PCl_5

$$R-OH + PCl_5 \rightarrow R-Cl + POCl_3 + HCl$$

Reactions involving breaking of C –O bond

Darzen's Method

Best method for chlorination due to by products are gases

With $SOCl_2$

$$R - OH + SOCl_2 \xrightarrow[\text{Reflux}]{\text{Pyridine}} R - Cl + SO_2 \uparrow + HCl \uparrow$$

MCQs

1. Alcohols on treatment with PCl_3, gives…

a) alkyl bromide

b) alkane

c) alkyl chloride ✓

d) None of these

2. Best method to prepare alkyl chloride is...

a) Reaction of alcohol with $SOCl_2$

b) Darzen's method

c) Reaction of alcohol with PCl_3

d) Both a & b ✓


Thank you...