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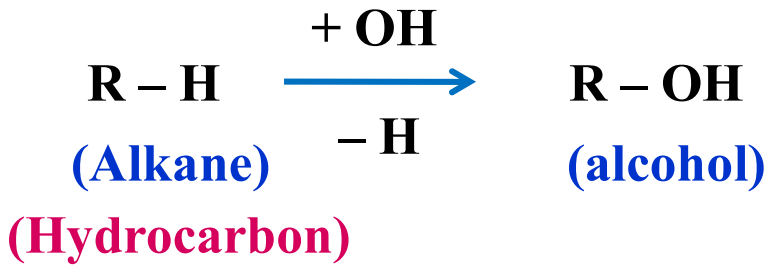
An Initiative by अमर उजाला

ALCOHOLS, PHENOLS AND ETHERS

INTRODUCTION TO ALCOHOLS

Alcohols



Now, replace hydrogen of alkane with hydroxyl group

Alcohols are the hydroxyl derivatives of hydrocarbons in which one or more hydrogen atoms are replaced by corresponding number of hydroxyl (– OH) group(s).

For e.g. H_3C – OH (Methyl alcohol),

H_5C_2 – OH (Ethyl alcohol), etc.

MCQs

1. R – H means…

a) Alkane

b) Alkynes

c) Alkene

d) Both a & b

2. Functional group of an alcohol is…

a) – O –

b) – OH

c) – C –OH
‖
O

d) –CHO

3. Alcohols are … derivatives of hydrocarbons

a) keto

b) hydroxyl

c) aldehyde

d) halogen

4. C_2H_5OH (Name of this compound is _____)

a) methyl alcohol

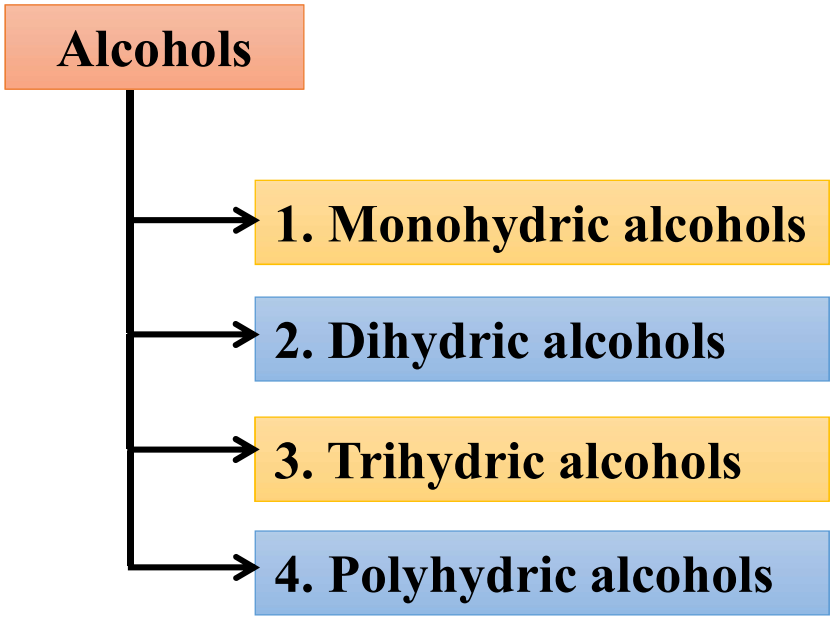
b) butyl alcohol

c) ethyl alcohol ✓

d) isopropyl alcohol

CLASSIFICATION OF ALCOHOL (PART-I)

Classification of alcohols



Classification of alcohols

1. Monohydric alcohols

(Contains only one – OH group)

How many hydroxyl groups does it contain?

For eg.

$CH_3 – OH$

(Methyl alcohol)

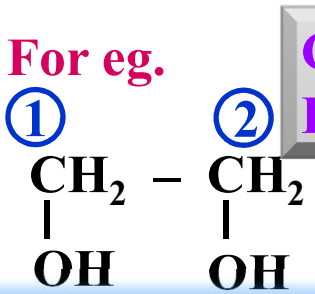
Classification of alcohols

2. Dihydric alcohols

(Contain two – OH groups)

What is the IUPAC name of this compound ?

For eg.



Common name:
Ethylene glycol

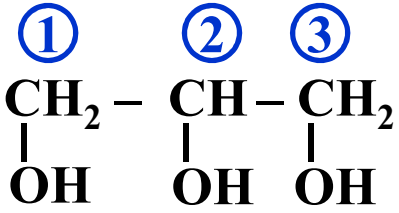
IUPAC name:
Ethane – 1, 2 – diol)

Classification of alcohols

3. Trihydric alcohols

(Contain three – OH groups)

For eg.



Common Name:
Glycerol / Glycerin

IUPAC Name:
Propane – 1, 2 ,3 – triol)

What is the IUPAC name of this compound ?

Classification of alcohols

4. Polyhydric alcohols

(Contains four or more than four – OH group)

For eg.

Common Name: Sorbitol

Classification of Monohydric alcohols

According to the type of hybridization of the Carbon atom to which the hydroxyl group is attached :

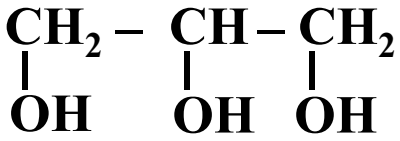
Monohydric alcohols

There are two types of monohydric alcohols

1. Alcohols Containing C_{sp3} – OH bond

2. Alcohols Containing C_{sp2} – OH bond

MCQs

1).  Is a

a) mono hydric alcohol

b) di hydric alcohol

c) tri hydric alcohol

d) Tetra hydric alcohol

CLASSIFICATION OF ALCOHOL (PART-II)

1. Alcohols Containing C_{sp3} – OH bond

Alkyl Alcohols

- **Primary (1^0) alcohols**
- **Secondary (2^0) alcohols**
- **Tertiary (3^0) alcohols**

There are three types of Alkyl alcohols

Alkyl Alcohols

Primary (1^0) alcohols

For eg. 1^0

$H_3C - CH_2 - OH$

IUPAC Name: Ethanol

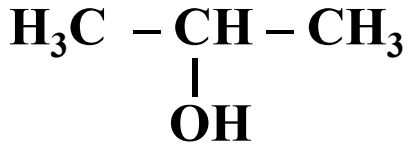
To what type of carbon OH group is attached?

In primary alcohols hydroxyl group is attached to 1^0 Carbon atom or Primary carbon.

Alkyl Alcohols **Secondary (2^0) alcohols**

In secondary alcohols hydroxyl group is attached to 2^0 Carbon atom.

For eg. **2^0 - Carbon**



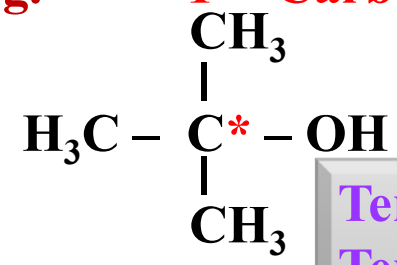
(Iso/sec – propyl alcohol)

IUPAC Name:
Propanol-2 or Propan-2-ol

Alkyl Alcohols | **Tertiary (3^0) alcohols**

In tertiary alcohols hydroxyl group is attached to 3^0 or Tertiary carbon atom)

For eg. **1^0 - Carbon**



*** is 3^0 - Carbon**

Tertiary – butyl alcohol (or)
Ter-butylalcohol

IUPAC Name:
2-methylpropan-2-ol

1. Alcohols Containing C_{sp3} – OH bond

Allylic Alcohols

There are three types of Allylic alcohols

(Hydroxyl group is attached to a sp^3 hybridised carbon atom next to the C = C i.e. to an allylic carbon

Allylic Alcohols

1^0 allylic alcohols

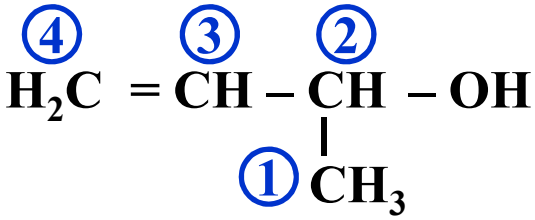
For eg.

(Prop – 2 – en – 1 – ol)

Allylic Alcohols

2^0 allylic alcohols

For eg.

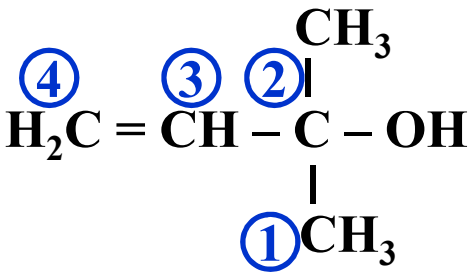


(But – 3 – en – 2 – ol)

Allylic Alcohols

3^0 allylic alcohols

For eg.



(2 – Methyl but – 3 –en – 2 – ol)

MCQs

1). $CH_2 = CH - CH_2 - OH$ is a…

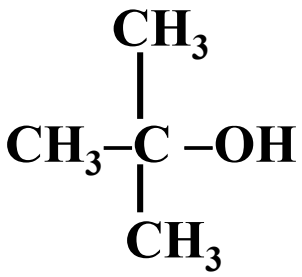
a) Primary alcohols

b) Secondary alcohols

c) Tertiary alcohols

d) Quaternary alcohols

MCQs

2). 

a) Primary alcohols

b) Secondary alcohols

c) Tertiary alcohols

d) Quaternary alcohols

3). Which one of the following is a secondary alcohol?

a) 2 – methyl -2- propanol

b) 1- propanol

c) 1- butanol

✔ d) 2- pentanol

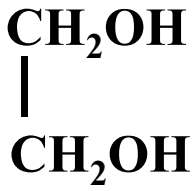
4). 2 - methyl pentanol -1 is a…

a) 1^0 alcohol

b) 2^0 alcohol

c) 3^0 alcohol

d) enol

5).  is a…

a) 1^0 alcohols

b) 2^0 alcohols

c) 3^0 alcohols

d) Carbinol

CLASSIFICATION OF ALCOHOL (PART-II)

1. Alcohols Containing C_{sp3} – OH bond

There are three types of Benzylic alcohols

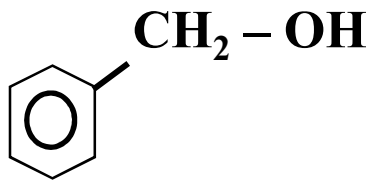
Benzylic alcohols

- 1^0 benzylic alcohols
- 2^0 benzylic alcohols
- 3^0 benzylic alcohols

Benzylic alcohols

1^0 benzylic alcohols

For eg.



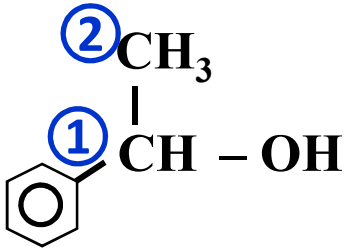
(Benzyl alcohol)

(Phenyl methanol)

Benzylic alcohols

2^0 benzylic alcohols

For eg.

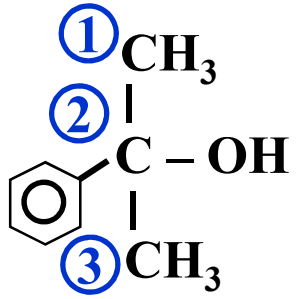


(1 – Phenyl ethanol)

Benzylic alcohols

3^0 benzylic alcohols

For eg.



(2 – Phenyl propan – 2 – ol)

Classification of Monohydric alcohols

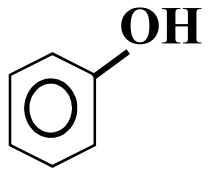
2. Alcohols Containing C_{sp2} – OH bond

- **– OH group is attached to a sp^2 hybridised carbon atom i.e. vinylic carbon or aryl carbon. these alcohols are also known as vinylic alcohols or phenols.**

For eg.

$H_2C = CH – OH$

(Vinyl alcohol)



(Phenol)

MCQs

1). In alkyl alcohol –OH group is attached to… hybridized carbon atom

a) sp^2

b) sp

c) sp^3 ✓

d) sp^3d

2). In secondary alcohol, hydroxyl group is attached to… carbon atom.

a) Primary (1^0)

b) Tertiary (3^0)

c) Secondary (2^0) ✓

d) None of these

3).  —CH_2OH is…

a) Primary benzylic alcohol

b) Secondary benzylic alcohol

c) Tertiary benzylic alcohol

d) None of these

4). In vinylic alcohols, – OH group is attached to…hybridized carbon atom.

a) sp

b) sp^2

c) sp^3

d) sp^3d

NOMENCLATURE

Nomenclature

No.	Structure	C
1.	$H_3C - OH$	Methyl alcohol

Common name:- common name of alkyl group(Methyl)+alcohol =Methyl alcohol

I.U.P.A.C. Name
Methanol

Root word +an + ol= Meth+an+ol=Methanol

Nomenclature

No.	Structure	Common Name
2.	$H_3C - CH_2 - OH$	Ethyl alcohol

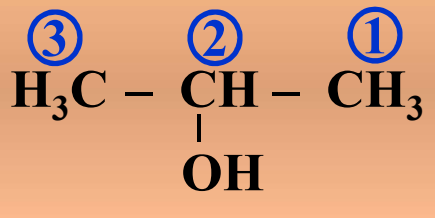
I.U.P.A.C. Name
Ethanol

Nomenclature

No.	Structure	Common Name
3.	$\overset{③}{H_3}C - \overset{②}{CH_2} - \overset{①}{CH_2} - OH$	n – propyl alcohol

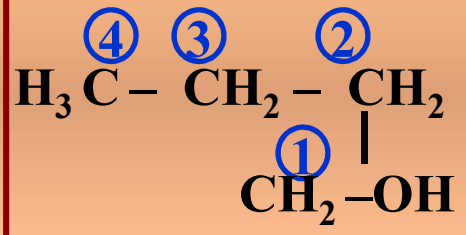
I.U.P.A.C. Name
Propan – 1 – ol

Nomenclature

No.	Structure	Common Name
4.		Iso / sec – propyl alcohol

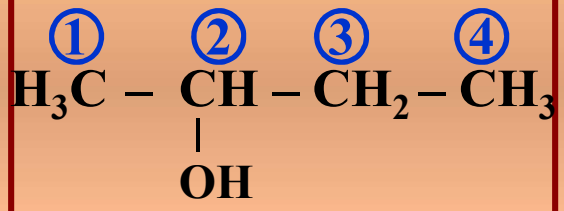
I.U.P.A.C. Name
Propan – 2 – ol

Nomenclature

No.	Structure	Common Name
5.		n – butyl alcohol

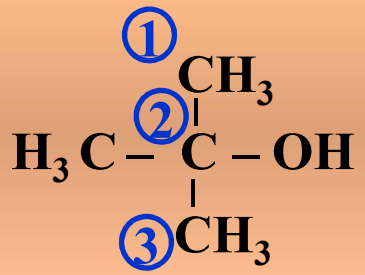
I.U.P.A.C. Name
Butan – 1 – ol

Nomenclature

No.	Structure	Common Name
6.		sec – butyl alcohol

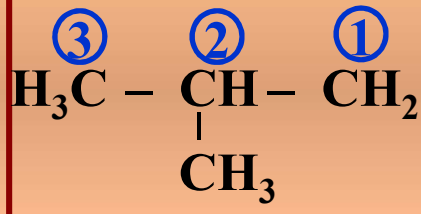
I.U.P.A.C. Name
Butan – 2 – ol

Nomenclature

No.	Structure	Common Name
7.		tert – butyl alcohol

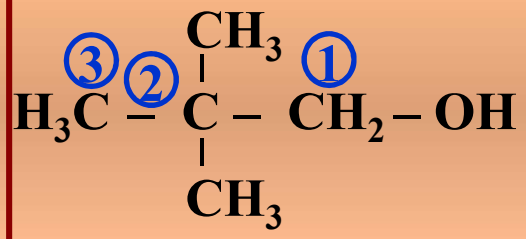
I.U.P.A.C. Name
2 – Methyl propan – 2 – ol

Nomenclature

No.	Structure	Common Name
8.		Isobutyl alcohol

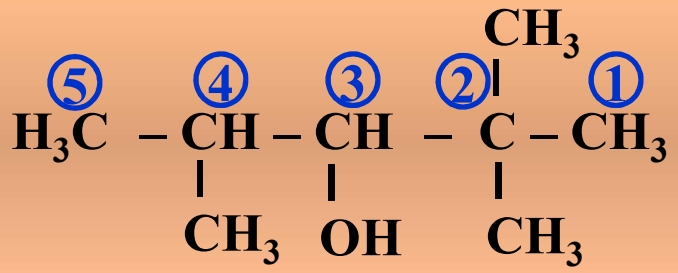
I.U.P.A.C. Name
2 – Methyl propan – 1 – ol

Nomenclature

No.	Structure	Common Name
9.		neo – pentyl alcohol

I.U.P.A.C. Name
2,2–Dimethyl propan – 1 – ol

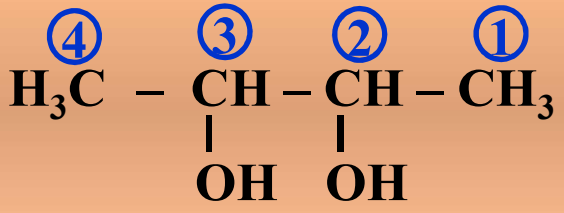
Nomenclature

No.	Structure
10.	

For complicated structure instead of common name IUPAC name is more preferred for example

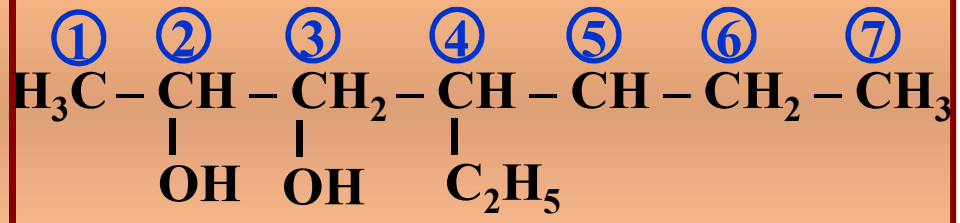
I.U.P.A.C. Name
2,2,4 – Trimethyl pentan – 3 – ol

Nomenclature

No.	Structure
11.	

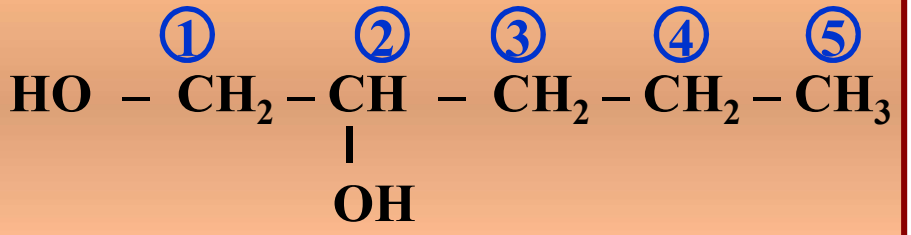
I.U.P.A.C. Name
Butane–2,3–diol

Nomenclature

No.	Structure
12.	

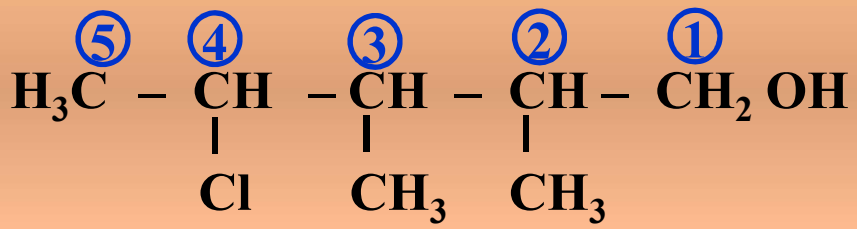
I.U.P.A.C. Name
4–Ethylheptane–2,3–diol

Nomenclature

No.	Structure
13.	

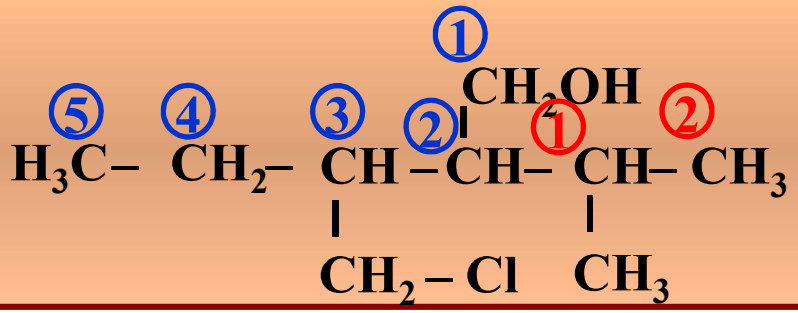
I.U.P.A.C. Name
Pentane –1,2 – diol

Nomenclature

No.	Structure
14	

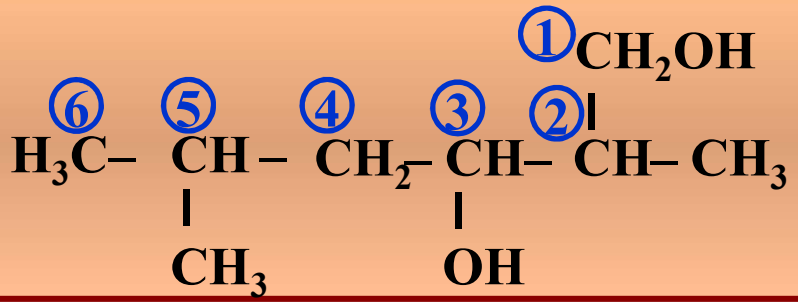
I.U.P.A.C. Name
4 – Chloro–2, 3 – dimethyl pentan – 1 – ol

Nomenclature

No.	Structure
15	

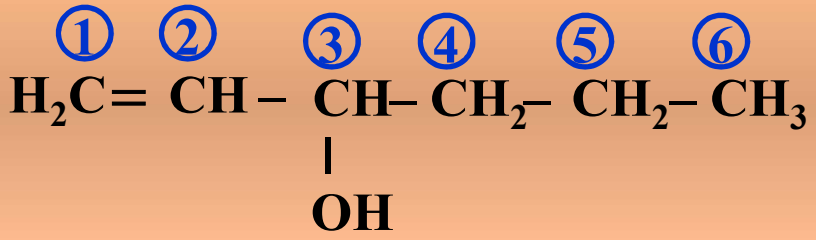
I.U.P.A.C. Name
3 –Chloro methyl – 2 – (1 – methyl ethyl) pentan – 1 – ol

Nomenclature

No.	Structure
16	

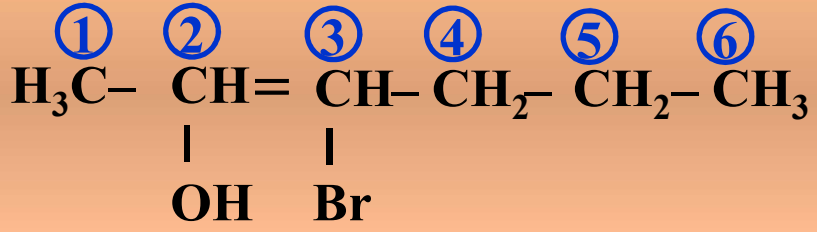
I.U.P.A.C. Name
2,5 – Dimethylhexane –1,3 – diol

Nomenclature

No.	Structure
17	

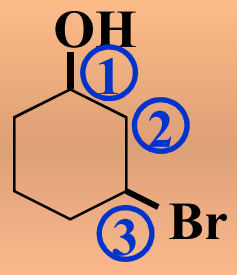
I.U.P.A.C. Name
Hex-1-en-3-ol

Nomenclature

No.	Structure
18	

I.U.P.A.C. Name
3 – Bromo – hex – 2 – en – 2 – ol

Nomenclature

No.	Structure
19	

I.U.P.A.C. Name
3 – Bromo – cyclohexan – 1 – ol

To find out no. of

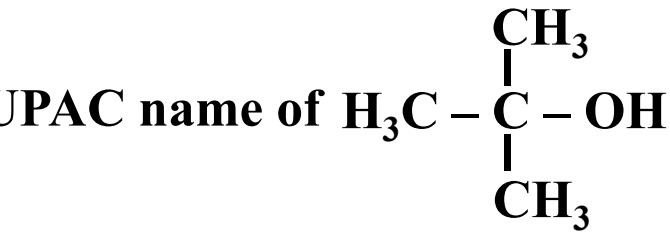
Possible isomers of alkyl alcohols = 2^{n-2}

Possible isomers of alkyl alcohols + ethers = $2^{n-1} - 1$

Possible isomers of ethers = $(2^{n-1} - 1) - (2^{n-2})$

Where, n = No. of Carbon atoms

MCQs

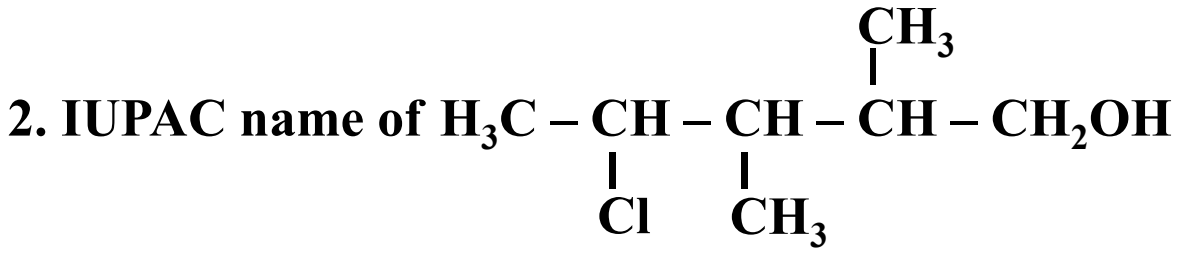
1. IUPAC name of 

a) 2 – Methylpropan – 1 – ol

b) 2 – Methylpropan – 2 – ol

c) 1 – Methylpropan – 3 – ol

d) 1 – Methylpropan – 2 – ol

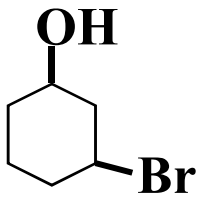
2. IUPAC name of 

a) 2 – Chloro –3, 4– dimethylpentan – 5 – ol

b) 4 – Chloro –2, 3 – dimethylpentan – 2 – ol

c) 4 – Chloro –2, 3 – dimethylpentan – 1 – ol

d) None of these

3. IUPAC name of 

a) 1 – Bromocyclohexanol

b) 5 – Bromocyclohexanol

c) 4 – Bromocyclohexanol

d) 3 – Bromocyclohexanol

4. Possible isomers of alkyl alcohols can be given by…

a) 2^{n-1}

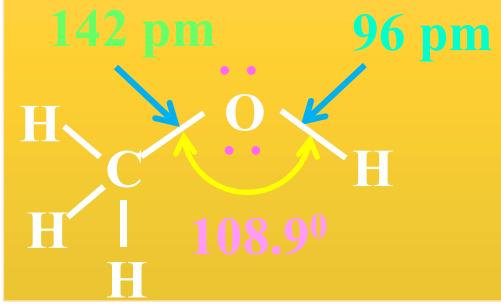
b) 2^{n}

c) 2^{n-2} ✓

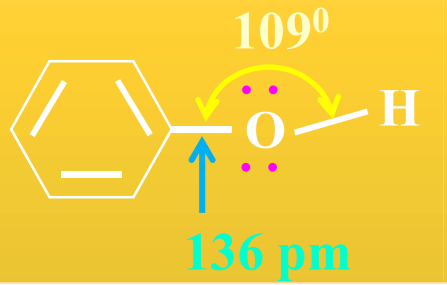
d) $2^{n-1} + 1$

STRUCTURE OF FUNCTIONAL GROUPS

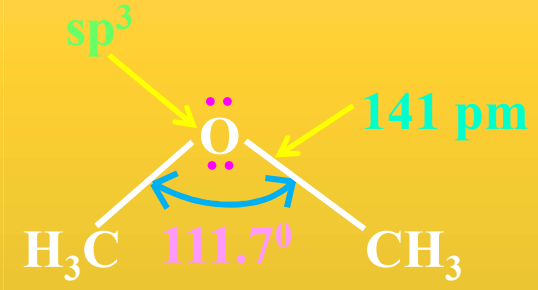
Structure of Methanol



Structure of Phenol



Structure of dimethyl ether



- **The bond angle $\angle$COH in alcohol is slightly less than the tetra hedral bond angle $109^0\ 28'$**
- **It's due to repulsion between the unshared electron pairs of oxygen .**
- **The carbon – oxygen bond length (136 pm) in phenol is slightly less than that in methanol.**
- **It's due to**

I. Partial double bond character (by delocalization)

II. SP^2 – carbon attached to – OH group of phenol.

Order of bond angle:-

Alcohol < Phenol < Ether

Due to big size alkyl groups around the oxygen

Order of bond length :-

Alcohol (or) Ether > Phenol

Uses of Methanol

- **Industrial solvent for oils , fats, gums etc.**
- **For dry cleaning & preparation of perfumes.**
- **As an antifreezing agent.**
- **To prepare chloromethane, dimethyl sulphate and formaldehyde etc.**

Uses of Ethanol :

- As a solvent for dyes, oils, perfumes, cosmetics and drugs
- Mixture of 10 – 20% Ethanol with petrol is used as motor fuel.
- As an alcoholic beverages
- Effective topical antiseptic
- Used to prepare chloroform, iodoform, acetic acid etc.

Note :

- **Rectified spirit = 95.6% ethyl alcohol + 4.4% water (azeotropic mixture)**
- **Power alcohol = 20% Absolute alcohol + 80% petrol**
- **Absolute alcohol = ethyl alcohol containing not more than 1% water (99% Pure ethyl alcohol)**

MCQs

1. **Alcohols have high boiling points than that of corresponding alkanes, due to…**

   a) Metallic bonding

   b) Intramolecular hydrogen bonding

   c) Intermolecular hydrogen bonding ✓

   d) None of these

2. Following is used as an “antifreezing agent”…

a) Methanol

b) Ethanol ✓

c) Propanol

d) None of these

3. Following is used as an alcoholic beverage…

a) Methanol

b) Ethanol ✓

c) Propanol

d) None of these

4. 95.6% ethyl alcohol and 4.4% water is…

a) Power alcohol

b) Rectified spirit ✓

c) Absolute alcohol

d) None of these

5. More CO bond length of CO is observed in ---

a) Alcohols

b) Phenols

c) Both are equal

d) Ethers

6. **Bond length of CO in phenol is slightly less than CO of methanol because...**

a) **partial double bond character**

b) **sp^2 – carbon attached to –OH group of phenol**

c) **Both a &b**

d) **none of these**

PREPARATION OF ALCOHOLS

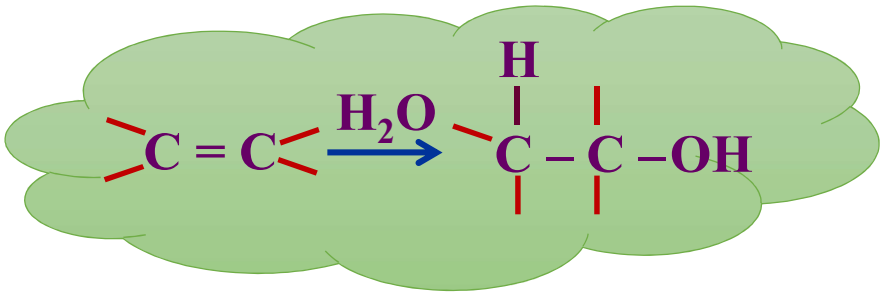
Methods of preparation of Alcohols (R – OH)

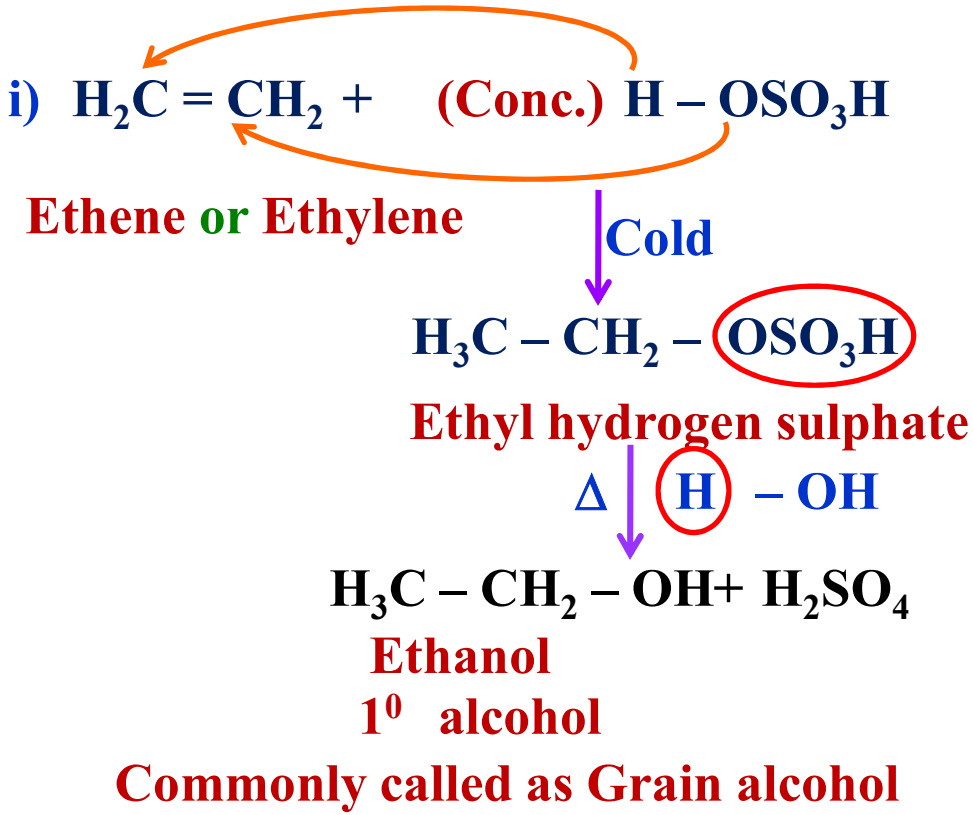
- **Hydration of Alkenes.**
- **Hydroboration – oxidation of alkenes.**
- **Reduction or hydrogenation of Carbonyl compounds.**
- **From Grignard's reagent (alkyl magnesium halide) (R – Mg – X).**

Methods of preparation of Alcohols (R – OH)

Hydration of Alkenes

(Commercial / Industrial method)

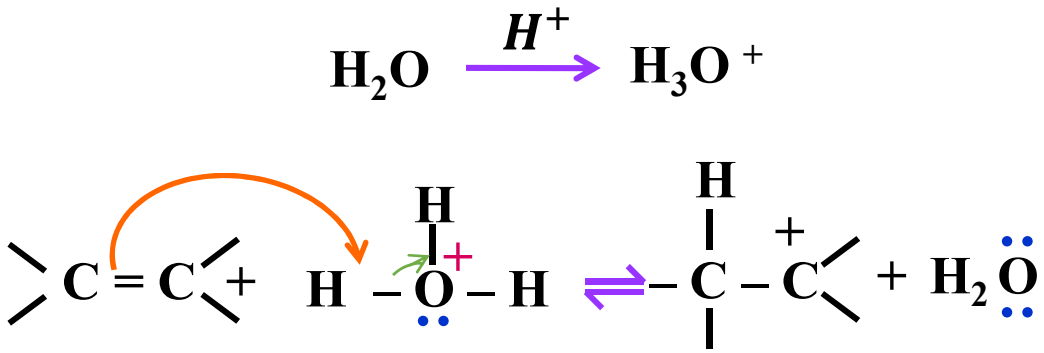



i) $H_2C = CH_2$ + (Conc.) $H - OSO_3H$
Ethene or Ethylene
Cold
$H_3C - CH_2 - OSO_3H$
Ethyl hydrogen sulphate
Δ
H – OH
$H_3C - CH_2 - OH + H_2SO_4$
Ethanol
1^0 alcohol
Commonly called as Grain alcohol

Mechanism of Hydration of alkenes :

Step I :

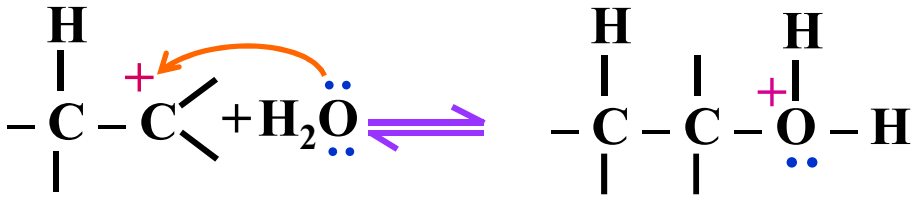
Protonation of alkene to form carbocation by Electrophilic attack of H_3O^+



Mechanism of Hydration of alkenes :

Step II :

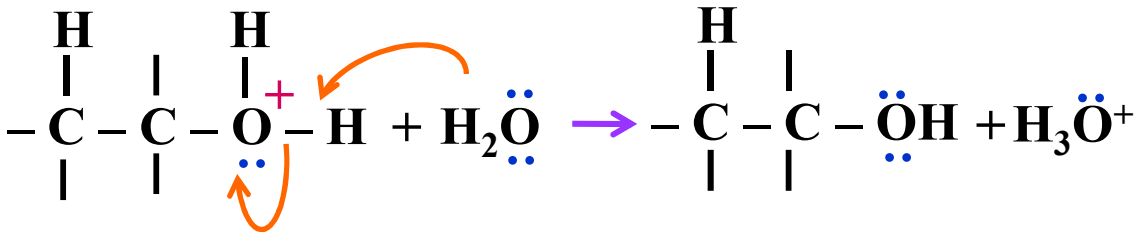
Nucleophilic attack of water on carbocation

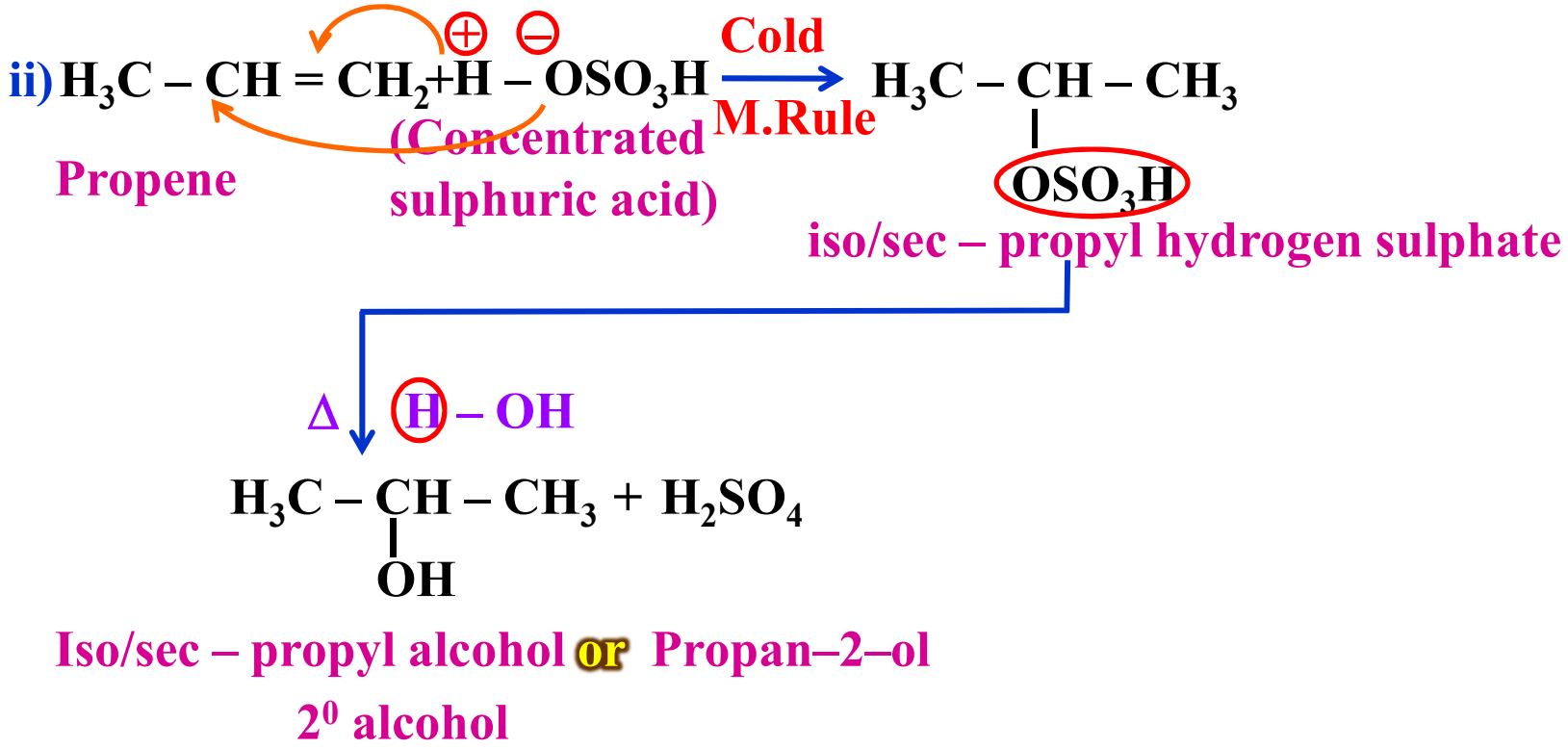


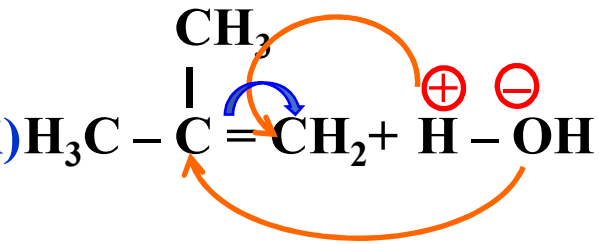
Mechanism of Hydration of alkenes :

Step III :

Deprotonation to form an alcohol



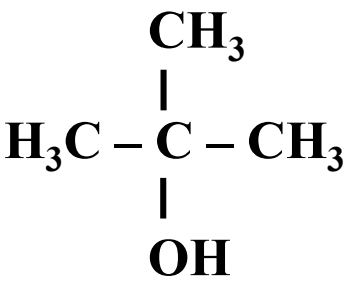

ii) H3C – CH = CH2 + H – OSO3H
Cold
M.Rule
H3C – CH – CH3
OSO3H
Propene
(Concentrated sulphuric acid)
iso/sec – propyl hydrogen sulphate
Δ
H – OH
H3C – CH – CH3 + H2SO4
OH
Iso/sec – propyl alcohol or Propan–2–ol
2⁰ alcohol

iii) 

Isobutylene

2-methylpropene

H^+ | M.R.



2-methyl-2-propanol

3^0 alcohol

Tert – butyl alcohol

Note :

i) **This method is used to prepare 2^0 and 3^0 alcohols.**

ii) **This method is not useful to prepare 1^0 alcohol except Ethanol.**

SOME COMMERCIALLY IMPORTANT ALCOHOLS

- **Methanol**
- **Ethanol**

Methanol :

Methanol, CH_3OH, also known as 'wood spirit', was produced by destructive distillation of wood.

$$CO + 2\,H_2 \xrightarrow[573–673K,\ 200–300\ Pressure]{Cr_2O_3 - ZnO} H_3C - OH$$

(Methanol) (Poisonous)

Methanol is a colourless liquid, boils at 337 K and highly poisonous in nature.

Methanol is used as a solvent in paints, varnishes.

Ethanol:

- **Ethanol, C_2H_5OH, is obtained commercially by fermentation.**

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

- **Ethanol is a colourless liquid with boiling point 351 K**

- **Ethanol is used as a solvent in paint industry and in the preparation of a number of carbon compounds.**

MCQs

1). Hydrolysis of 1-bromopentane by an aq NaOH gives…

a) 1 - propanol

b) 2 - propanol

✓c) 1 - pentanol

d) 2 - pentanol

2). Hydration of ethene produces ---

a) Propanol

b) 2-butanol

c) ethanol

d) methanol

3). Hydration of 2 - methyl but – 2 - ene produces...

a) 1 – methyl butanol

b) 2 – methyl pentan – 2 - ol

c) 2 – methyl butan - 2 - ol

d) 2 – ethyl butan – 2 - ol

HYDROBORATION
- OXIDATION OF ALKENES

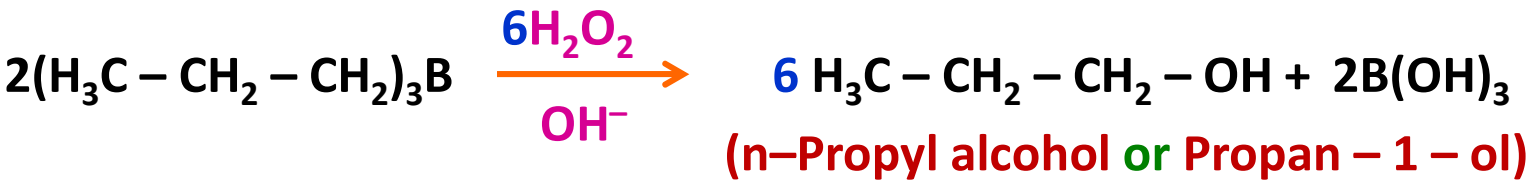
Methods of preparation of Alcohols (R – OH)

Hydroboration – oxidation of alkenes

(Excellent yield of primary alcohol)

$$6(CH_3 – CH=CH_2) + B_2H_6 \longrightarrow 2(H_3C – CH_2 – CH_2)_3B$$

(Propene) **Tripropylborane**



Note :

This reaction gives AntiMarkownikoff's product.

1). The only primary alcohol that can be prepared by hydration of alkene is…

a) Propanol

b) Butanol

c) Ethanol ✓

d) Ethene

2). Hydroboration…oxidation reaction follows

a) Markownikoffs rule

b) Anti – Markownikoff's rule

c) Saytzeff rule

d) Hoffmann

3). Isobutylene on hydration in presence of 50% H_2SO_4 gives…

a) n-butyl alcohol

b) Isobutyl alcohol

c) ✓ Tert–butyl alcohol

d) All of these

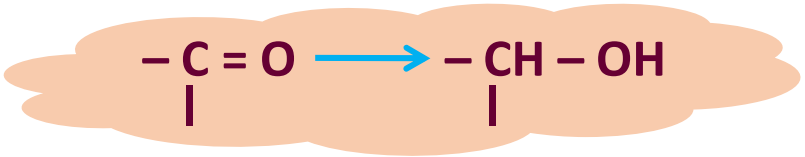
REDUCTION
OR
HYDROGENATION OF CARBONYL COMPOUNDS.

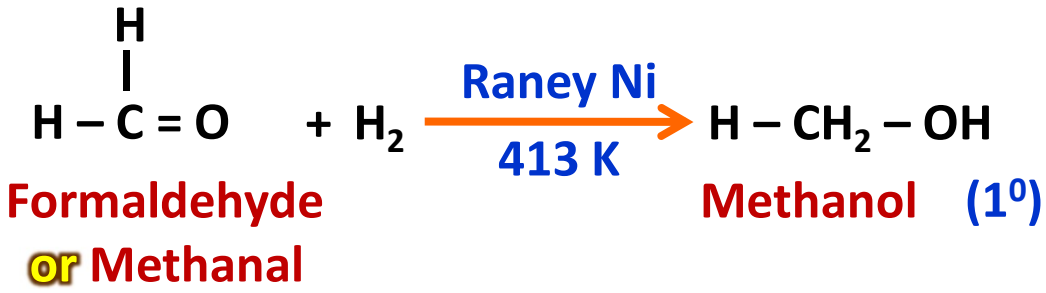
Methods of preparation of Alcohols (R – OH)

Reduction

Reduction or Hydrogenation of Carbonyl compounds

- **Catalytic hydrogenation**
- **Using 2[H]**





Formaldehyde or Methanal

Methanol (1^0)

Acetaldehyde or Ethanal

Ethanol (1^0)

Acetone

or

Dimethyl ketone

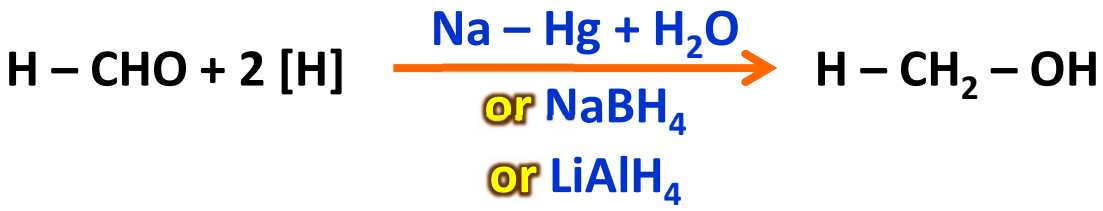
or

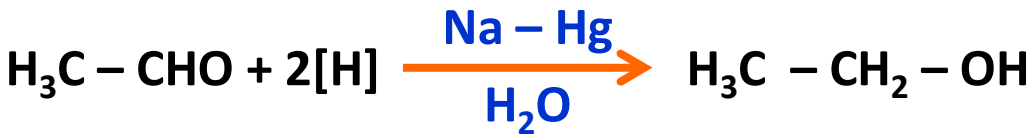
Propanone

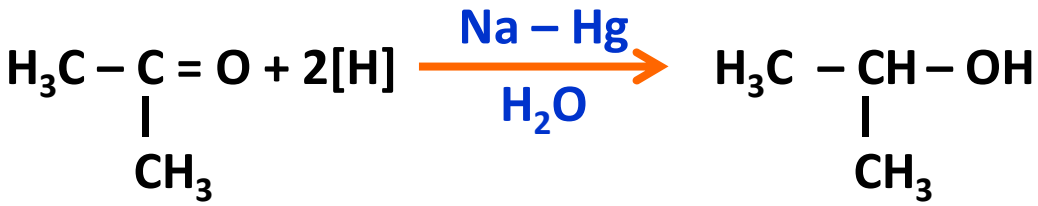
Iso/sec – propyl alcohol

or

Propan – 2 – ol) (2^0)


H – CHO + 2 [H]
Na – Hg + H2O
or NaBH4
or LiAlH4
H – CH2 – OH


H3C – CHO + 2[H]
Na – Hg
H2O
H3C – CH2 – OH


H3C – C = O + 2[H]
CH3
Na – Hg
H2O
H3C – CH – OH
CH3

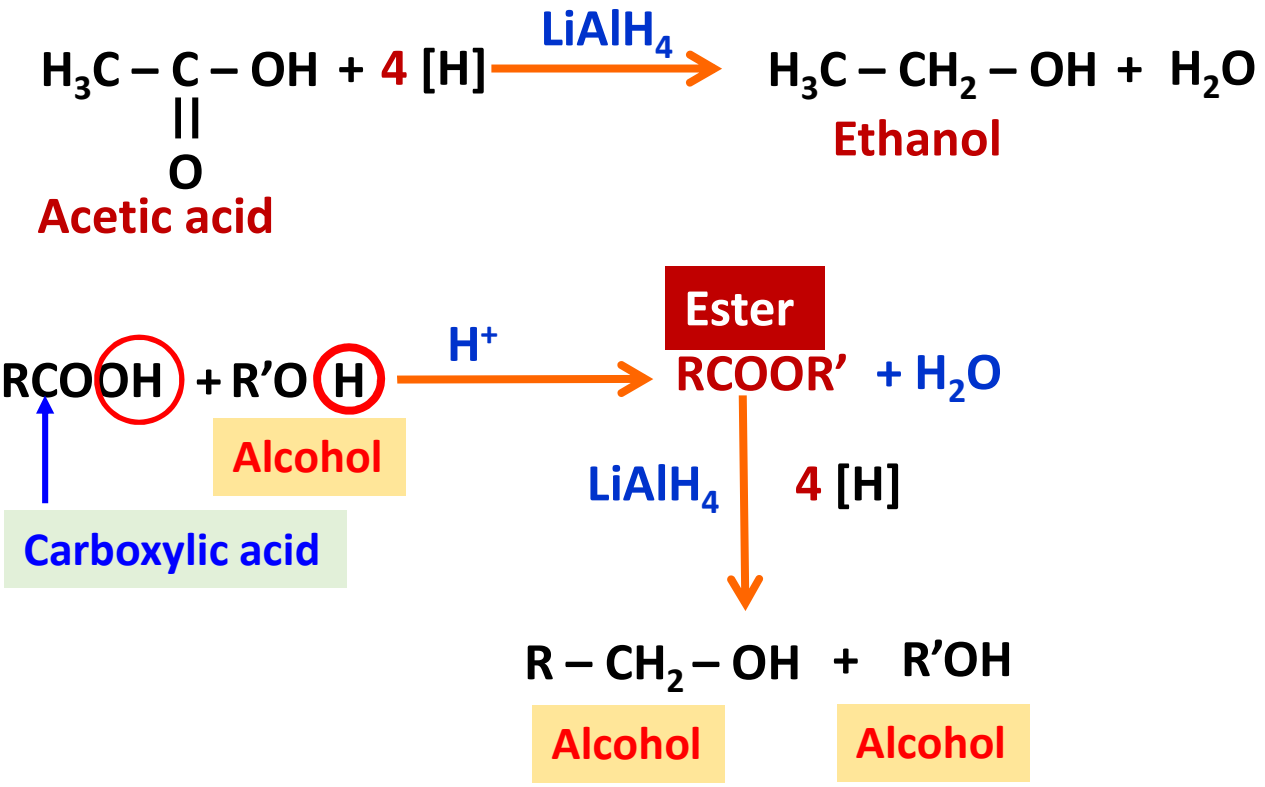
Note :

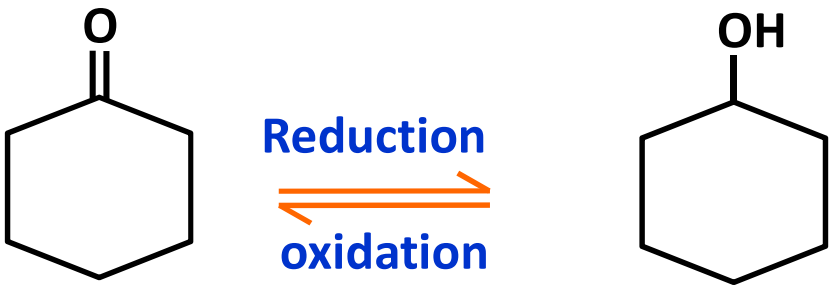
i) **Aldehyde gives 1^0 alcohol on reduction.**

ii) **Ketone gives 2^0 alcohol on reduction.**

iii) **3^0 alcohol can not be prepared by reduction.**

iv) **$LiAlH_4$ is an expensive reagent, so used for preparing special chemicals only. Acids are reduced to alcohols by converting them to the esters followed by their catalytic reduction.**


H3C – C – OH + 4 [H]
LiAlH4
H3C – CH2 – OH + H2O
Ethanol
Acetic acid
RCOOH + R'O H
H+
Ester
RCOOR' + H2O
Alcohol
Carboxylic acid
LiAlH4
4 [H]
R – CH2 – OH + R'OH
Alcohol
Alcohol



Cyclohexanone

Cyclohexanol

MCQs

1. The reagent used for converting ethanoic acid to ethanol is…

a) $LiAlH_4$

b) BH_3

c) PCl_5

d) $K_2Cr_2O_7/H^+$

2. **Esterification of carboxylic acid followed by reduction with lithium aluminum hydride yields…**

a) esters

b) ethers

c) alcohols ✓

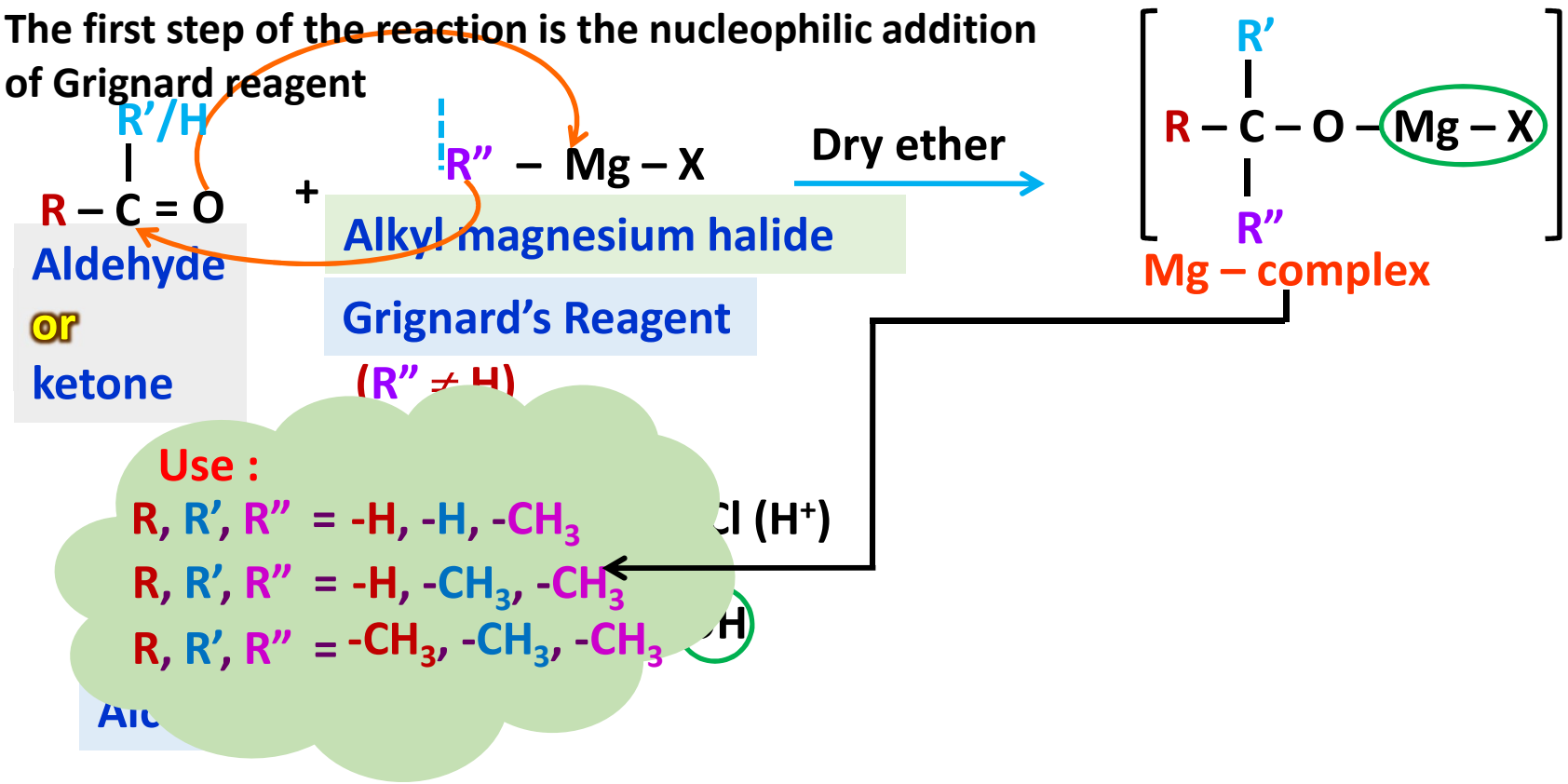
d) aldehyde

FROM:GRIGNARD'S REAGENT

Methods of preparation of Alcohols (R – OH)

From Grignard's reagent (alkyl magnesium halide)(R – Mg – X)

The first step of the reaction is the nucleophilic addition of Grignard reagent



Note:

i) Formaldehyde + G.R. $\rightarrow$ 1^0 alcohol

ii) Aldehyde except formaldehyde + G.R. $\rightarrow$ 2^0 alcohol

ii) ketone + G.R. $\rightarrow$ 3^0 alcohol

Note:

i) By Grignard's reagent we can't prepare Methanol.

ii) By G.R. we can't prepare any compound which contains only one carbon atom.

MCQs

1). Alcohols can be obtained from carbonyl compounds by…

a) Oxidation

b) Reduction ✓

c) Hydration

d) Dehydration

2). Acetaldehyde on reduction gives…

a) Methanol

b) Propanol

c) Ethanol ✓

d) Ethene

3. sec-propyl alcohol is obtained from reduction of…

a) acetaldehyde

b) acetone ✓

c) formaldehyde

d) propanol

4). By using Grignard reagent, we can't prepare…

a) Methanol

b) ethanol

c) propanol

d) butanol

5). Identify the reagent to form t-butyl alcohol from acetone…

a) CH_3MgI

b) $AgNO_3$

c) $CuSO_4$

d) Zn-Hg

6). When C_2H_5MgCl is treated with formaldehyde to form..

a) Pentanol-1

b) Propan-1-ol ✓

c) pentanol-2

d) Propan - 2 - ol

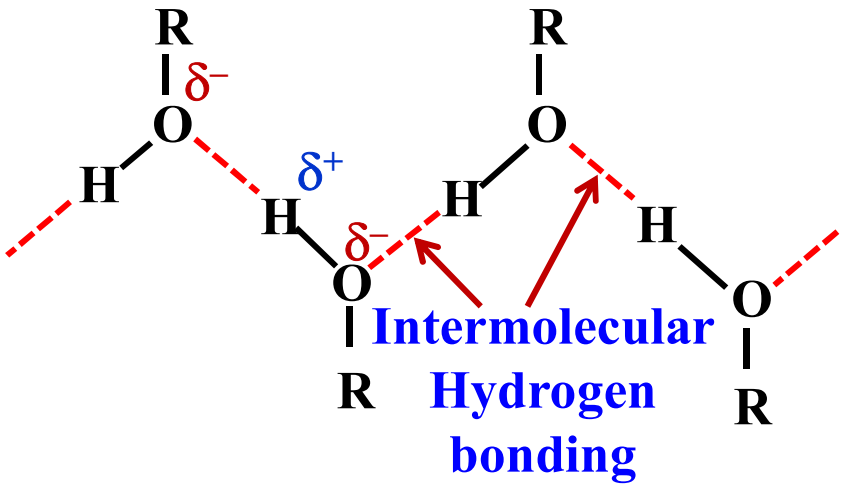
PROPERTIES OF ALCOHOLS

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.**



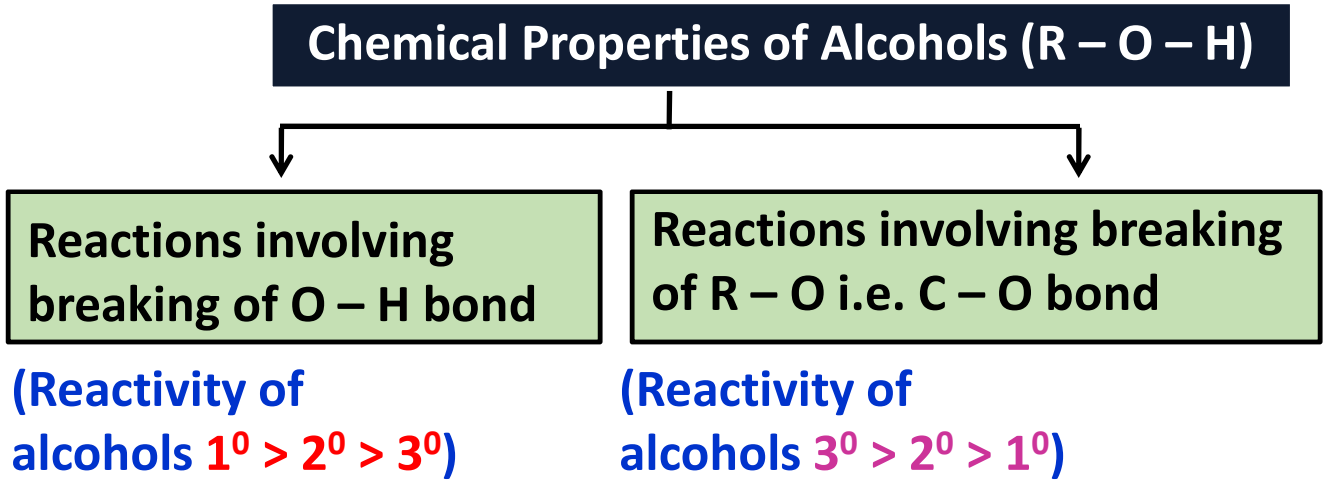
Physical properties of alcohols

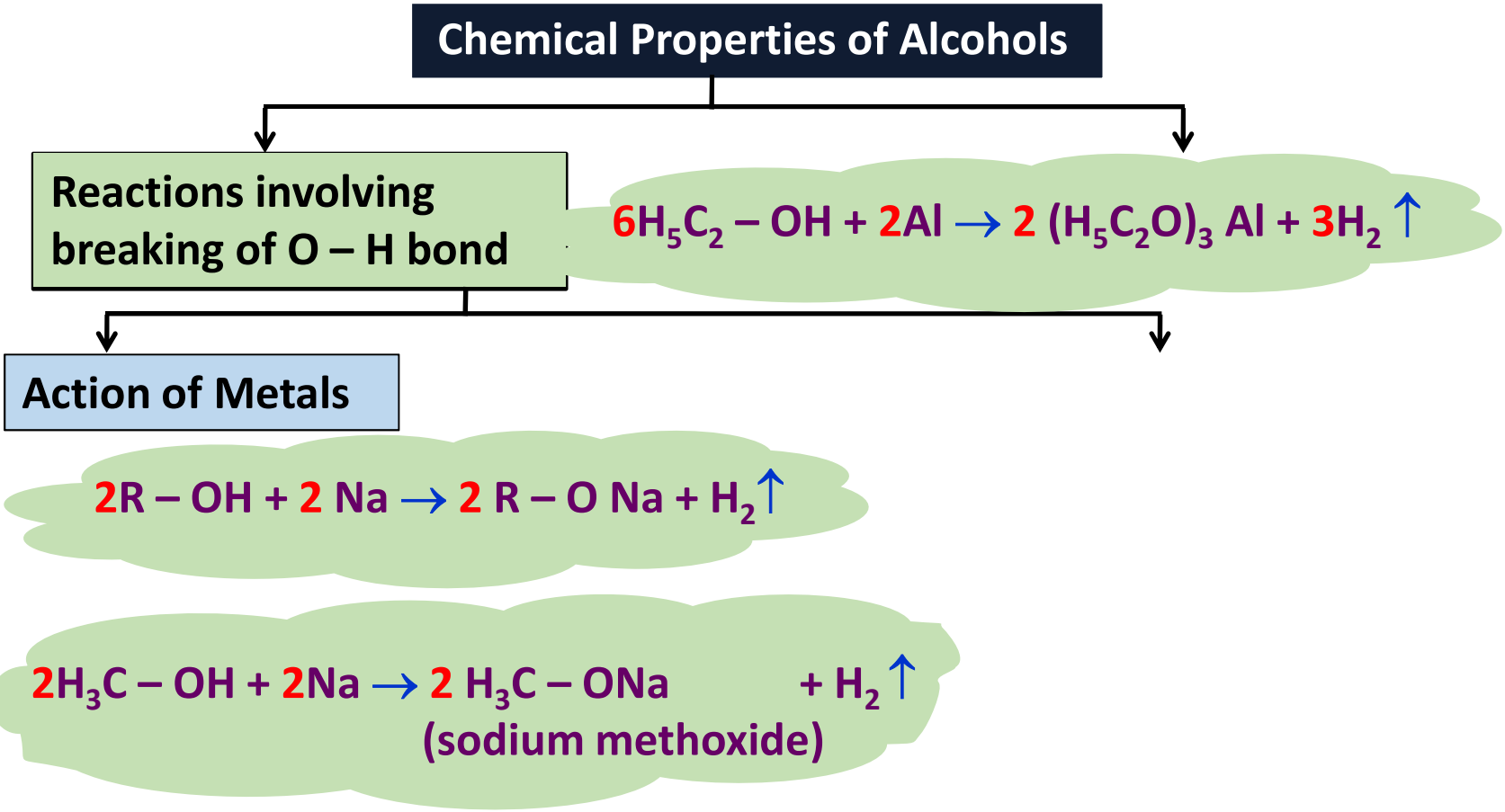
- **Such hydrogen bonding is absent in alkyl halide, aldehydes, ketones, etc. and we require more energy to break this hydrogen bonding in case of alcohol, therefore, Alcohols have more boiling points than that of corresponding alkanes, alkyl halides, aldehydes, ketones, etc.**

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

Note :

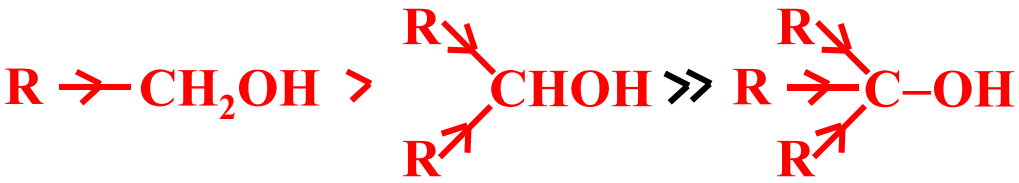
- **Branched chain alcohols have low boiling points due to weak *Vander Waals forces.***
- **Alcohols are neutral to litmus.**
- **Alcohols are acting as Bronsted acids as well as lewis bases, therefore they are reactive.**


Chemical Properties of Alcohols (R – O – H)
Reactions involving breaking of O – H bond
Reactions involving breaking of R – O i.e. C – O bond
(Reactivity of alcohols $1^0 > 2^0 > 3^0$)
(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.

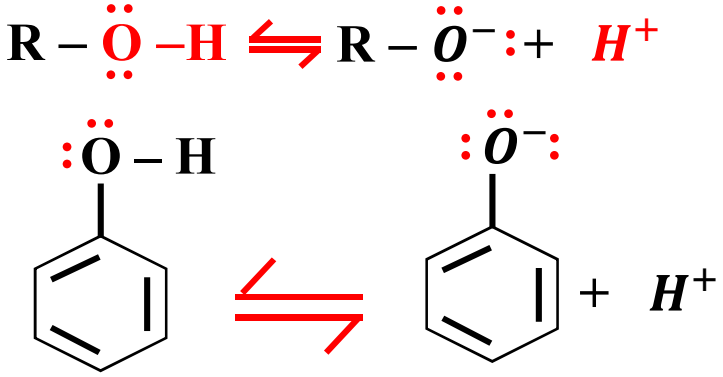
- **Ethers do not have H-bond, so they have boiling points similar to hydrocarbons.**

- **Ethers are only slightly soluble in water and are highly flammable.**

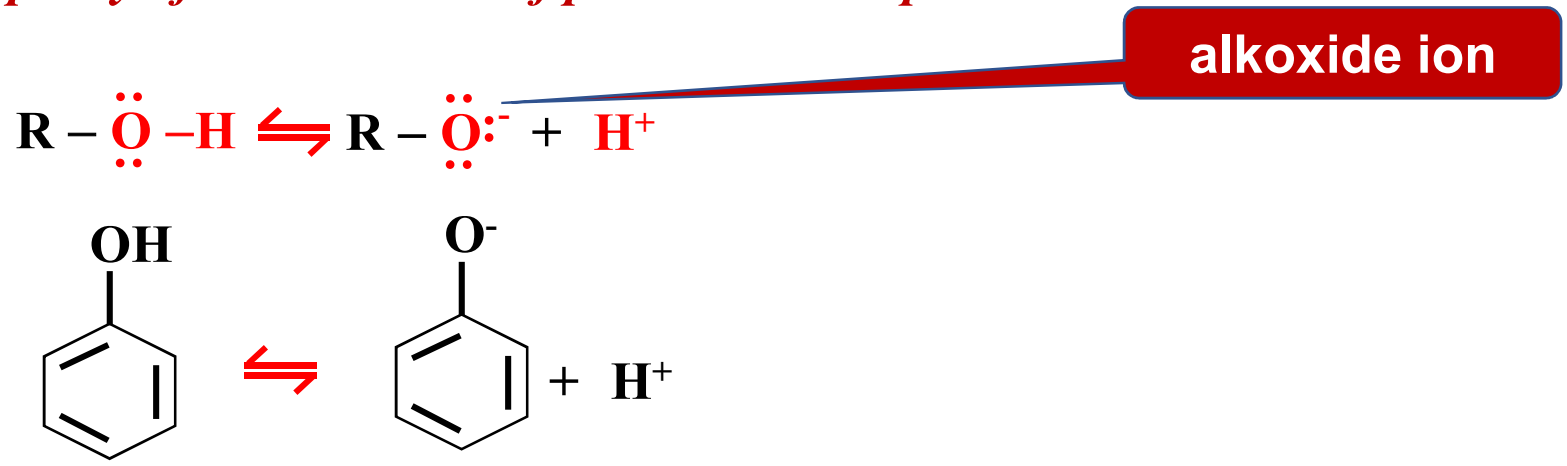
Acidity of phenols:

- **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.


R – O –H
R – O⁻ : + H⁺
: O – H
: O⁻ :
+ H⁺

Comparity of acidic nature of phenols and aliphatic alcohols



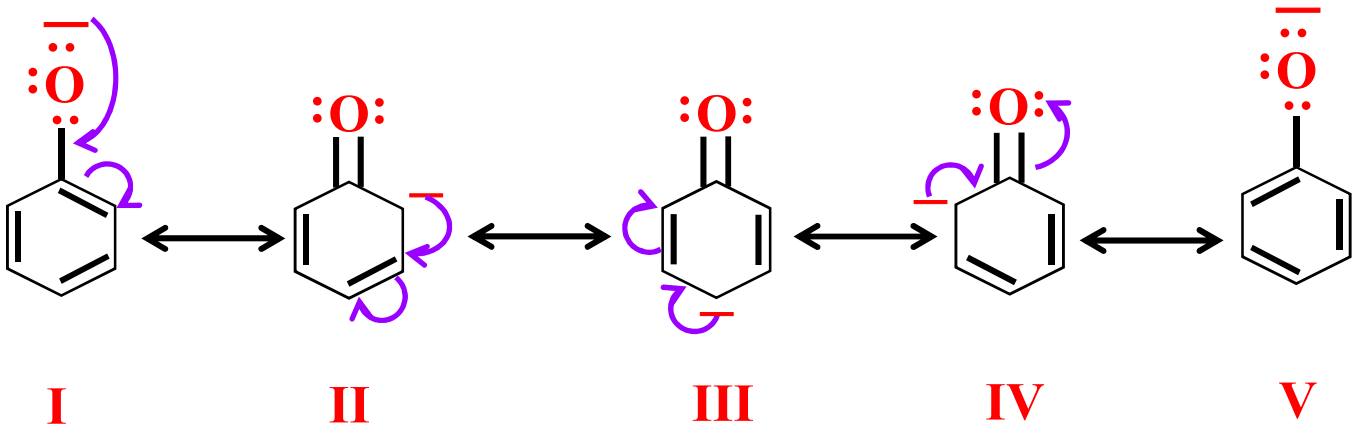
Phenoxide ion

- **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.**

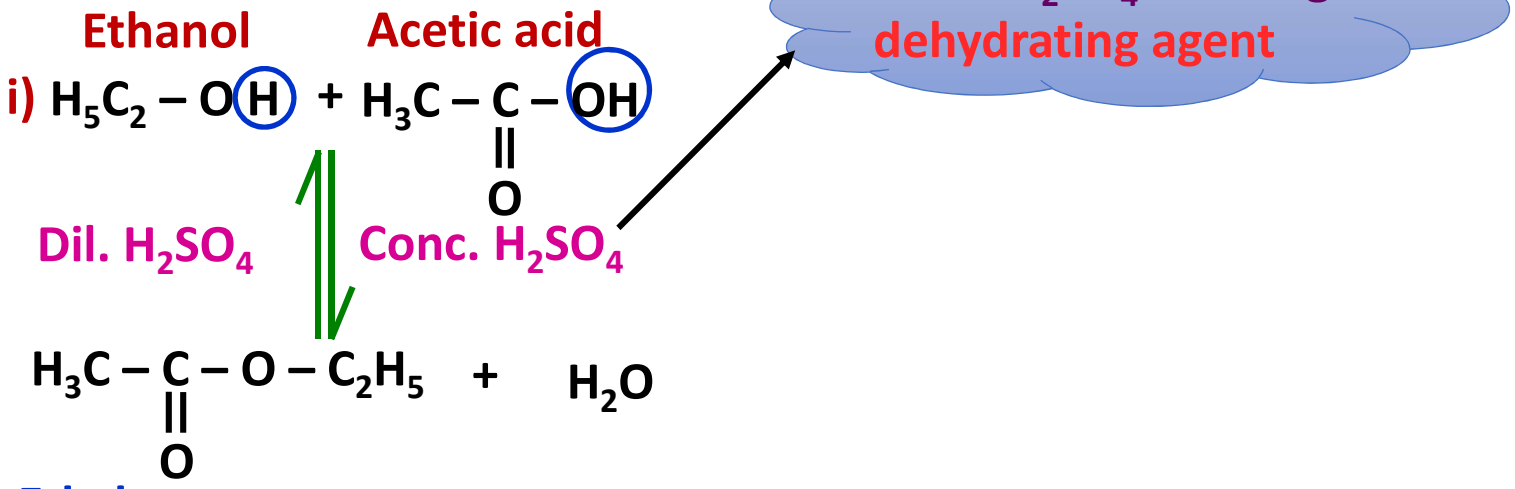
- **In alkoxide ion, the negative charge is localised on oxygen while in phenoxide ion, the charge is delocalised.**

- **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



Ethyl acetate

or

Ethylethanoate

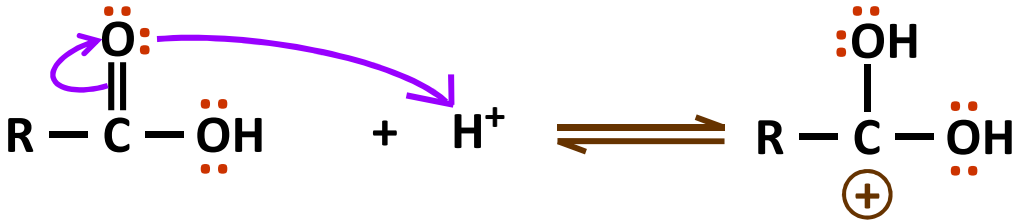
Note :

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

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

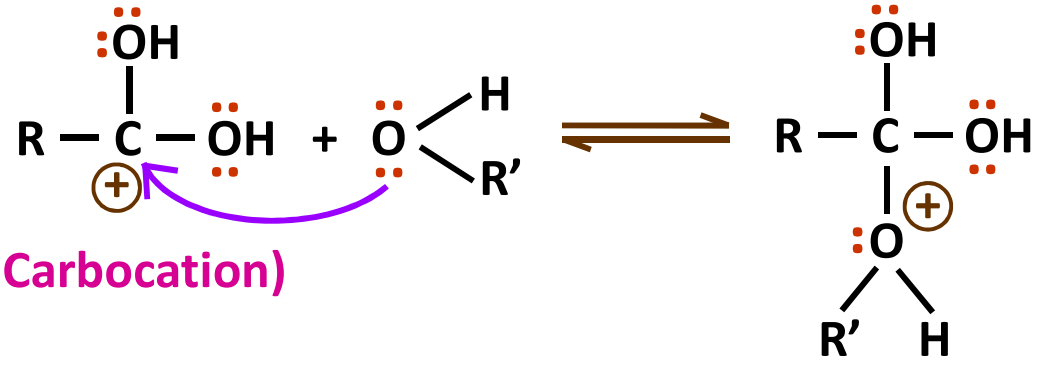
Mechanism : It involves following 3 steps :

Step I : Protonation of the carbonyl group:



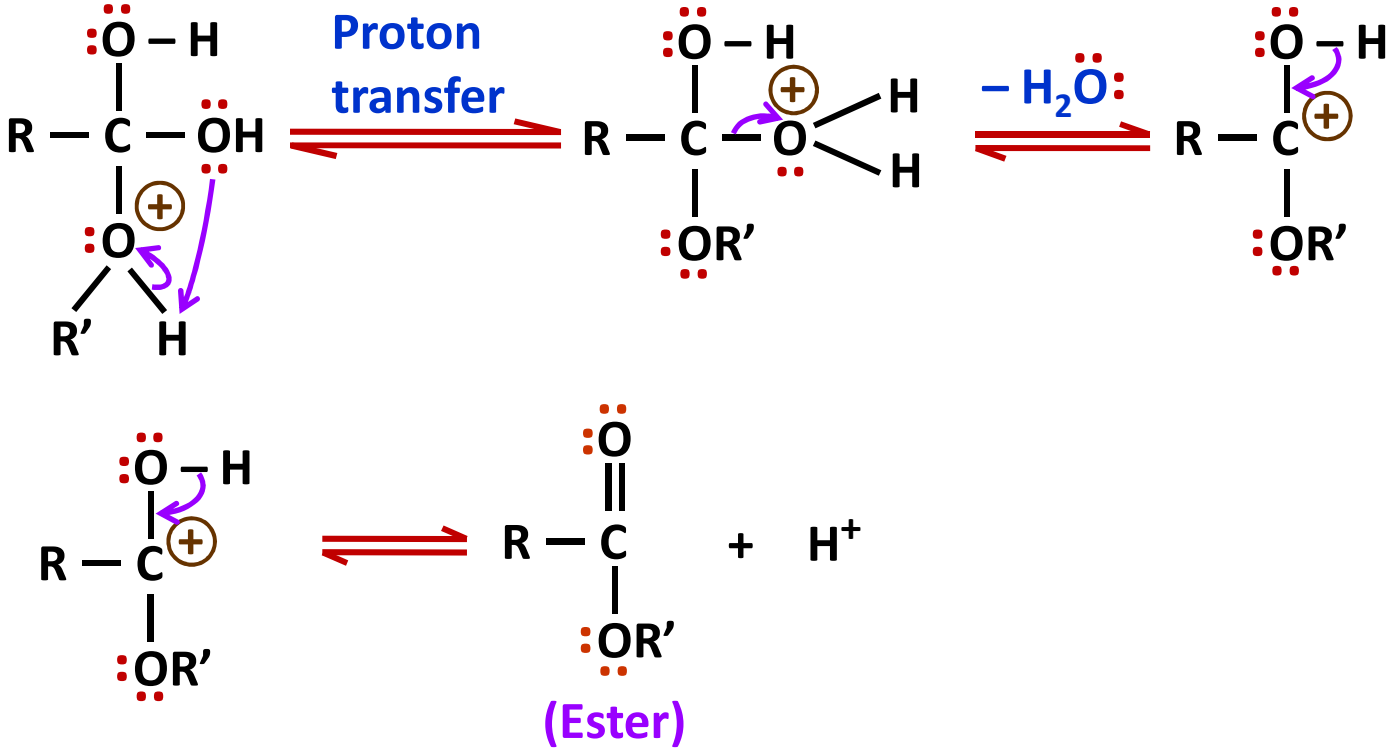
(Carbocation)

Step II : Nucleophilic attack by the alcohol molecule:



(Carbocation)

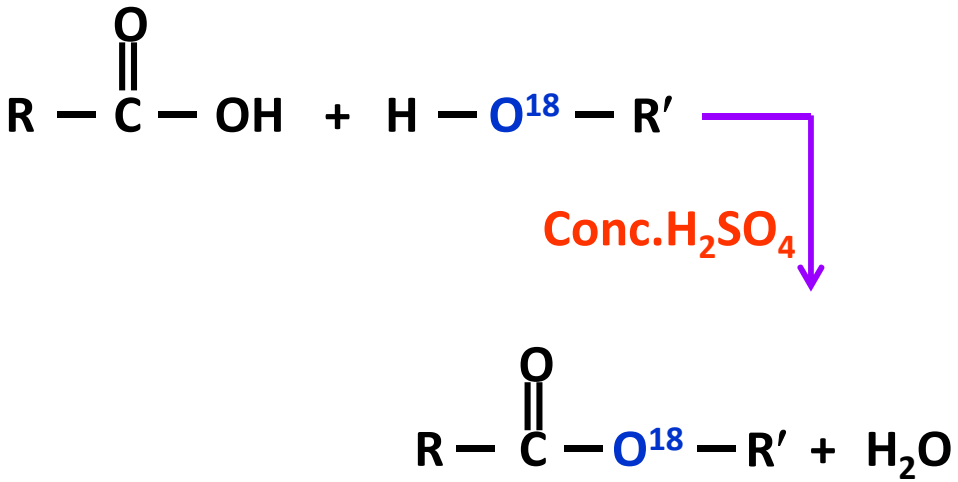
Step III : Loss of water molecule and a proton transfer :



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

$$R - \boxed{OH + H} X \longrightarrow R - X + H_2O$$

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)

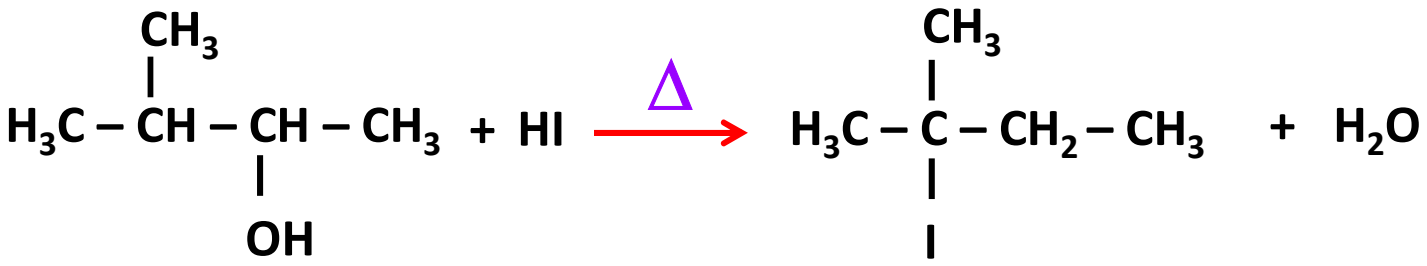
Note : Distinguishable reaction between 1^0, 2^0 and 3^0 alcohol

⇒ 3^0 alcohol $\xrightarrow{\text{Lucas reagent}}$ Immediate appearance of turbidity.

⇒ 2^0 alcohol $\xrightarrow{\text{Lucas reagent}}$ Turbidity within 5 min.

⇒ 1^0 alcohol $\xrightarrow{\text{Lucas reagent}}$ Do not produce turbidity at room temp.

Note :

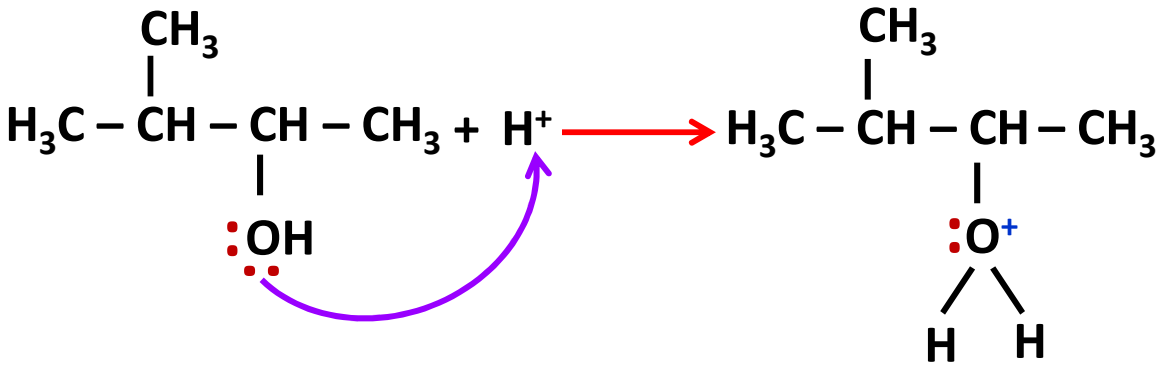


(2^0 alcohol)

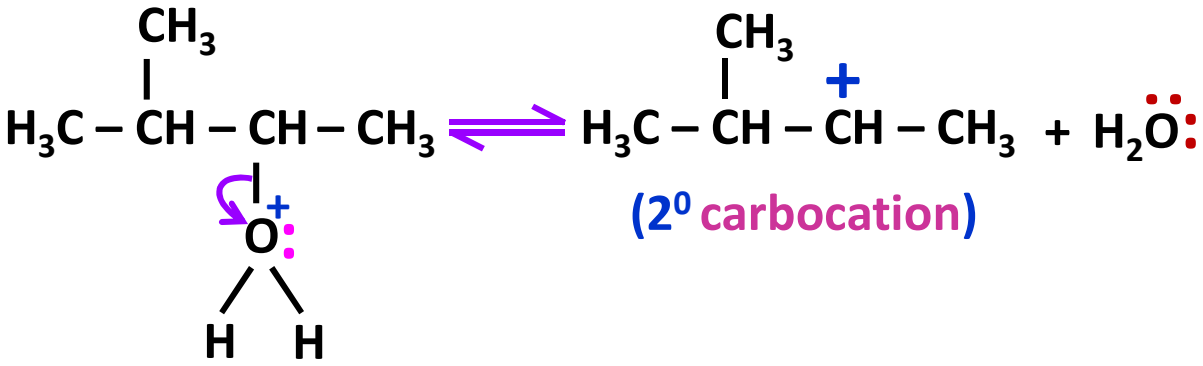
(ter-pentyliodide) (3^0)

Mechanism :

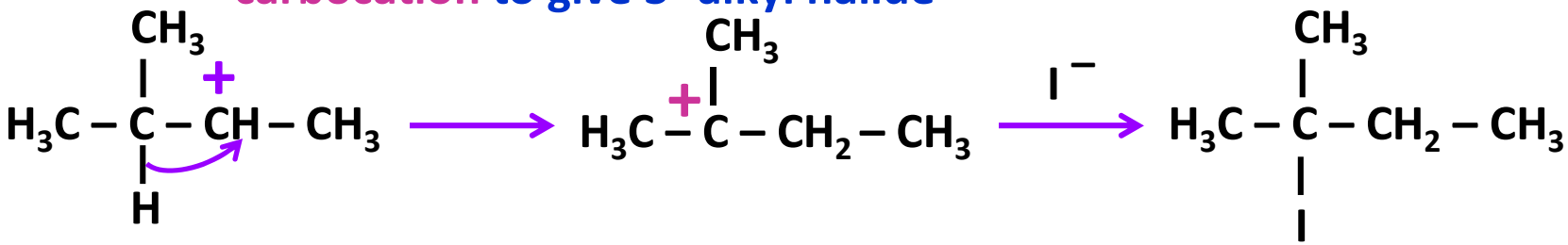
Step I : **The alcohol is protonated by an acid :**



Step II : **Formation of carbocation :**



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



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…

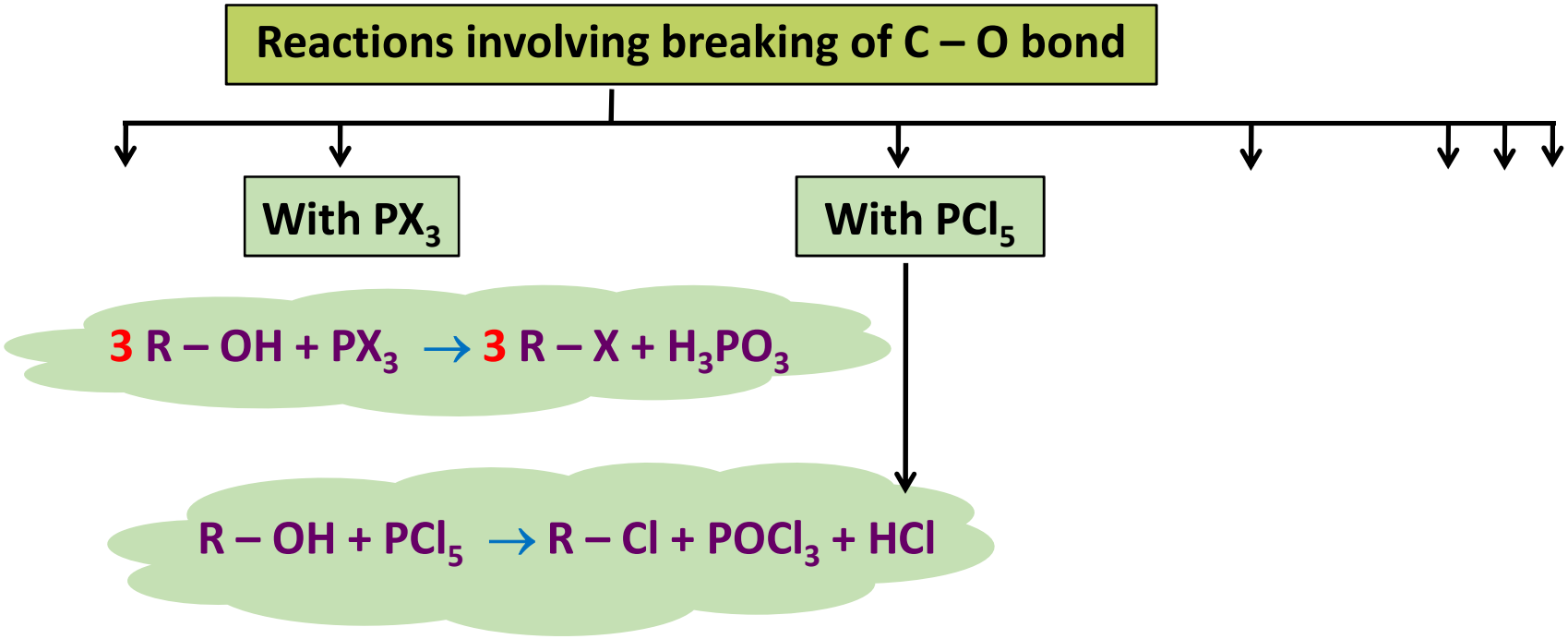
a) Conc. HNO_3 + anhydrous $MgCl_2$

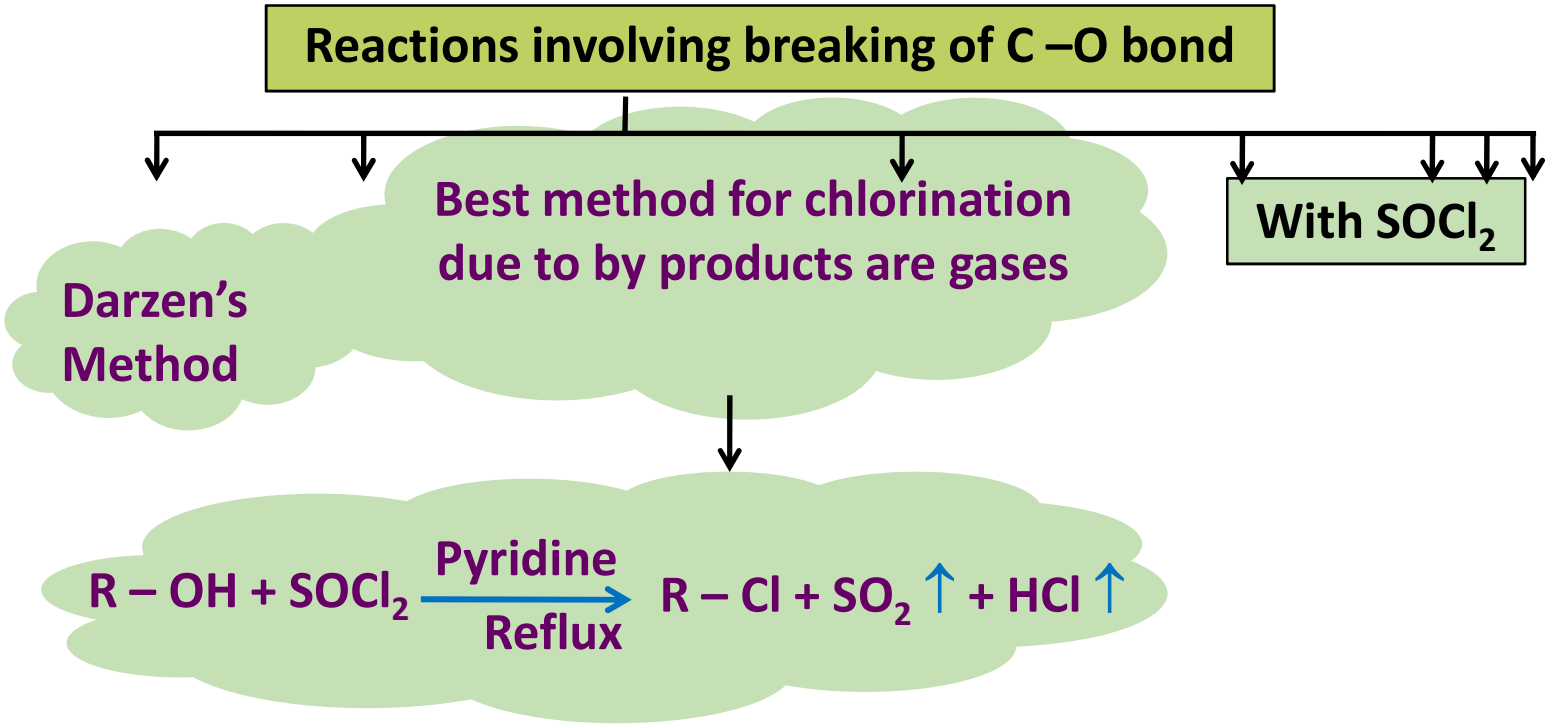
b) dil. HCl + anhydrous $ZnCl_2$

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
With PCl_5
$3\ R-OH + PX_3 \rightarrow 3\ R-X + H_3PO_3$
$R-OH + PCl_5 \rightarrow R-Cl + POCl_3 + HCl$


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...

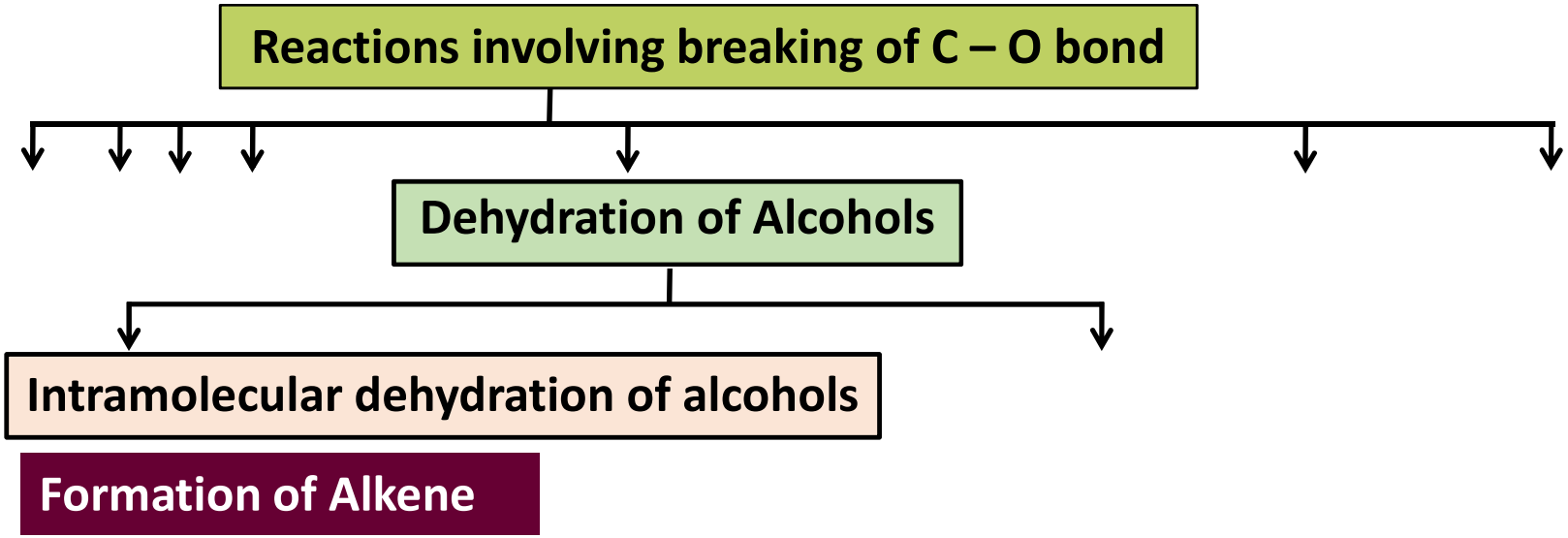
a) Reaction of alcohol with $SOCl_2$

b) Darzen's method

c) Reaction of alcohol with PCl_3

d) Both a & b ✓

DEHYDRATION OF ALCOHOLS


Reactions involving breaking of C – O bond
Dehydration of Alcohols
Intramolecular dehydration of alcohols
Formation of Alkene

i) $H_3C - CH_2 - OH$ —(95% H_2SO_4 , 443 K / or Al_2O_3 , 623 K)→ $H_2C = CH_2 + H_2O$

Ethanol (1^0) — Ethene

ii) $H_3C - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_3$ —(60% H_2SO_4 , 373 K / or Al_2O_3 , 523 K)→ $H_3C - CH = CH_2 + H_2O$

Propan – 2 – ol (2^0) — Propene

iii)

(tert – butyl alcohol)

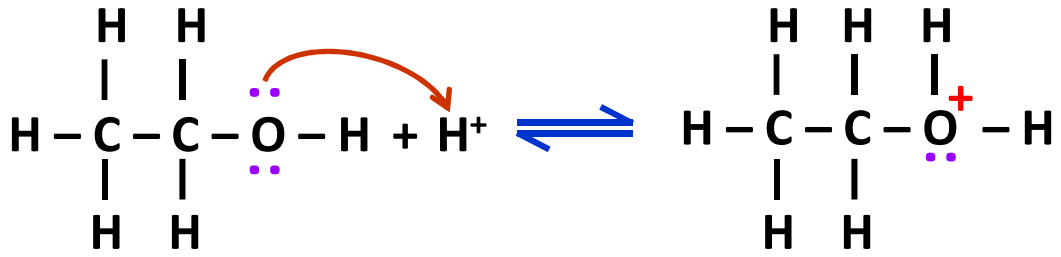
(3^0)

(isobutylene or

2- Methyl propene)

Mechanism : Dehydration of Ethanol :

Step I : Formation of Protonated alcohol

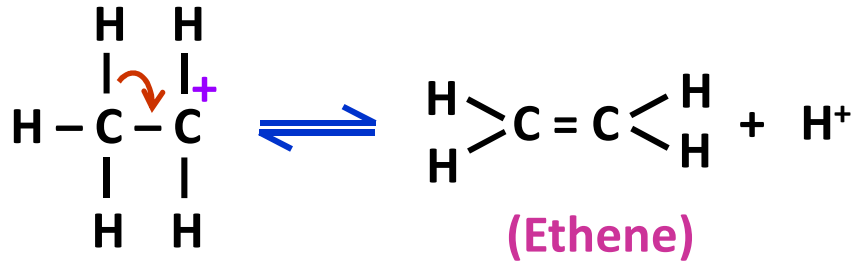


Step II : Formation of Carbocation

Carbocation

R.D.S =Rate Determining Step.

Step III : **Formation of Ethene by deprotonation**



(Ethene)

Order of ease of dehydration of alcohols .

Tertiary > Secondary > Primary

MCQs

1) $C_2H_4 \xrightarrow[AlCl_3]{HCl} A \xrightarrow{KOH(aq.)} B \xrightarrow[170^0C]{Conc.H_2SO_4} C$

a) C_2H_4

b) $C_2H_5 - O - C_2H_5$

c) C_2H_5OH

d) $C_2H_5 - O - SO_3H$

2) $C_2H_5OH \xrightarrow[350^0C]{X} C_2H_4$ What is 'X'?

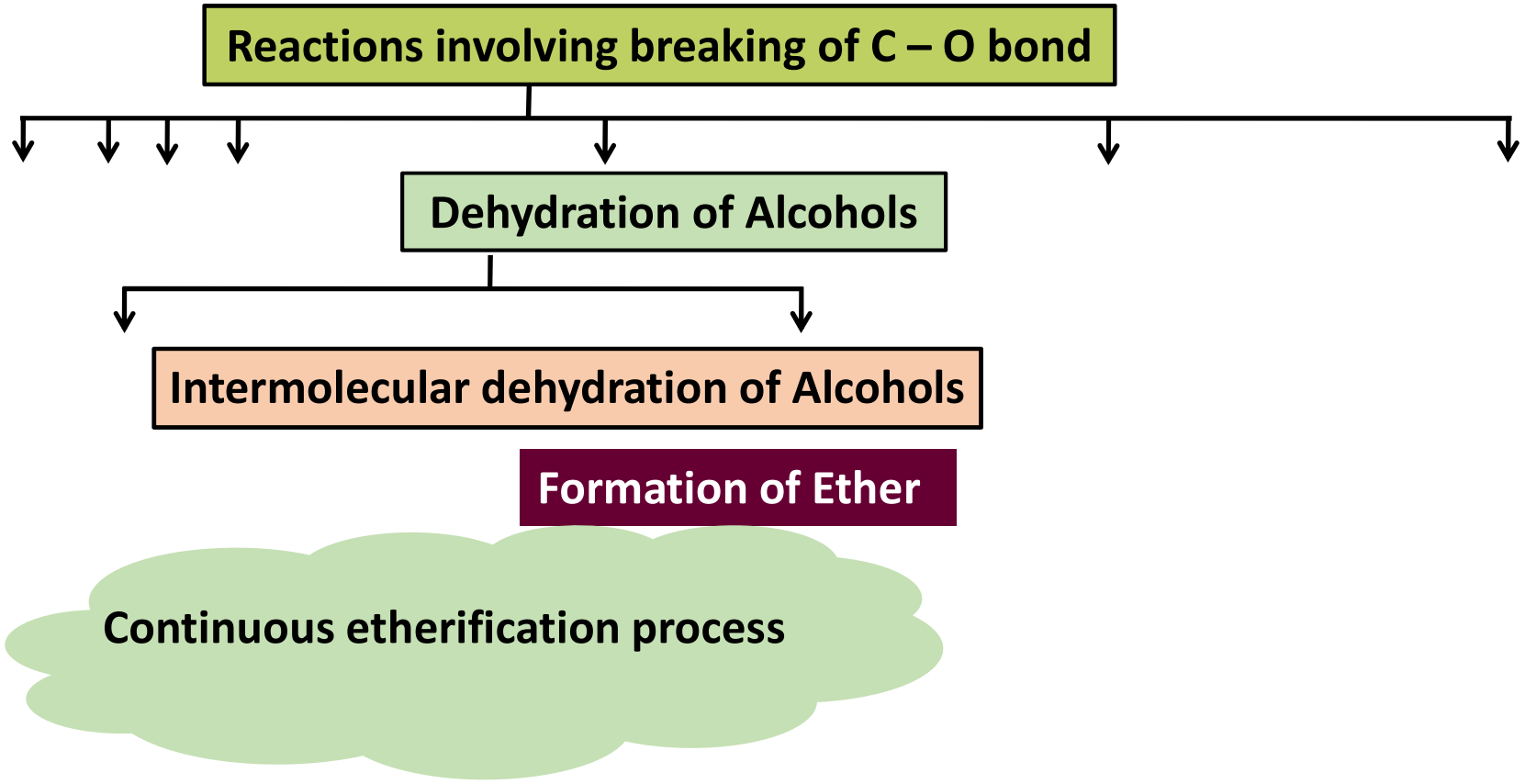
a) Conc. H_2SO_4

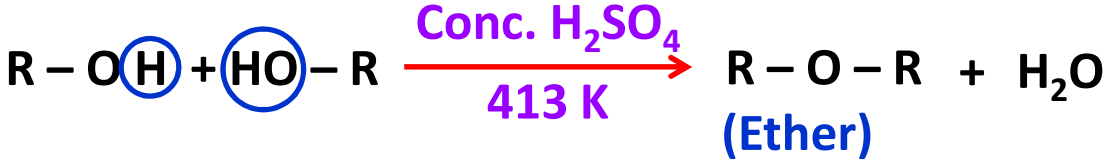
b) $CaCl_2$

c) CaO

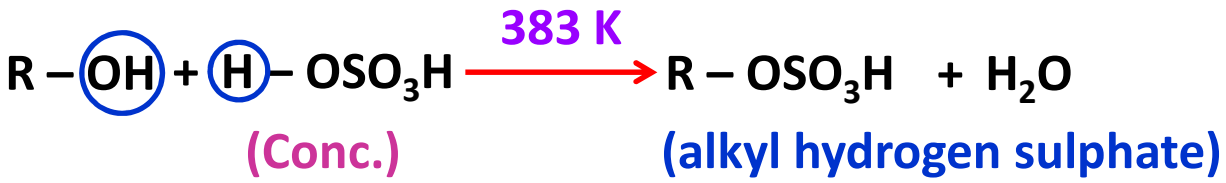
d) Al_2O_3

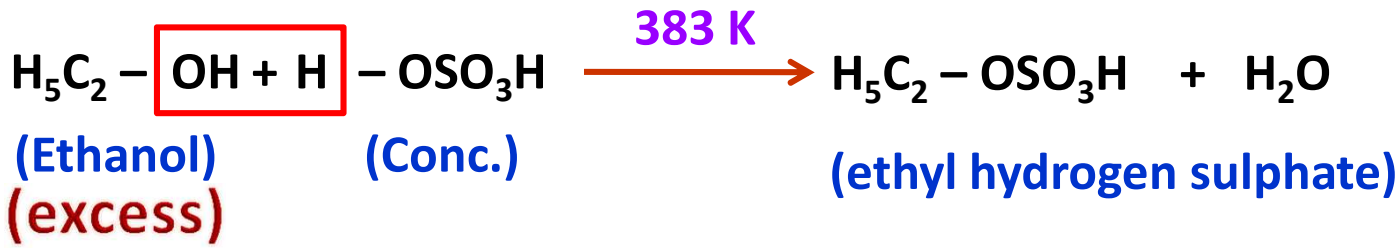
DEHYDRATION OF ALCOHOLS FORMATION OF ETHER.

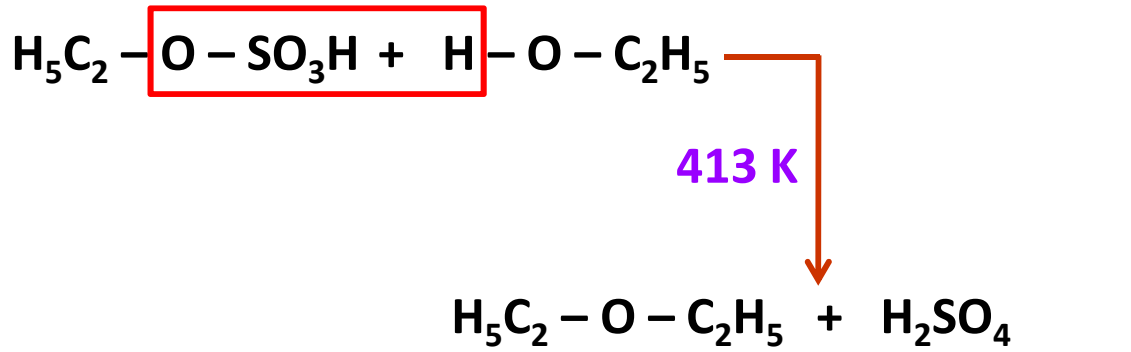

Reactions involving breaking of C – O bond
Dehydration of Alcohols
Intermolecular dehydration of Alcohols
Formation of Ether
Continuous etherification process


R – OH + HO – R
Conc. H2SO4
413 K
R – O – R + H2O
(Ether)

Note :

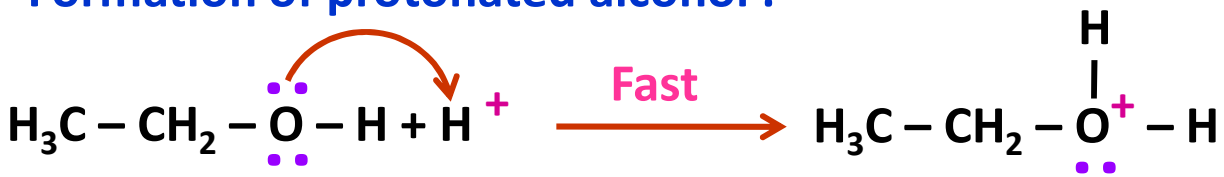

R – OH + H – OSO3H
383 K
R – OSO3H + H2O
(Conc.)
(alkyl hydrogen sulphate)


383 K
H5C2 – OH + H – OSO3H
H5C2 – OSO3H + H2O
(Ethanol)
(excess)
(Conc.)
(ethyl hydrogen sulphate)

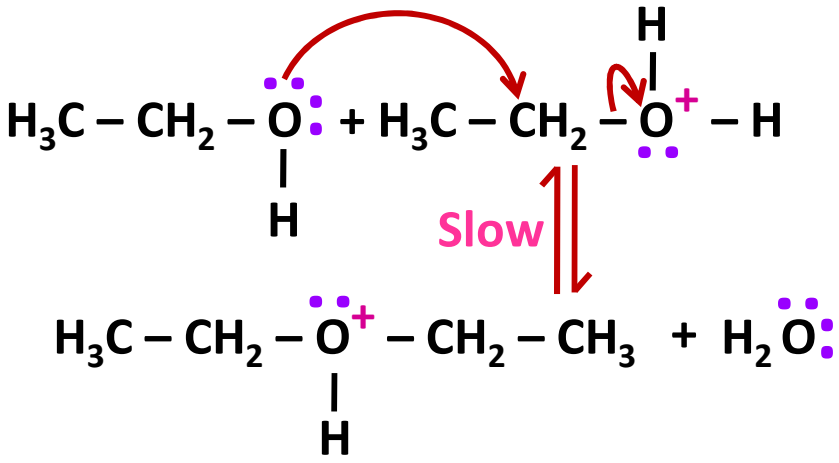

H5C2 – O – SO3H + H – O – C2H5
413 K
H5C2 – O – C2H5 + H2SO4
(diethyl ether or Ethoxyethane)

Mechanism

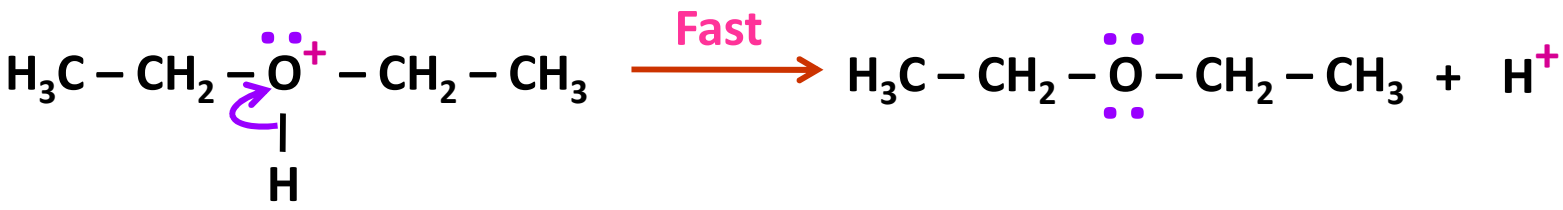
i) **Formation of protonated alcohol :**



ii) **Attack of Nucleophilic alcohol on protonated alcohol :**

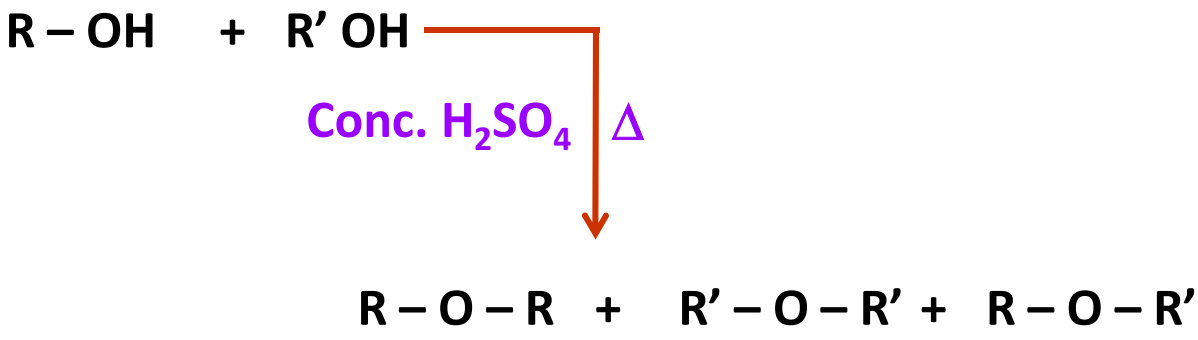


iii) Deprotonation to give ether



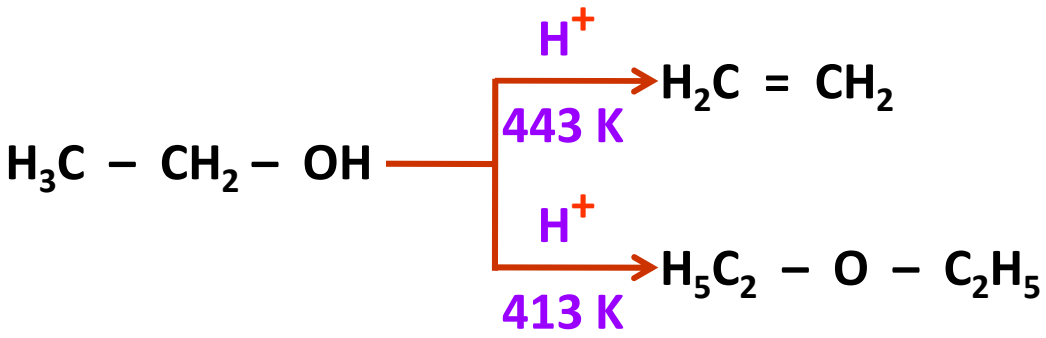
Limitations

i) **Only simple ethers are prepared by this method, if a mixture of two different alcohols is used then a mixture of three different ethers is obtained which is difficult to separate.**



ii) Ethers prepared from this method is from only 1^0 alcohol because 2^0 & 3^0 alcohols gives alkene by elimination.

iii) If temp rises above 413 K then alcohol gives formation of an alkene.



MCQs

1). Removal of water molecule from an alcohol is called…of alcohols.

a) hydration

b) dehydration ✓

c) hydrogenation

d) dehydrogenation

2). Dehydrating agent used for dehydration of alcohols is…

a) Conc. HCl

b) Conc. H_2SO_4 ✓

c) Conc. HNO_3

d) None of these

3). Ethyl alcohol when treated with concentrated sulphuric acid at 413K gives…

a) Ethene

b) Ethyl ether

c) Diethyl ether ✓

d) None of these

4). $C_2H_4 \xrightarrow[AlCl_3]{HCl} A \xrightarrow{KOH(aq.)} B \xrightarrow[140^0C]{Conc.H_2SO_4} C$ .What is C?

a) C_2H_4

b) $C_2H_5 - O - C_2H_5$

c) C_2H_5OH

d) $C_2H_5 - O - SO_3H$

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