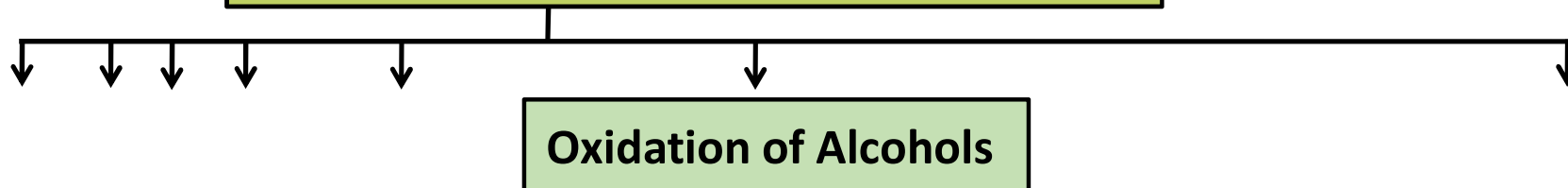




OXIDATION OF ALCOHOLS

Reactions involving breaking of C – O bond

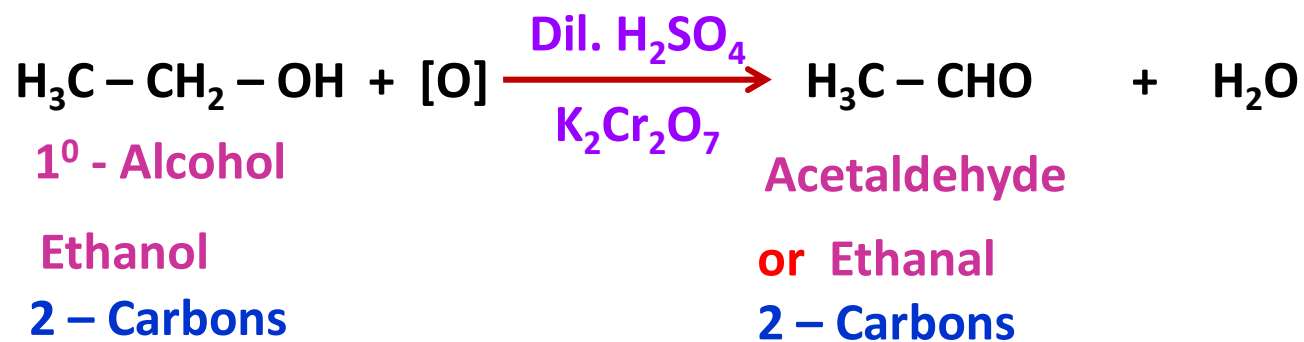


Distinguishable reaction Between 1^o, 2^o and 3^o alcohols

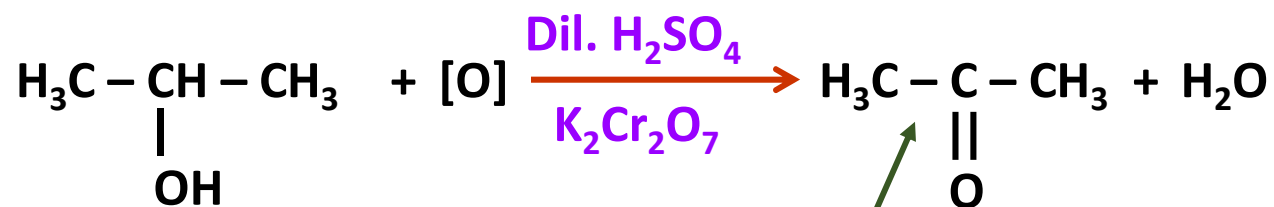
Oxidation

pyridinium dichromate (PDC)
Oxidation of alcohols is used to differentiate between 1^o, 2^o and 3^o alcohols

(i) Oxidation of 1^o alcohol



(ii) Oxidation of 2^o alcohol



Iso/sec – propyl alcohol

or

Propan – 2 – ol

2^o -Alcohol

3 – Carbons

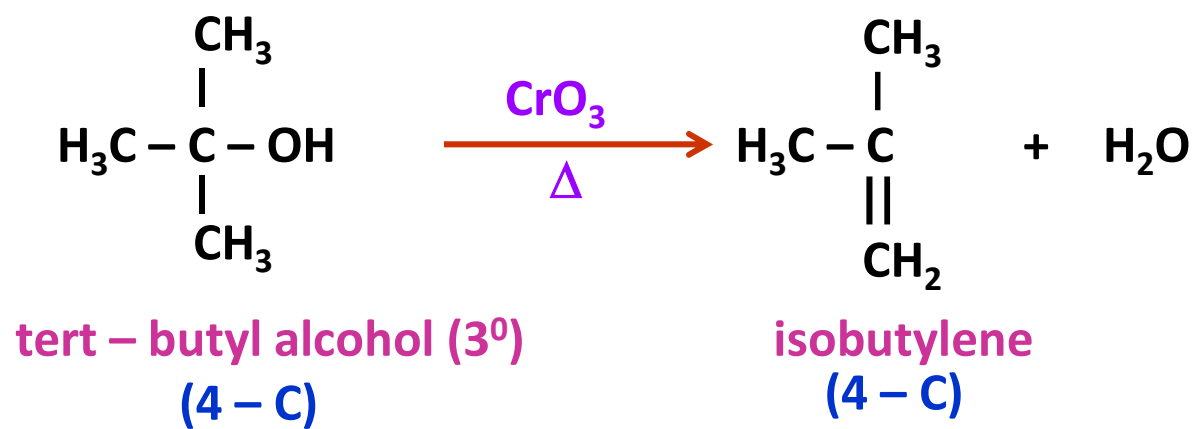
Acetone

Propan-2-one

Dimethyl ketone

3 – Carbons

iii) Oxidation of 3^o alcohol



Note :

1° , 2° and 3° alcohol on vigorous oxidation gives carboxylic acid but 1° alcohol gives carboxylic acid with same no. of 'C' atom, 2° alcohol gives carboxylic acid with one 'C' atom less and 3° alcohol gives carboxylic acid with two 'C' atoms less.

MCQs

1. Oxidation of alcohols is carried out by using...

a) dilute H_2SO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$

b) pyridinium chlorochromate

c) pyridinium dichromate

d)  All of these

2. Primary alcohol on oxidation gives...

a)  aldehyde

b) ketone

c) Both a & b

d) None of these

3. Secondary alcohol on oxidation gives...

a) aldehyde

 **b) ketone**

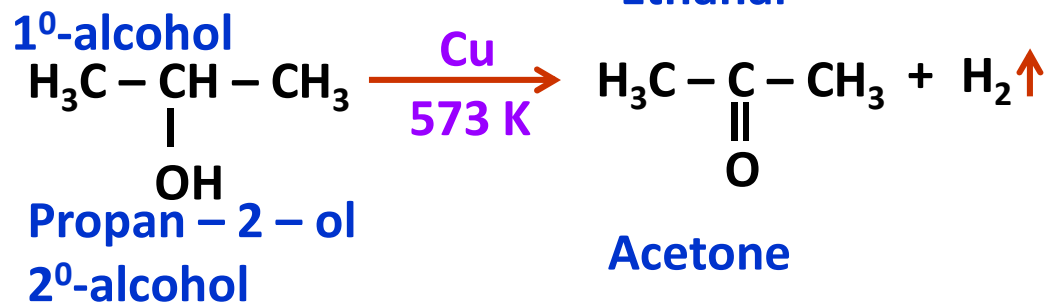
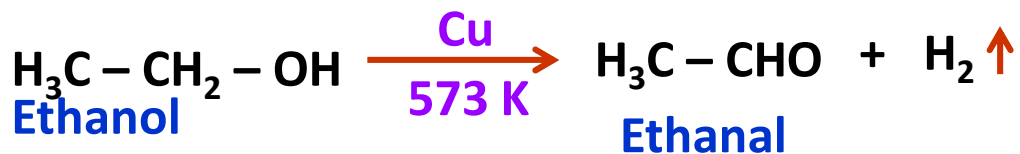
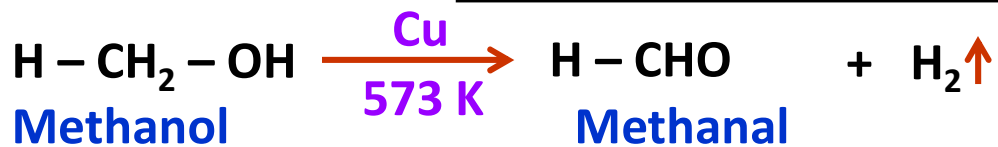
c) Both a & b

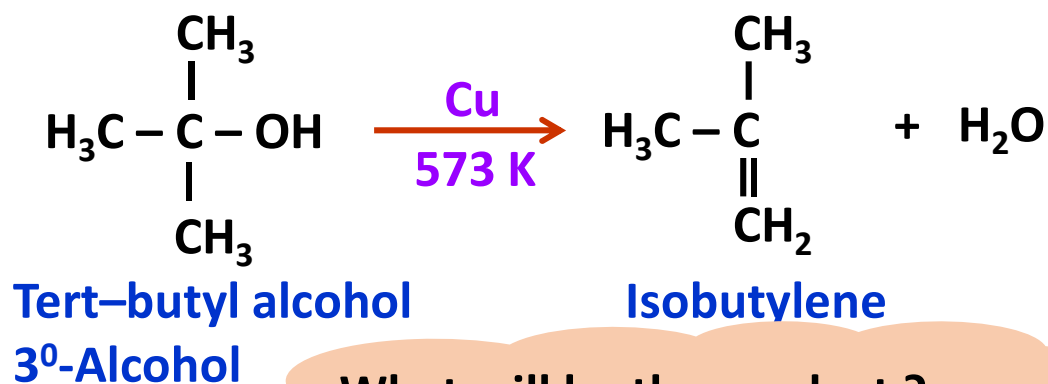
d) None of these

DEHYDROGENATION OF ALCOHOLS WITH 'Cu' AT 573 K

Reactions involving breaking of C – O bond

Dehydration of alcohols with Cu at 573 K (300°C)





What will be the product ?

Catalytic dehydrogenation is also
 useful to distinguish 1^o, 2^o and 3^o
 alcohols

MCQs

1. Primary alcohols on dehydrogenation with Cu at 573 K gives

a) ketone

 **b) aldehyde**

c) acid

d) None of these

2. Ethanol on dehydrogenation gives...

a) Methanol

 **b) Ethanal**

c) Both a & b

d) Ethyl chloride

3. Propan – 2– ol on dehydrogenation gives --

a) acetaldehyde

b) Formaldehyde

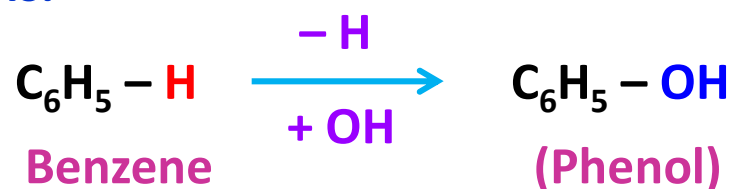
 **c) acetone**

d) All of these

INTRODUCTION OF PHENOLS

Phenols

The aromatic hydroxyl compounds in which one or more hydroxyl groups are directly attached to the aromatic nucleus (i.e. Benzene ring) are called Phenols.



Classification of Phenols

```
graph TD; A[Classification of Phenols] --> B[Monohydric Phenols<br/>(One -OH group)]; A --> C[Dihydric Phenols<br/>(Two - OH groups)]; A --> D[Trihydric Phenols<br/>(Three - OH groups)];
```

Monohydric Phenols

(One -OH group)

Dihydric Phenols

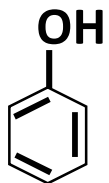
(Two - OH groups)

Trihydric Phenols

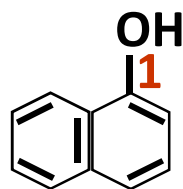
(Three - OH groups)

Phenols are classified into three types

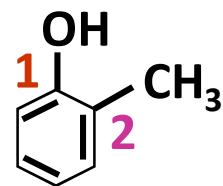
Monohydric phenols



Phenol
Carbolic acid

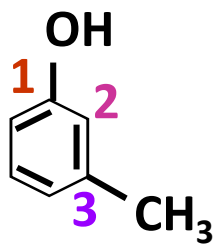


α – Naphthol
1 – Naphthol



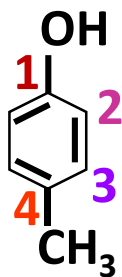
o – Cresol
2-Methylphenol

Monohydric phenols



m – Cresol

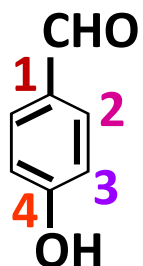
3 – Methylphenol



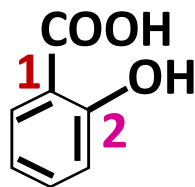
p – Cresol

4 – Methylphenol

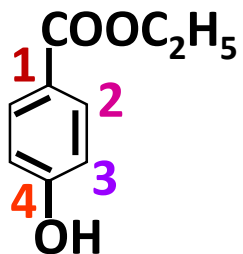
Monohydric phenols



(4 – Hydroxybenzaldehyde)

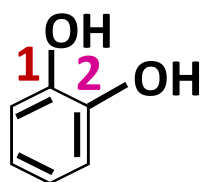


(2 – Hydroxybenzoic acid)



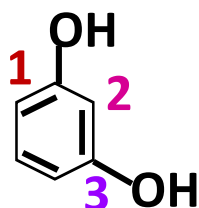
(4 – Hydroxyethylbenzoate)

Dihydric phenols



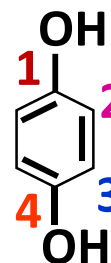
Catechol

Benzene-1,2-diol



Resorcinol

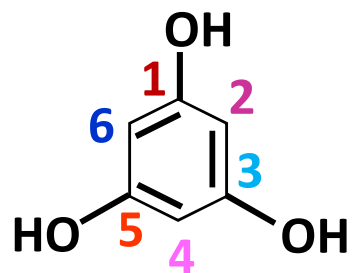
Benzene -1,3- diol



Hydroquinone
(or)
Quinol

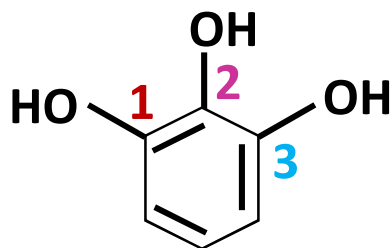
Benzene -1,4-diol

Trihydric phenols



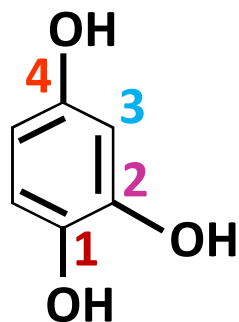
Phloroglucinol

Benzene – 1,3,5 – triol



Pyrogallol

Benzene-1,2,3-triol



Benzene – 1, 2, 4 – triol

MCQs

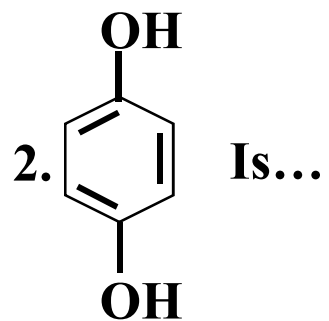
1. Phenols are classified as..

a) Monohydric Phenols

b) Dihydric Phenols

c) Trihydric Phenols

d)  all of these

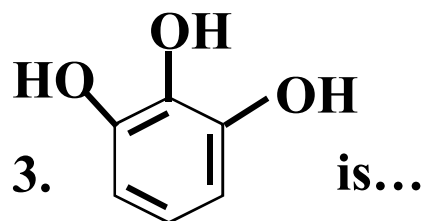


a) Benzene-1,4-diol

b) Hydroquinone

 **c) Both (a) and (b)**

d) None of these



a) trihydric phenol

b) dihydric phenol

c) benzene-1,2,3-triol

 **d) both (a) and (c)**

4. p-cresol is an example of...

a) dihydric phenol

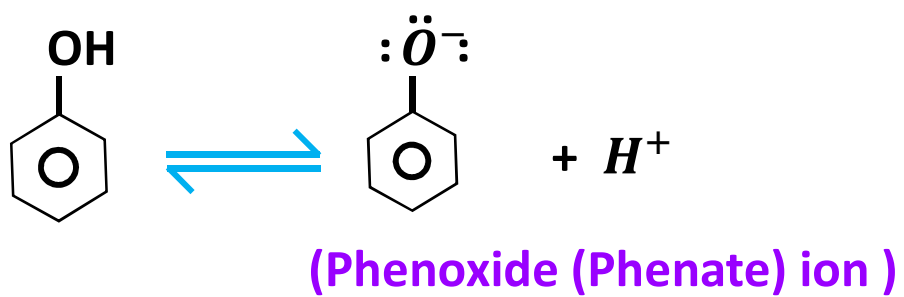
b) trihydric phenol

 c) monohydric phenol

d) monohydric alcohol

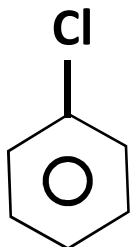
PREPARATION OF PHENOLS

Acidic character of phenol (According to Lowry - Bronsted)

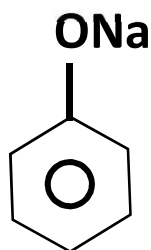


Methods of preparation of Phenol

Dow's process



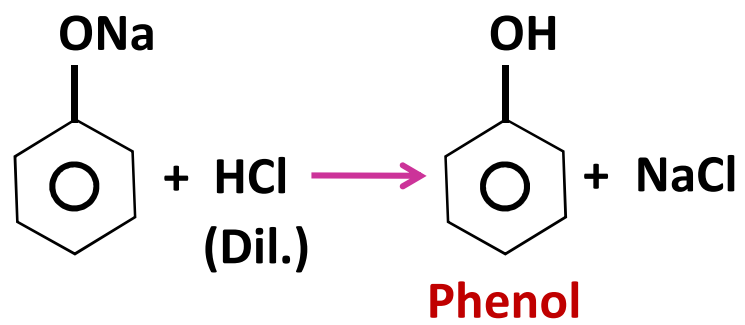
Chlorobenzene
(or)
Phenyl chloride



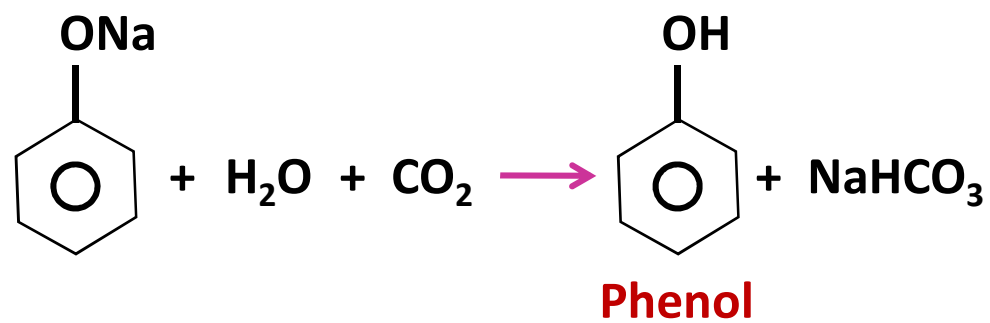
Sodium phenoxide (phenate)



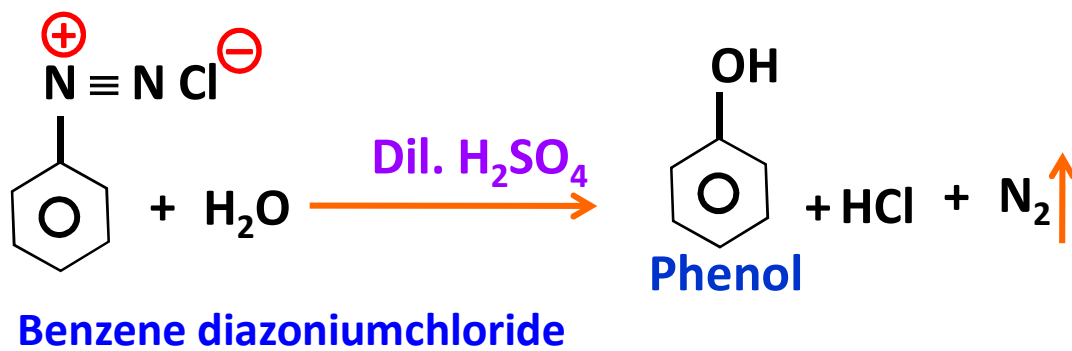
Phenol can be prepared from
First is Dow's process



or



Phenol can be prepared
from diazonium salt

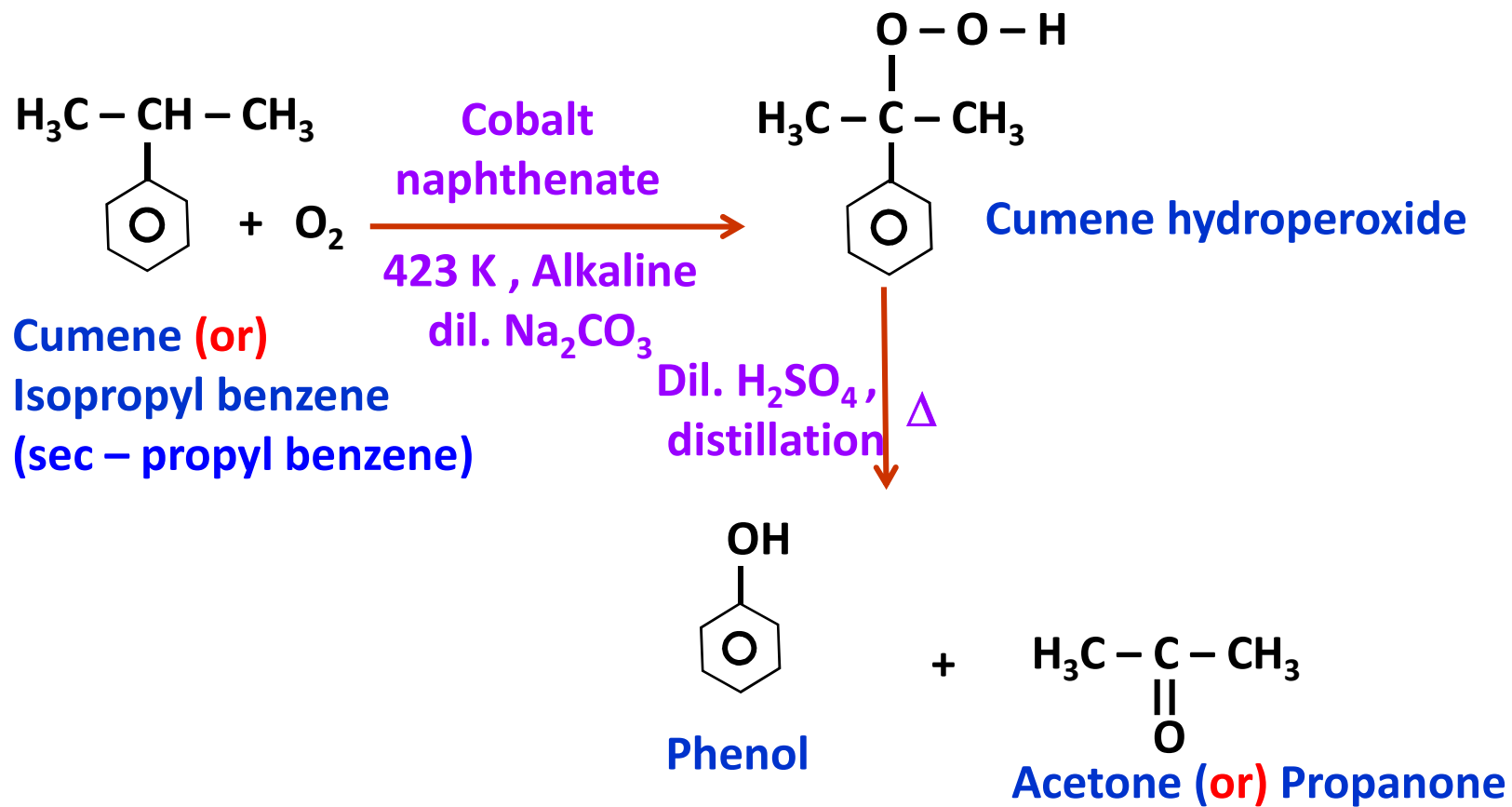


From Cumene

Commercial method

**Phenol can be prepared
commercially from Cumene.**

**Cumene is
Isopropyl benzene**



MCQs

1. Cumene is nothing but...

a) Isopropyl benzene

b) n-propyl alcohol

c) sec-propyl benzene

d)  Both a & c

2. Phenol can be obtained commercially from...

a) chlorobenzene

b) aniline

c)  cumene

d) benzene sulphonic acid

ELECTROPHILIC SUBSTITUTION
REACTION,
BROMINATION & NITRATION

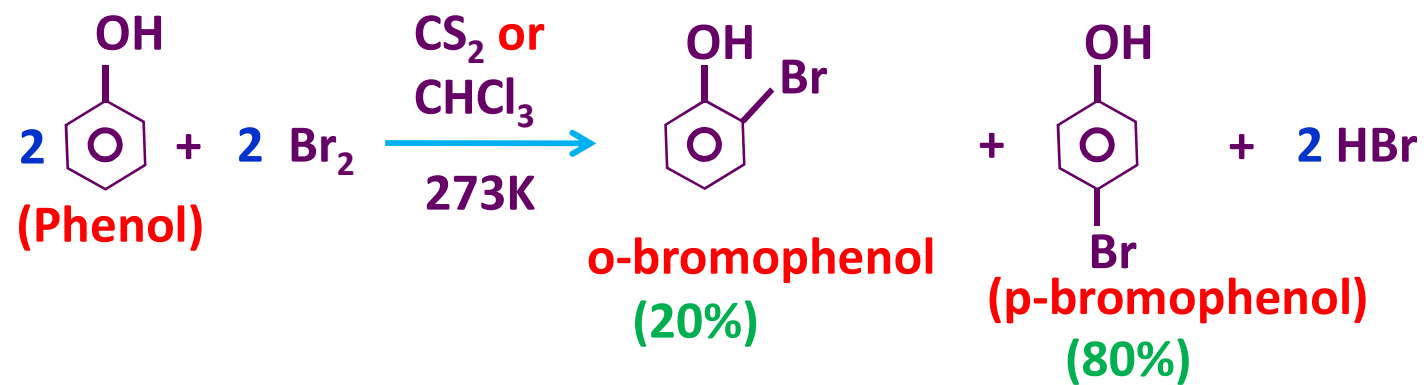
Chemical properties of Phenol

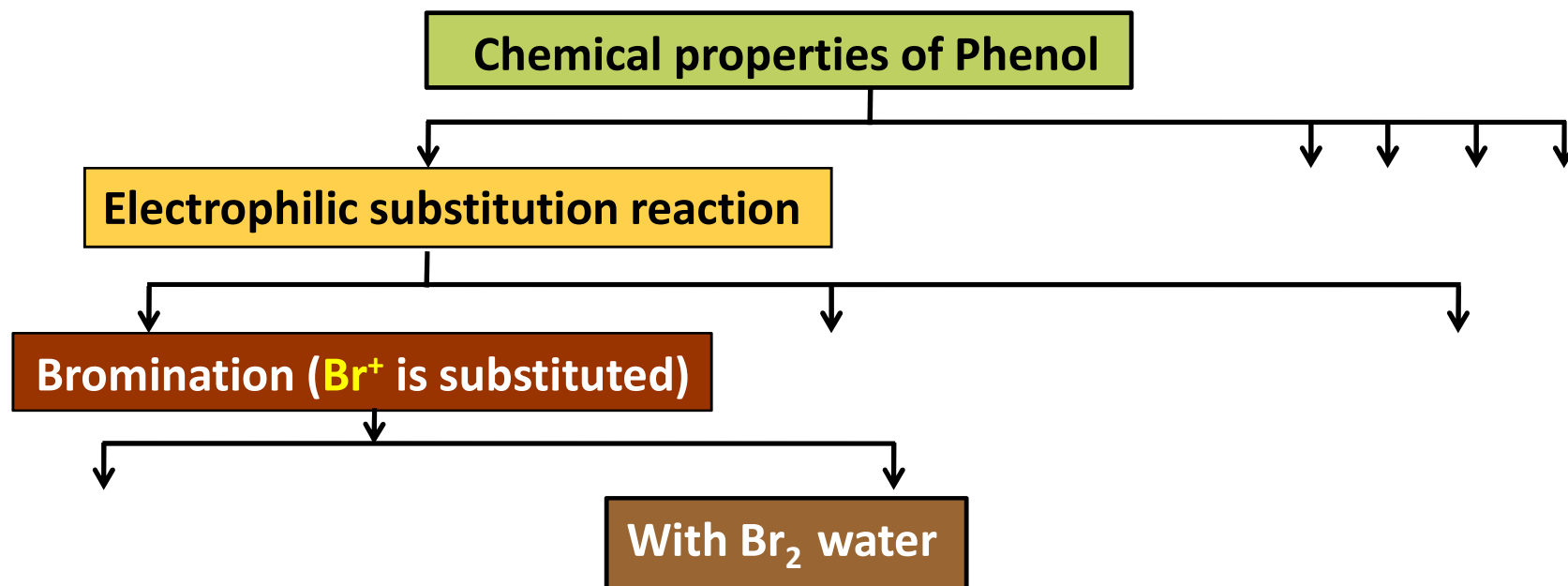
Electrophilic substitution reaction

Bromination

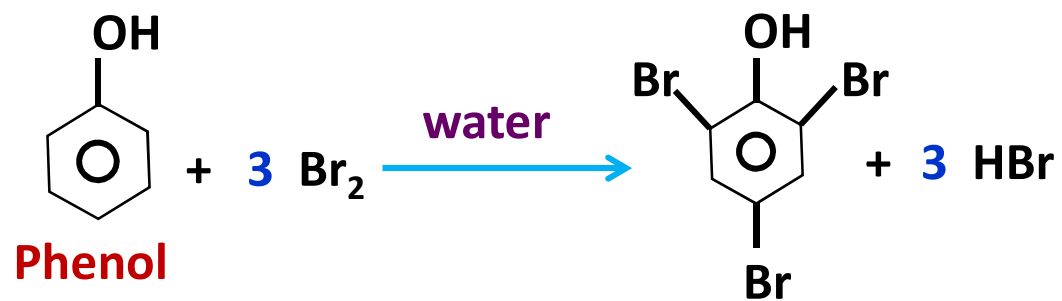
Let us see action of phenol
with liquid Br_2

With liquid Br_2





Let us see action of phenol
with Br₂ water



2,4,6 – tribromophenol

white ppt

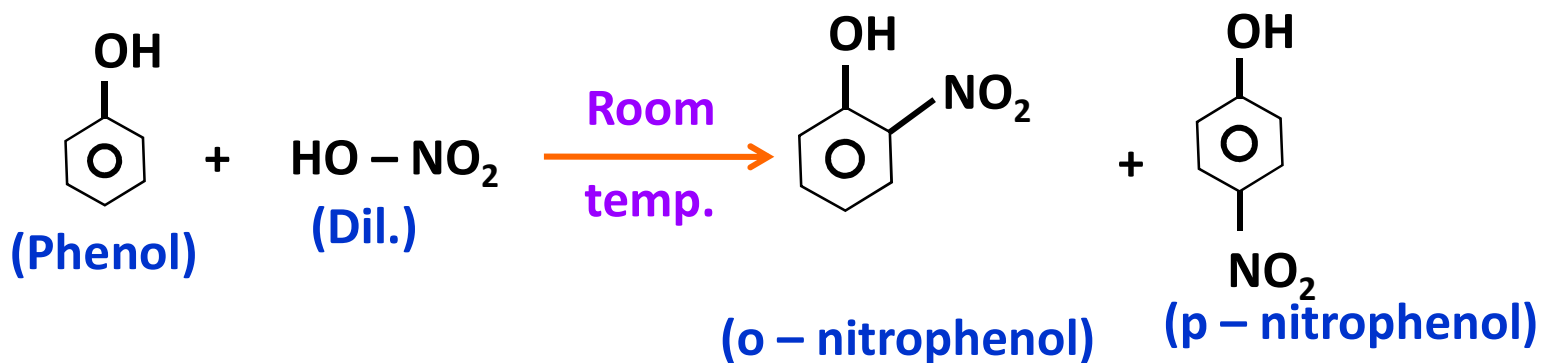
Chemical properties of Phenol

Electrophilic substitution reaction

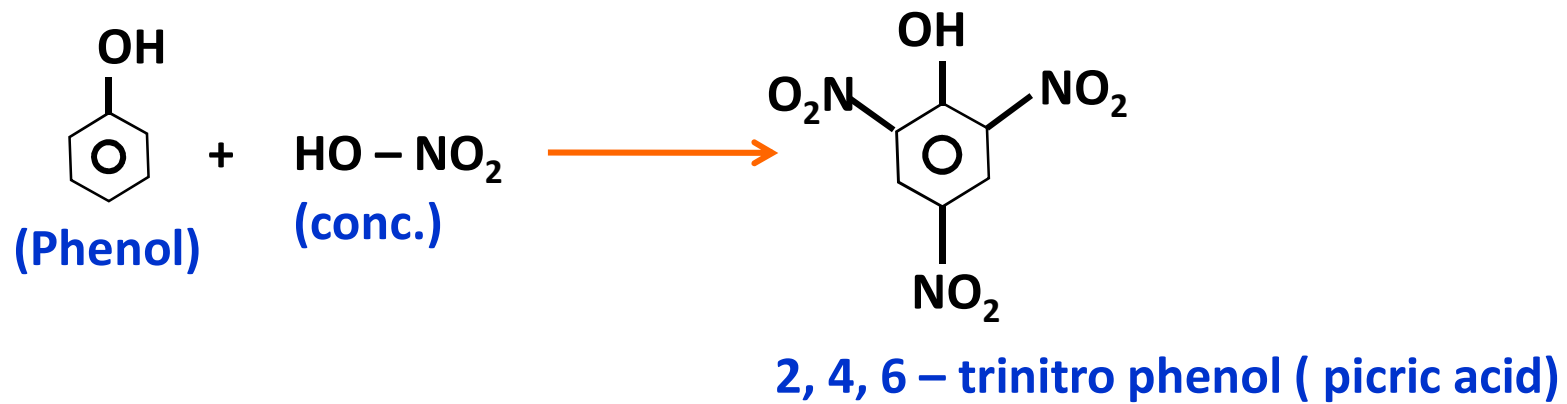
Nitration
(Nitronium ion (NO_2^+) is substituted)

With Dil.

Let us see reaction of phenol
with Dil. HNO_3 (Nitric acid)

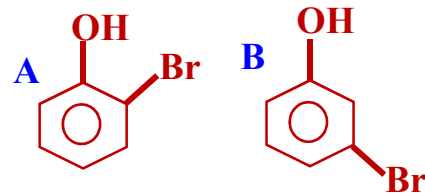
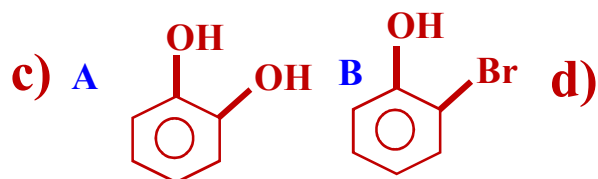
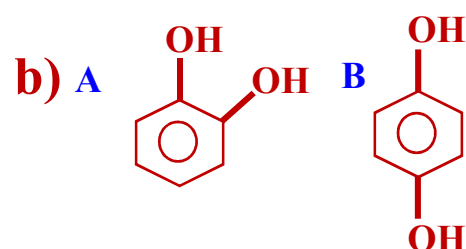
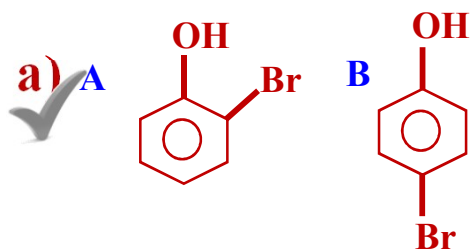


o – nitrophenol is steam volatile due to intramolecular hydrogen bonding , while p – nitrophenol is less volatile due to intermolecular hydrogen bonding.



MCQs

1. Phenol $\xrightarrow[\text{Cs}_2]{\text{Br}_2}$ A + B identify A & B





a) 2,4,6 – Trihydroxy nitro benzene

b) 2,4,6 – Trihydroxy benzene

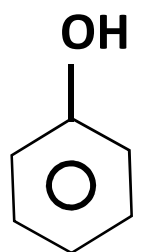
c) 2,4,6 – Trinitro benzene

d)  Picric acid

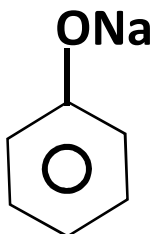
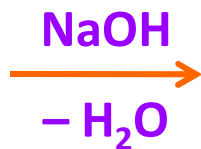
KOLBE'S
&
REIMER – TIEMANN
REACTION

Chemical properties of Phenol

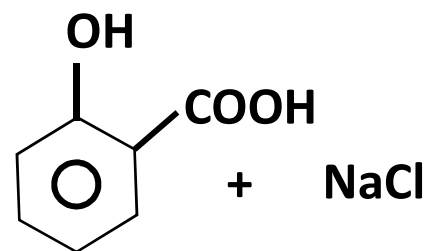
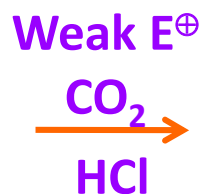
Kolbe's Reaction



Phenol



Sodium phenoxide



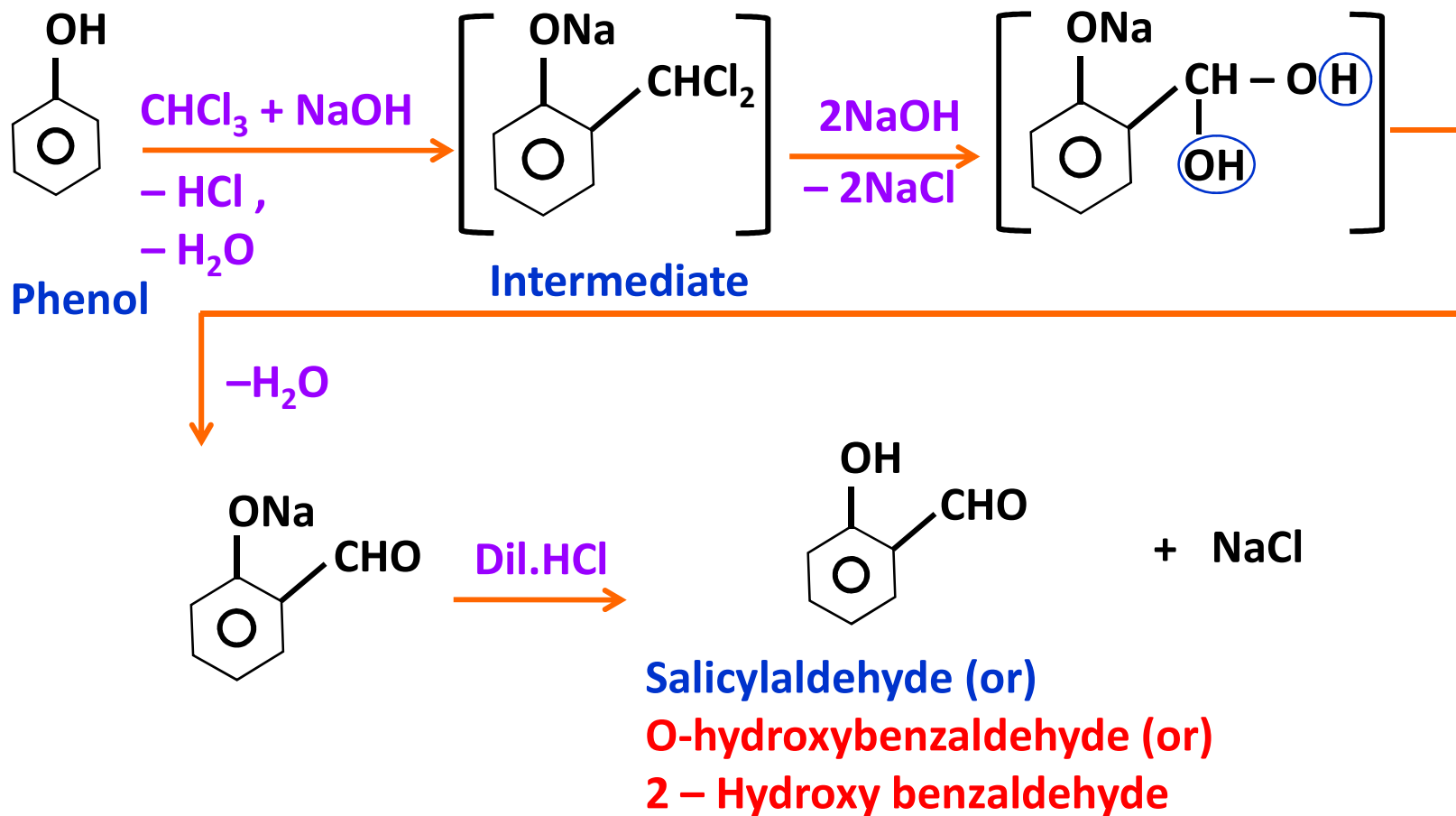
Salicylic acid (or)

O – Hydroxy benzoic acid (or)
2 – Hydroxy benzoic acid

Chemical properties of Phenol

```
graph TD; A[Chemical properties of Phenol] --> B[Reimer – Tiemann reaction]; A --> C[ ]; A --> D[ ]; A --> E[ ]; A --> F[ ]
```

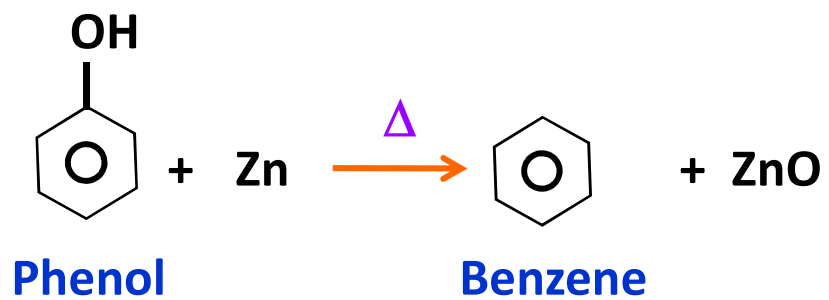
Reimer – Tiemann reaction



Chemical properties of Phenol

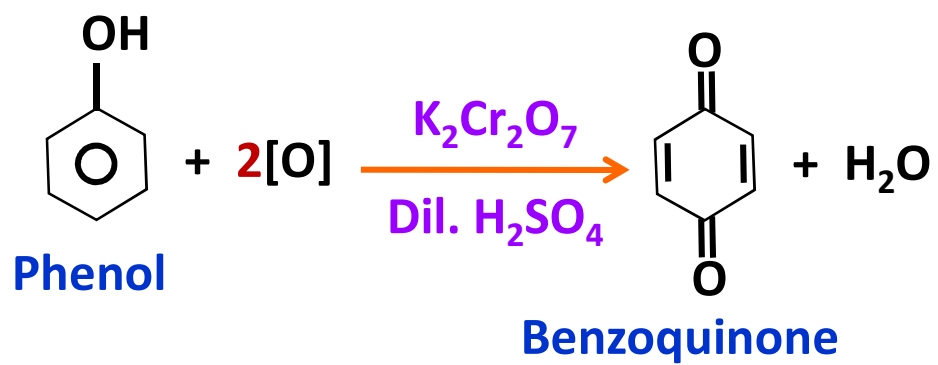
Reaction with Zn dust

Reduction



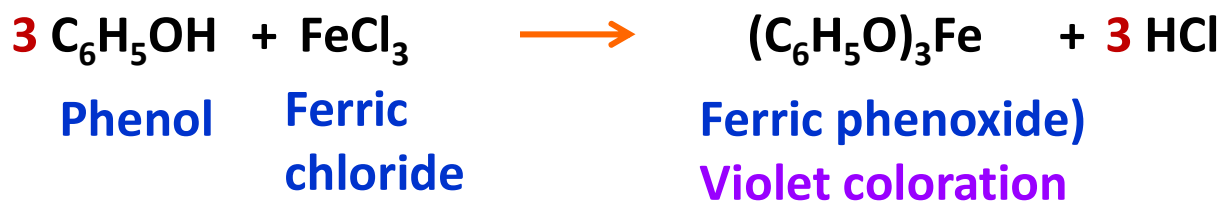
Chemical properties of Phenol

oxidation



Distinguishing test between Alcohol and Phenol

- Alcohol + Neutral FeCl_3 solution does not phenols turns blue
 - Phenol + Neutral FeCl_3 solution turns violet coloration with aq. FeCl_3
- Let us see how we can differentiate between alcohol and phenol



1. Riemer Tiemann reaction gives formation of ...

a) salicylic acid

 **b) salicylaldehyde**

c) sodium phenoxide

d) Both b & c

2. Phenol gives violet coloration when treated with...

a) litmus paper

b) acidic FeCl_3 solution

 **c) aq. Neutral FeCl_3 solution**

d) None of these

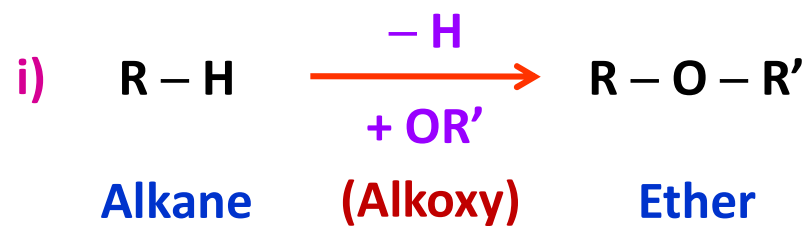
INTRODUCTION TO ETHERS

Ethers

Ethers

Alkoxy or Aryloxy derivatives of alkane

IUPAC Name: Alkoxyalkane or Aryloxy alkane



Functional group of Ether is $\begin{array}{c} | \\ -\text{C}-\text{O}-\text{C}- \\ | \end{array}$
(Ether linkage)

G.F. for aliphatic ethers $\Rightarrow \text{C}_n\text{H}_{2n+2}\text{O}$ (or) $\text{C}_n\text{H}_{2n+1}-\text{O}-\text{C}_n\text{H}_{2n+1}$

Which is same as monohydric alcohols therefore they are functional isomers

For eg. $\text{H}_3\text{C}-\text{CH}_2-\text{OH}$ Ethanol

& $\text{H}_3\text{C}-\text{O}-\text{CH}_3$ Dimethyl ether

MCQs

1. Ethers are...derivatives of alkane

a) alkoxy

b) aryloxy

c) Both a & b

d) Alkyl or aryl

2. General representation of Ether is...



3. Ethers are functional isomers of...

a) Aldehydes

b) Dihydric alcohols

c) Trihydric alcohols

 **d) Monohydric alcohols**

4. General formula for aliphatic ethers is...



d) None of these

ISOMERISM OF ETHERS

Classification of Ethers

Ethers

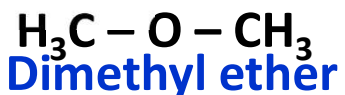
Ethers are of two types

Simple **or**
symmetrical ethers

G.R. : $R - O - R$

(Both the alkyl groups which are attached to the oxygen atom are

same) For eg.



(**or**) Methoxymethane

Mixed **or**
Unsymmetrical ethers

G.R. : $R - O - R'$

(Both the alkyl groups which are attached to the oxygen atom are **different**)

For eg.



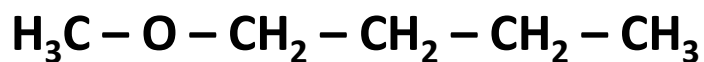
Ethyl methyl ether(**or**) Methoxyethane

Isomerism of Ethers

Chain isomerism

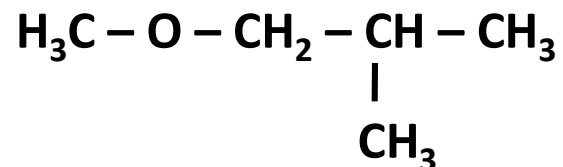
(Different arrangement of carbon chain)

For eg.



n – butyl methyl ether

&

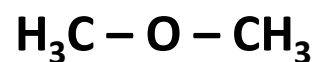


Isobutyl methyl ether

Functional isomerism

(Functional groups are different)

For eg.



Dimethyl ether

&



Ethanol

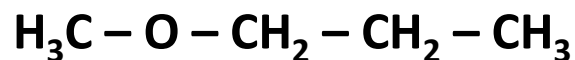
Metamerism

For eg.

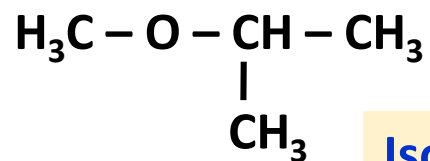
Compounds having M.F. $C_4H_{10}O$ has the following metamers :



Diethyl ether
Ethoxy ethane



Methyl n – propyl ether
1-methoxypropane



Isopropyl methyl ether
2-methoxypropane

Metamerism

Metamers are either chain **or** position isomers with same functional group **&** have different alkyl groups attached to oxygen atom

Eg.



MCQs

1. $\text{C}_2\text{H}_5 - \text{O} - \text{CH}_3$ is an example of...

a) symmetrical ether

b) Mixed ether

c) unsymmetrical ether

 d) Both b & c

2. $\text{H}_3\text{C} - \text{O} - \text{CH}_3$ and $\text{H}_3\text{C} - \text{CH}_2 - \text{OH}$ are...of each other

a) Chain isomers

b) metamers

 c) Functional isomers

d) All of these

3. Ethers having same molecular formula but different alkyl groups on either side of oxygen atom, called as...

a) chain isomers

 **b) metamers**

c) functional isomers

d) All of these

4. Ethers in which both alkyl groups attached to oxygen are same, are called...

a) simple ethers

b) mixed ethers

c) symmetrical ethers

 **d) Both a & c**

NOMENCLATURE OF ETHERS

No.	Structure	Common Name
1.	$\text{H}_3\text{C} - \text{O} - \text{CH}_3$	Dimethyl ether

I.U.P.A.C. Name (Alkoxyalkane)
Methoxymethane

Think about its IUPAC name.

Nomenclature of Ethers

No.	Structure	Common Name
2.	$\text{H}_3\text{C} - \text{O} - \text{CH}_2 - \text{CH}_3$	Ethyl methyl ether

Think about its IUPAC name.

I.U.P.A.C. Name (Alkoxyalkane)

Methoxyethane

Nomenclature of Ethers

No.	Structure	Common Name
3.	$\text{CH}_3 - \text{H}_2\text{C} - \text{O} - \text{CH}_2 - \text{CH}_3$	Diethyl ether

I.U.P.A.C. Name (Alkoxyalkane)

Ethoxyethane

✓
It's IUPAC name is

Nomenclature of Ethers

No.	Structure	Common Name
4.	$\text{H}_3\text{C} - \text{O} - \overset{\textcircled{1}}{\text{CH}_2} - \overset{\textcircled{2}}{\text{CH}_2} - \overset{\textcircled{3}}{\text{CH}_3}$	Methyl n -propyl ether

✓
IUPAC name of it is--

I.U.P.A.C. Name (Alkoxyalkane)

1 – Methoxypropane

Nomenclature of Ethers

No.	Structure	Common Name
5.	$ \begin{array}{c} \textcircled{2} \quad \textcircled{1} \\ \text{H}_3\text{C} - \text{O} - \text{CH} - \text{CH}_3 \\ \\ \textcircled{3} \text{CH}_3 \end{array} $	isopropyl methyl ether

Now, can you tell me the IUPAC name ?

I.U.P.A.C. Name (Alkoxyalkane)

2 – Methoxypropane

Nomenclature of Ethers

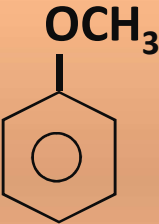
No.	Structure	Common Name
6.	$ \begin{array}{c} \textcircled{1} \text{CH}_3 \\ \\ \text{H}_3\text{C} - \text{O} - \textcircled{2} \text{C} - \text{CH}_3 \\ \\ \textcircled{3} \text{CH}_3 \end{array} $	tert-butyl methyl ether

Now, can you tell me the IUPAC name ?

I.U.P.A.C. Name (Alkoxyalkane)

2 – Methoxy – 2 – methylpropane

Nomenclature of Ethers

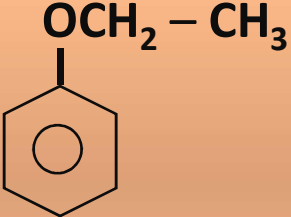
No.	Structure	Common Name
7.		<p>Most common called as Anisole</p> <p>Other name based on alkyl and aryl groups Methyl phenyl ether</p>

I.U.P.A.C. Name (**Alkoxyalkane**)

Methoxybenzene

IUPAC name of it is --

Nomenclature of Ethers

No.	Structure	Common Name
8.	 <chem>CCOC1=CC=CC=C1</chem>	Phenetole Other name: Ethyl phenyl ether


I.U.P.A.C. Name (Alkoxyalkane)

Ethoxybenzene

IUPAC name of it is --

MCQs

1. IUPAC name of ether in general is...

- a)  Alkoxyalkane**
- b) Alkylalkane**
- c) Allylalkane**
- d) None of these**

2. What is the IUPAC name of $\text{H}_3\text{C} - \text{O} - \text{C}(\text{CH}_3)_2 - \text{CH}_3$

a) 2-Methyl-2-Methoxypropane

b) 2, 2-Dimethyl-2-methoxy ethane

c)  2-Methoxy-2-methylpropane

d) All of these



a) Phenyl ethoxy

b) Ethylbenzoxy

 c) Ethoxy benzene

d) All of these

PHYSICAL PROPERTIES OF ETHERS

Physical properties of Ethers

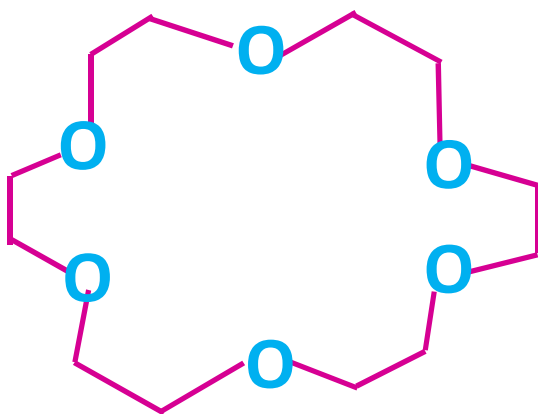
Let us go through
physical properties
carefully.

- ➡ Boiling points of ethers are slightly higher than alcohols but much lower than that of alcohols.
- ➡ Ethers are immiscible with water because they do not form H – bonding with water molecule readily due to alkyl groups or hydrocarbon part.
- ➡ Dipole moment for diethyl ether is 1.18 D.
- ➡ Some ethers are Volatile and are highly inflammable.

Uses of Diethyl ether

Some important uses of Diethyl ether....

- ➡ Used as industrial solvent for oils, fats, etc.
- ➡ Used as solvent in the reaction of Grignards reagent.
- ➡ Used as refrigerant.
- ➡ A mixture of diethyl ether & ethyl alcohol, known as **Natalite**, which is used as fuel (substitute for petrol)



Did you come
across this type of
structure so far?

Imagine what it
could be?

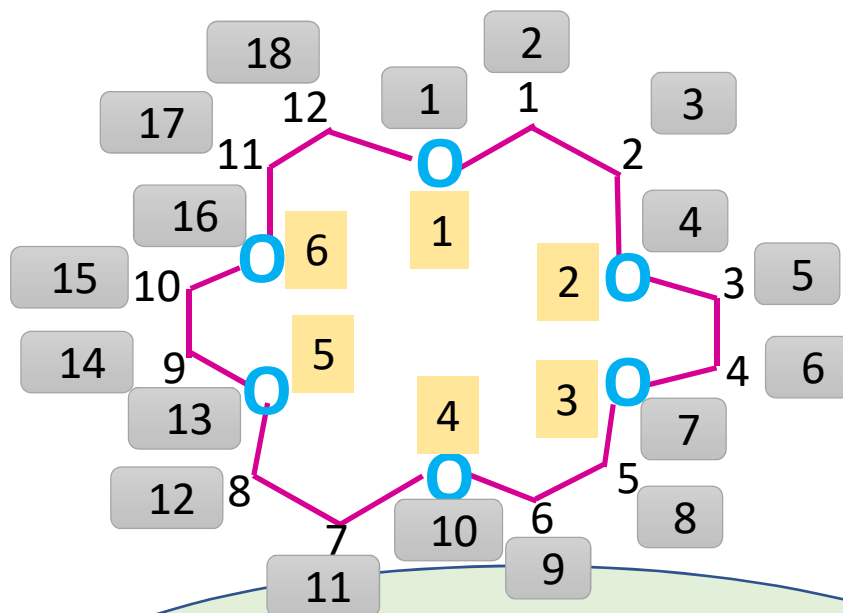
Let us travel to next slide for
better understanding

Crown ethers

Charles J. Pederson discovered Macroscopic polyethers, which are the organic compounds with molecules containing large rings of carbon & oxygen atoms, called crown ethers.

Crown ethers are named as $n - \text{crown} - m$, where n is the total number of atoms and m is the number of oxygen atoms in the ring.

The number of carbons = total number of atoms - number of oxygen atoms.
The first crown ether synthesized is $18 - \text{crown} - 6$.



Structure of 18 – crown – 6

1 to 6 are oxygens

1 to 12 are carbons

1 to 18 total number of atoms.

6-indicates number of oxygens
 18 -indicates number of atoms
 including carbons
 Number of carbons = $18 - 6 = 12$

MCQs

1. Boiling points of ethers are lower than that of...

a) Carboxylic acids

 **b) Alcohol**

c) Amides

d) all of these

2. Those ethers which are... in nature, are highly inflammable


a) Non – volatile

 **b) Volatile**

c) Both a & b

d) None of these

3. Natalite is...

- a) diethyl ether and methyl alcohol**
- b) dimethyl ether and methyl alcohol**
-  c) diethyl ether and ethyl alcohol**
- d) diethyl ether and propyl alcohol**

4. The first crown ether to be synthesized was...

a) 16 – crown – 6

b) 14 – crown – 6

c) 17 – crown – 6

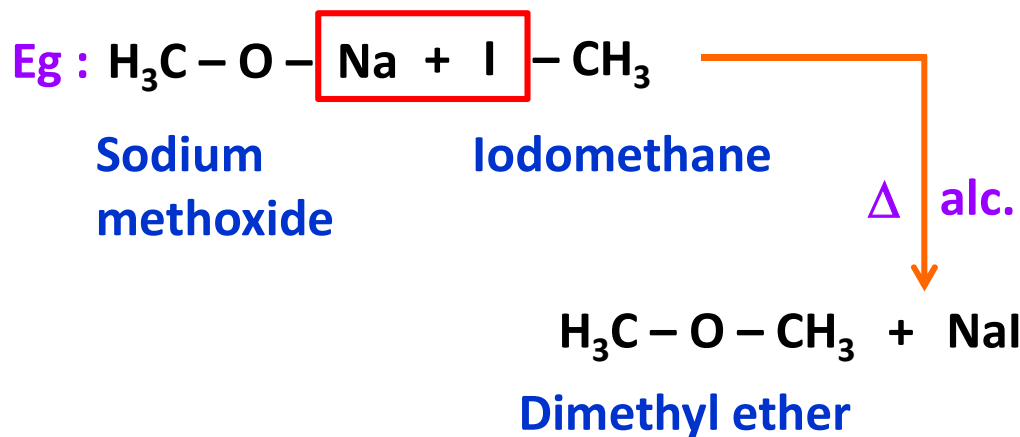
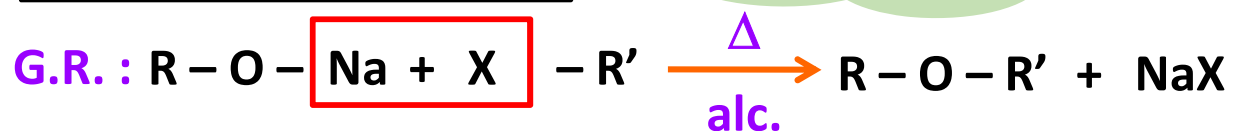
 **d) 18 – crown – 6**

PREPARATION OF ETHERS

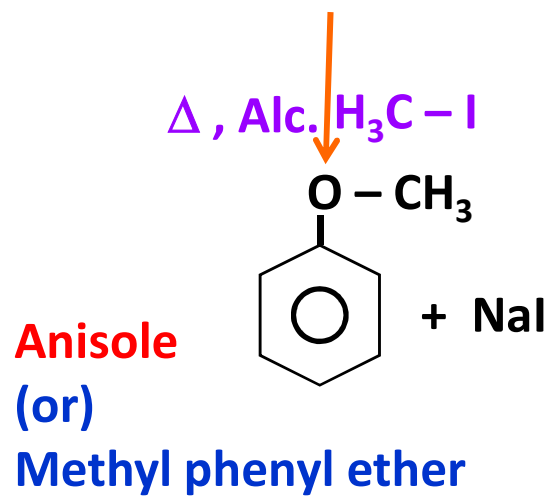
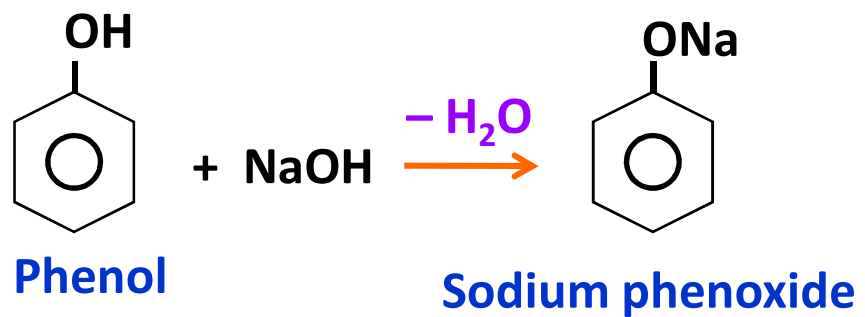
Methods of preparation of Ethers

There are 3 methods of preparation of ethers

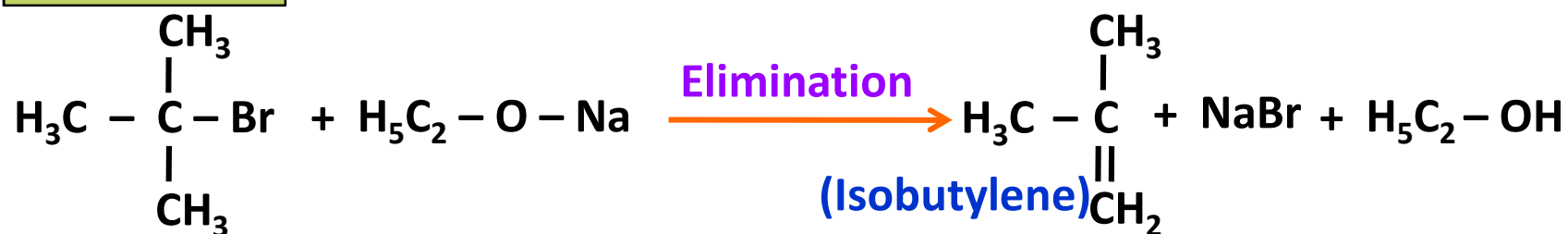
Williamson's Synthesis







Limitation



Tert – butyl
bromide (3°)

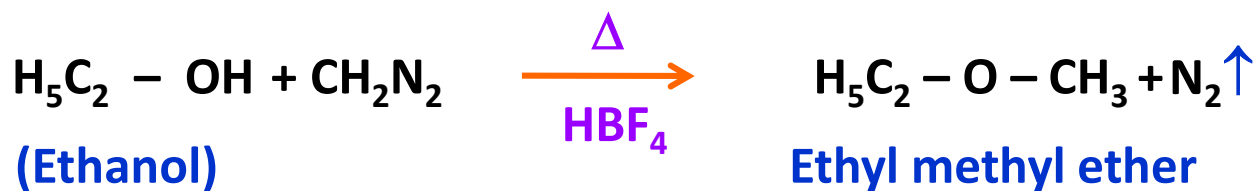
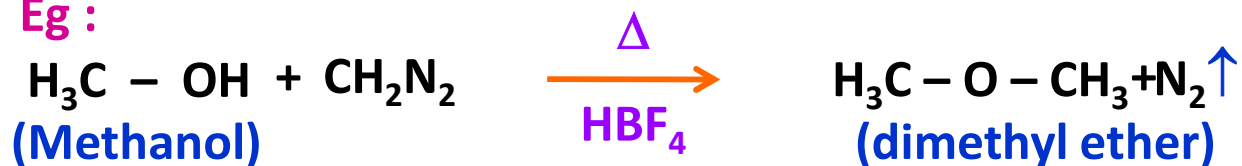
Only 1° alkyl halide is used in this method, because 2° & 3° alkyl halide gives alkene on Elimination.

Methods of preparation of Ethers

From Alcohol & Diazomethane



Eg :



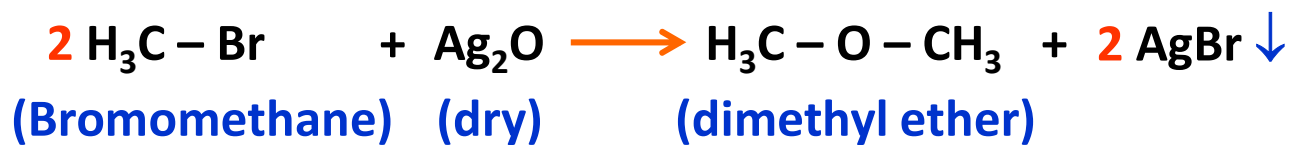
Limitation

Only Methyl ethers are obtained by this method.

Diethyl ether can't be prepared by this method.

Methods of preparation of Ethers

With dry Ag_2O



MCQs

1. Methyl iodide when heated with alcoholic sodium ethoxide, product is...

a) diethyl ether

 **b) ethyl methyl ether**

c) diethyl ether

d) all of these

2. In Williamson's synthesis, only...alkyl halide is used

a) Secondary (2°)

b) Tertiary (3°)

 c) Primary (1°)

d) all of these

3. Only...ethers are obtained from alcohols and diazomethane

a) ethyl

b) diethyl

c) dimethyl

 **d) methyl**

4. Bromomethane on treatment with dry Ag_2O , gives...

a) diethyl ether

b) ethyl methyl ether

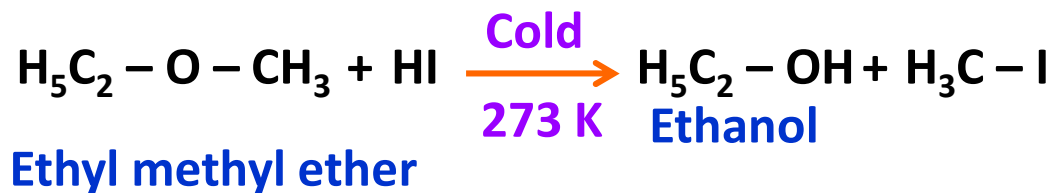
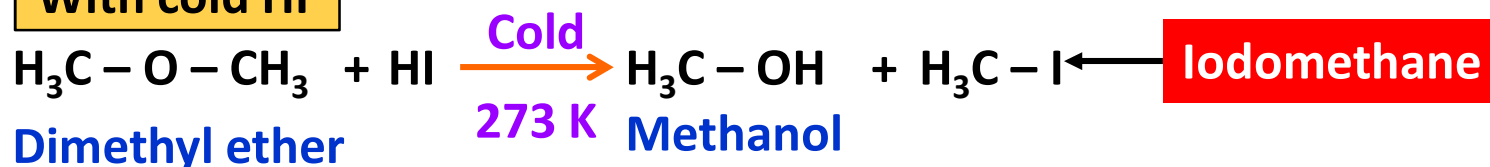
 c) dimethyl ether

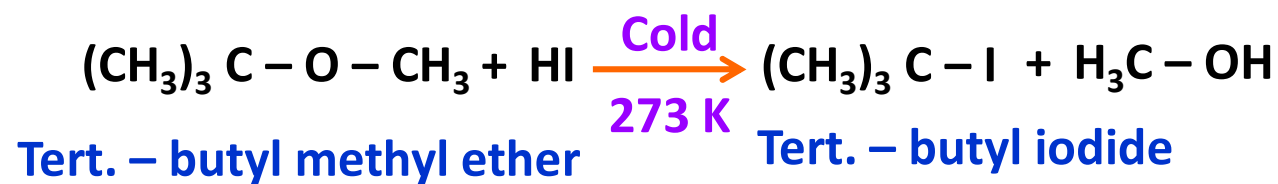
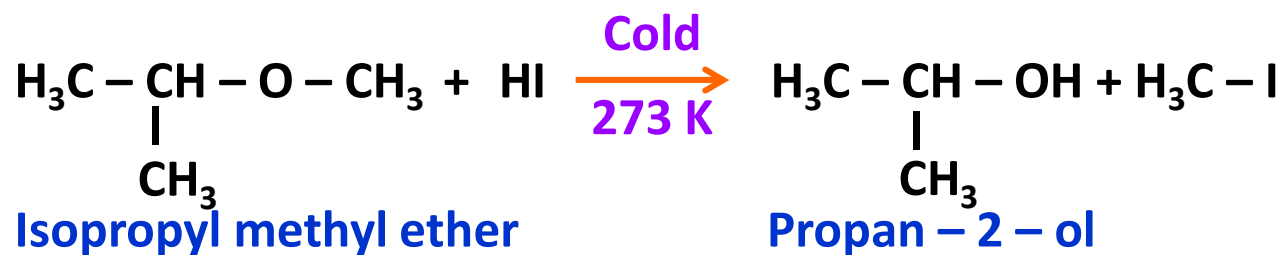
d) All of these

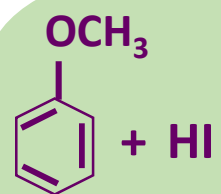
CHEMICAL PROPERTIES OF ETHERS

Chemical properties of Ethers

With cold HI

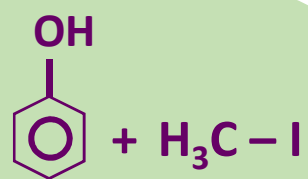






Anisole

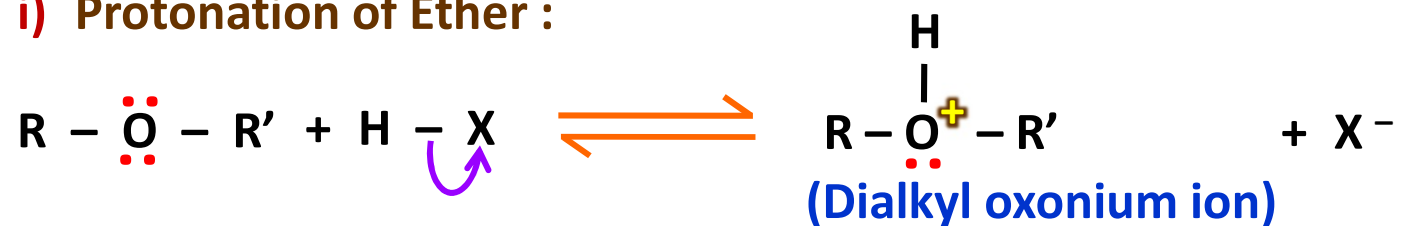
Cold
→



Phenol

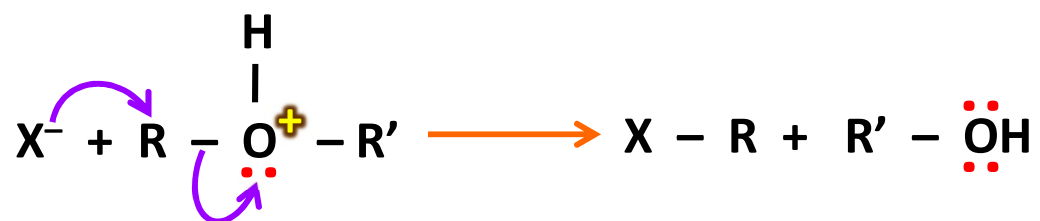
Mechanism

i) Protonation of Ether :

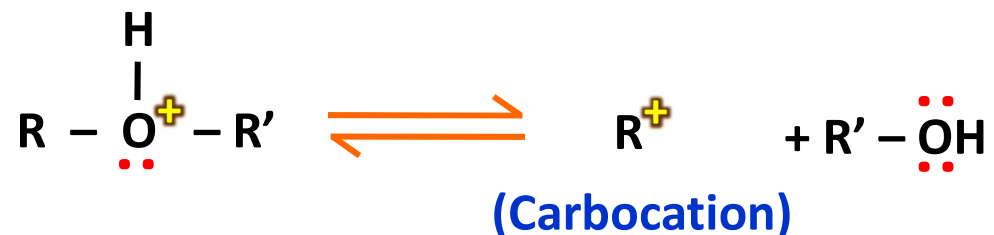


ii) $\text{S}_{\text{N}}2$ cleavage :

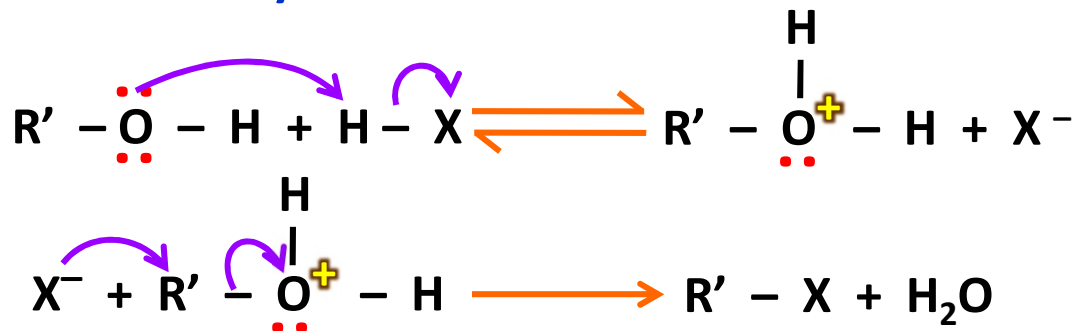
(a) If alkyl groups are 1° or 2° then lower alkyl group forms alkyl halide



(b) If alkyl group is tertiary then tertiary alkyl halide is formed.

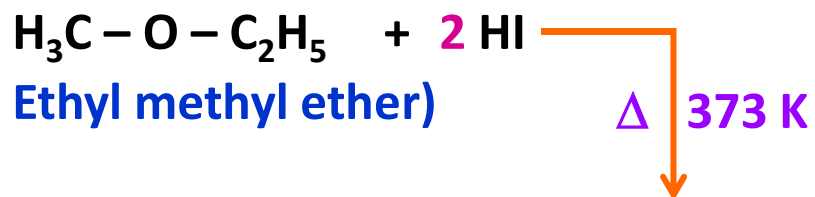


iii) At high temperature alcohol molecule reacts with excess of HX to give alkyl halide :



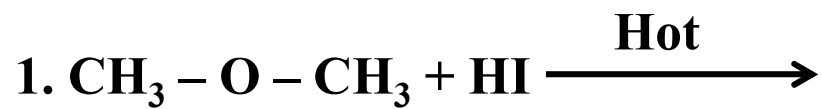
Chemical properties of Ethers

Let us see reaction of
ether with Hot HI





MCQs

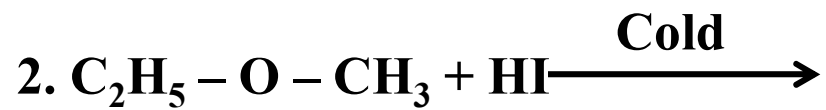


a) CH_3I , CH_3OH

b) CH_3I , CH_4

c) CH_3OH , CH_3OH

d)  CH_3I



a) $\text{C}_2\text{H}_5\text{I}$, CH_3OH

b) CH_3I , $\text{C}_2\text{H}_5\text{I}$

c) ✓ CH_3I , $\text{C}_2\text{H}_5\text{OH}$

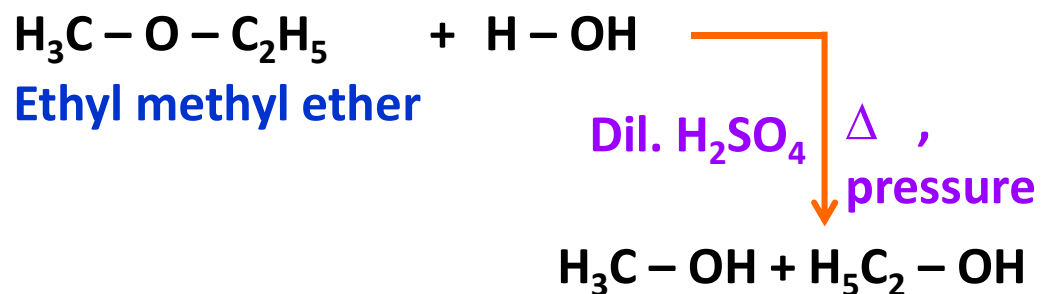
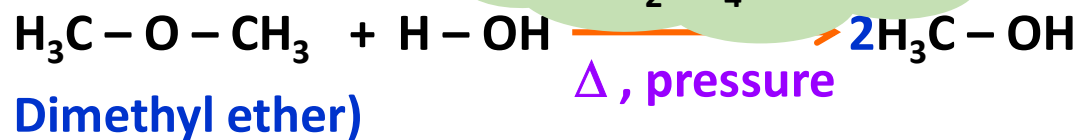
d) $\text{C}_2\text{H}_5\text{OH}$, CH_3OH

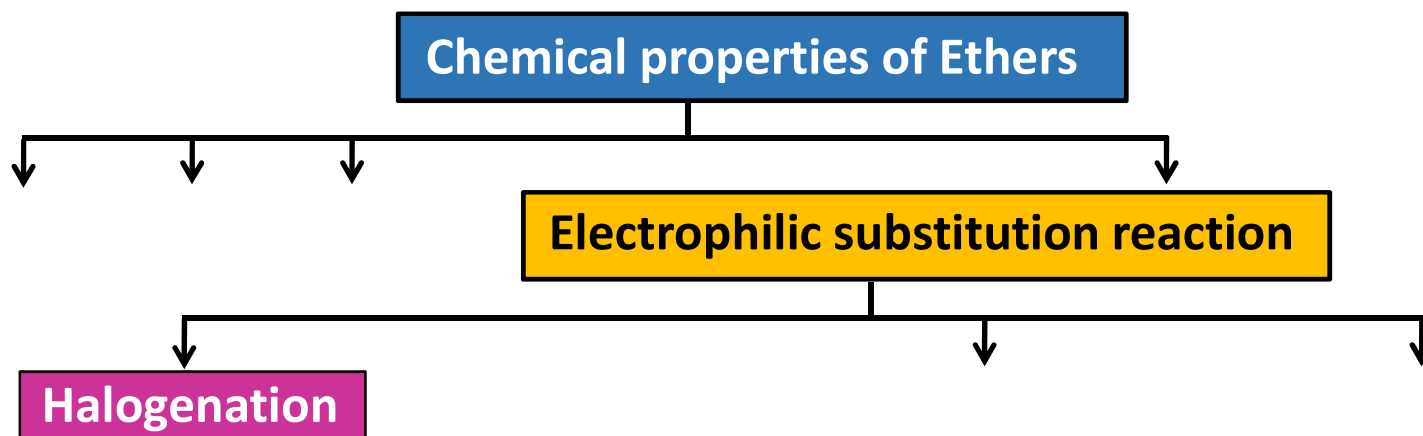
ELECTROPHILIC SUBSTITUTION REACTION OF ETHERS

Chemical properties of Ethers

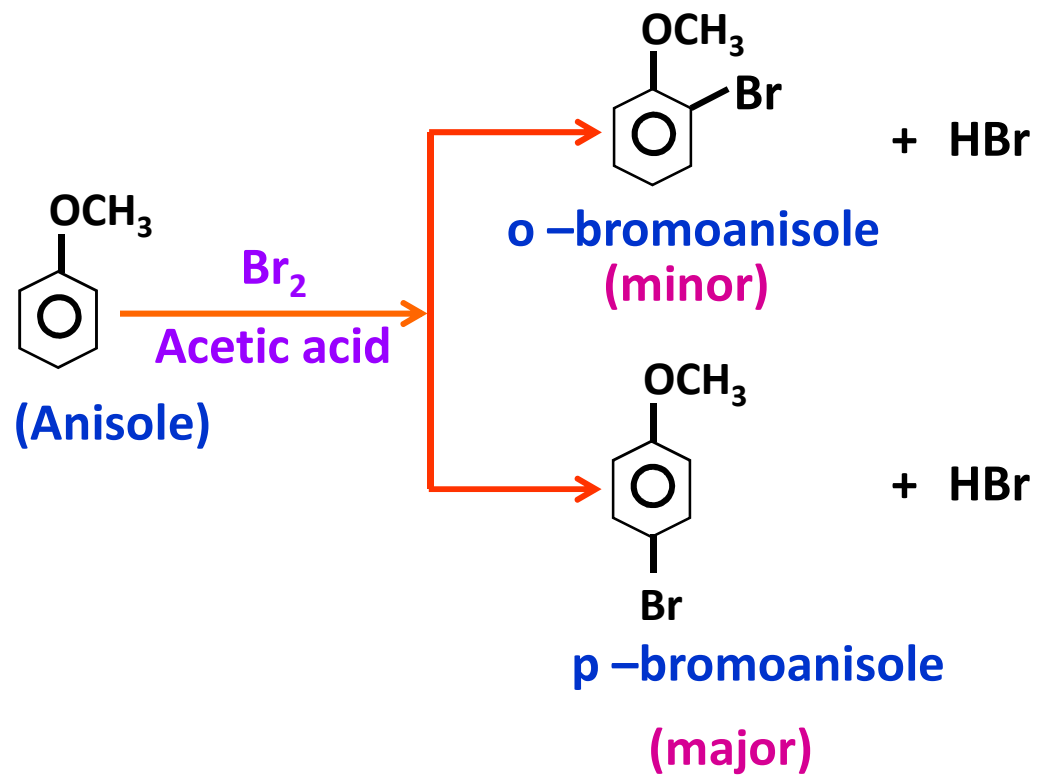
Acid-catalyzed cleavage (Hydrolysis)

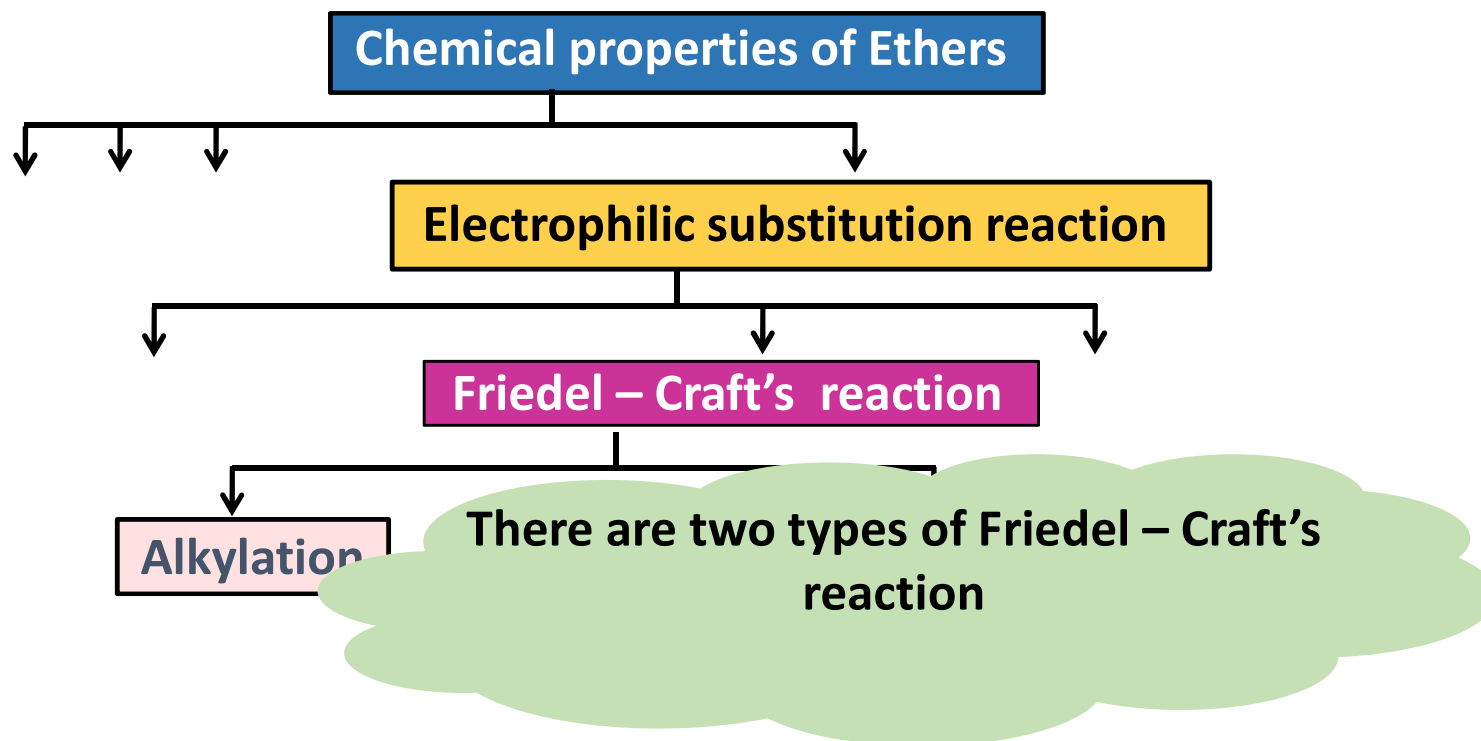
Let us see action of
dil. H_2SO_4 on ethers

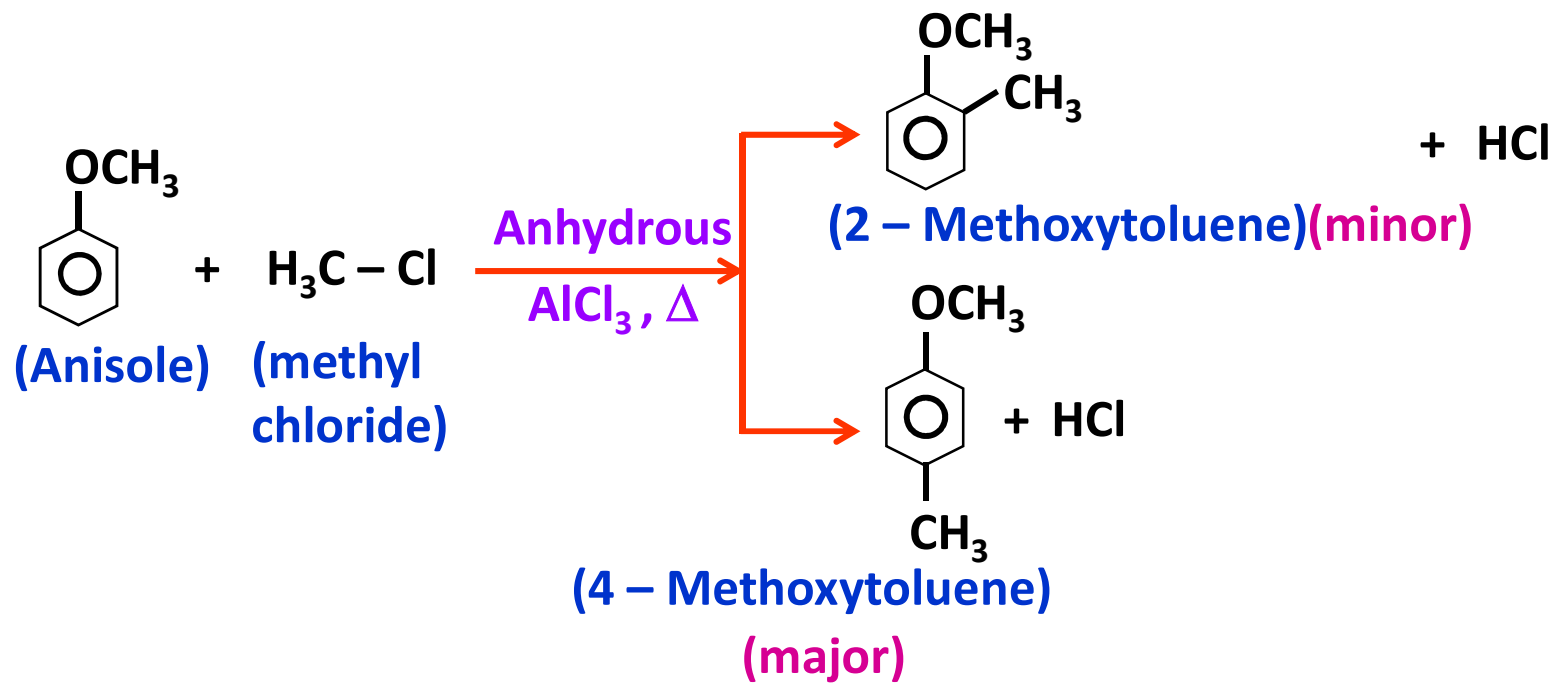


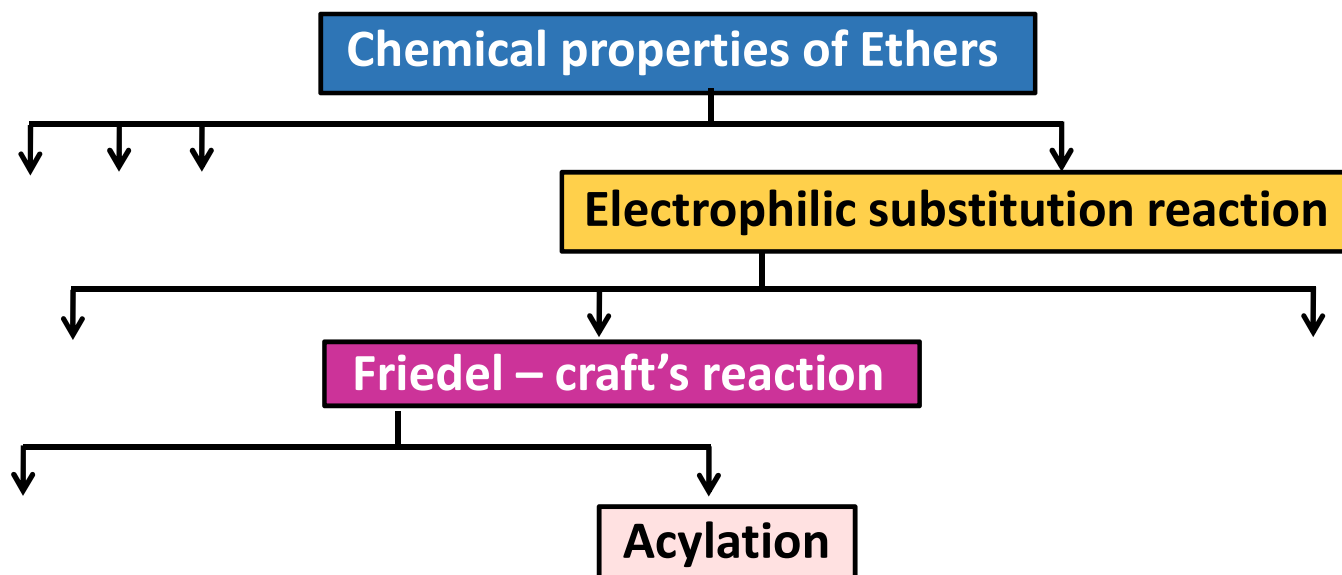


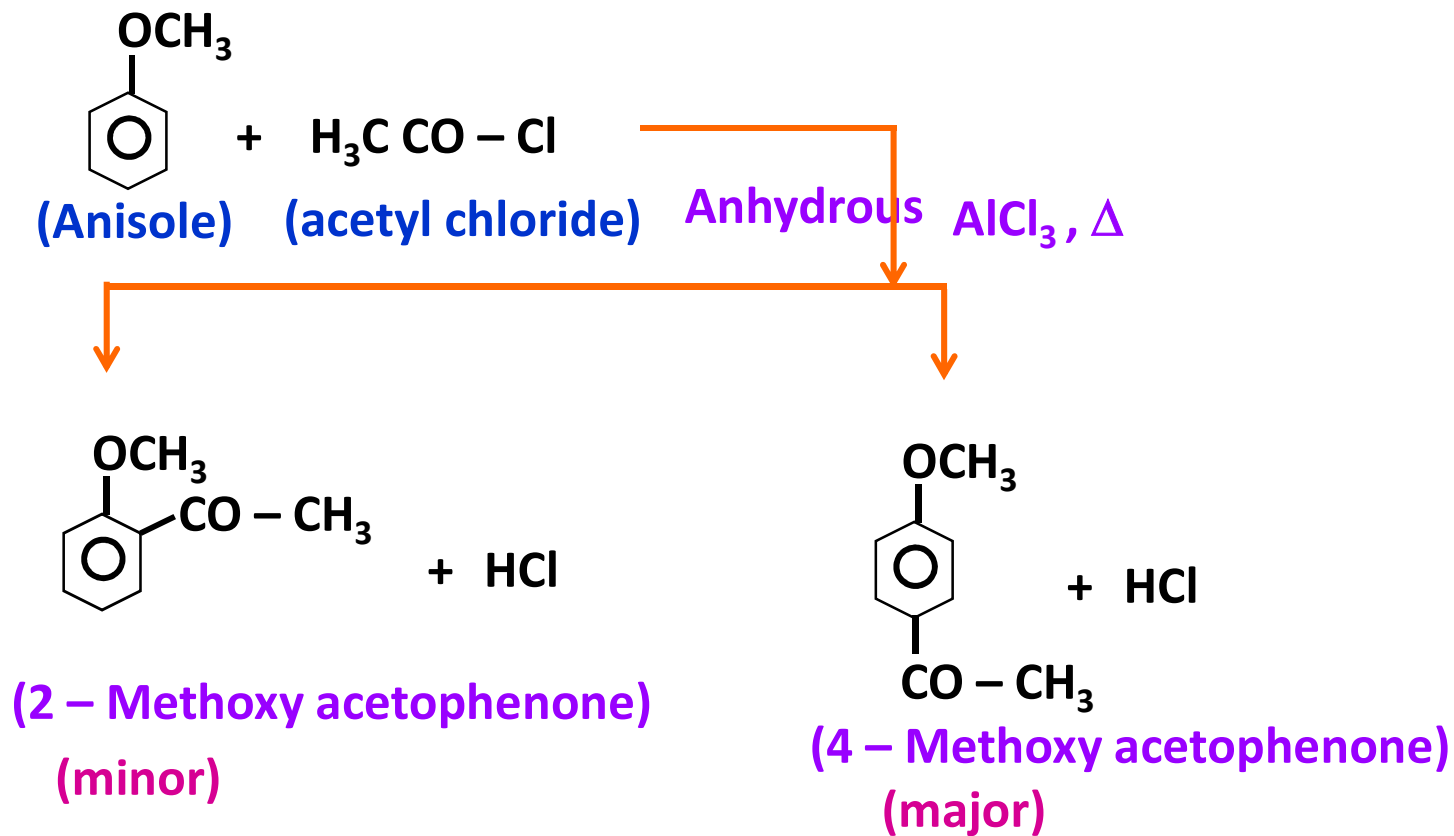
There are three types of electrophilic substitution reactions

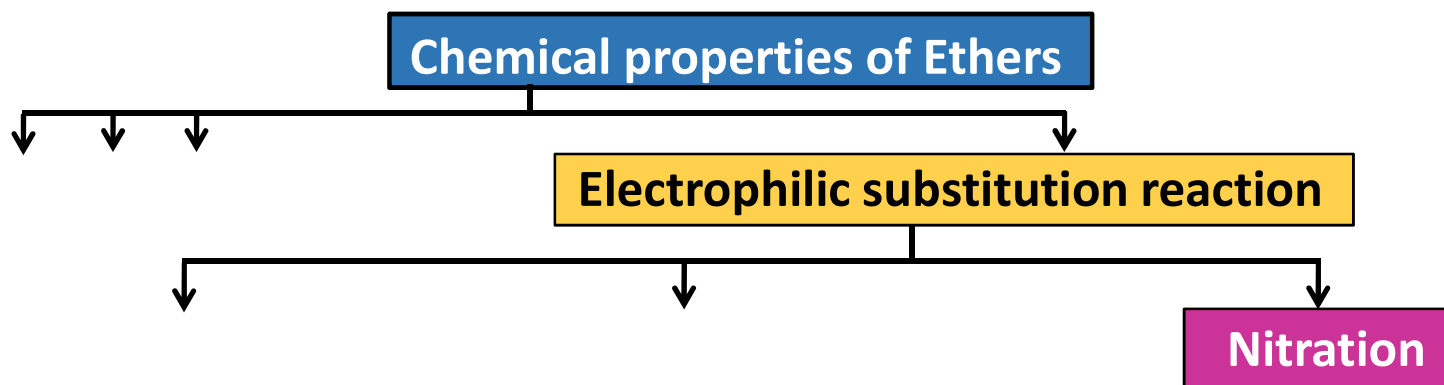


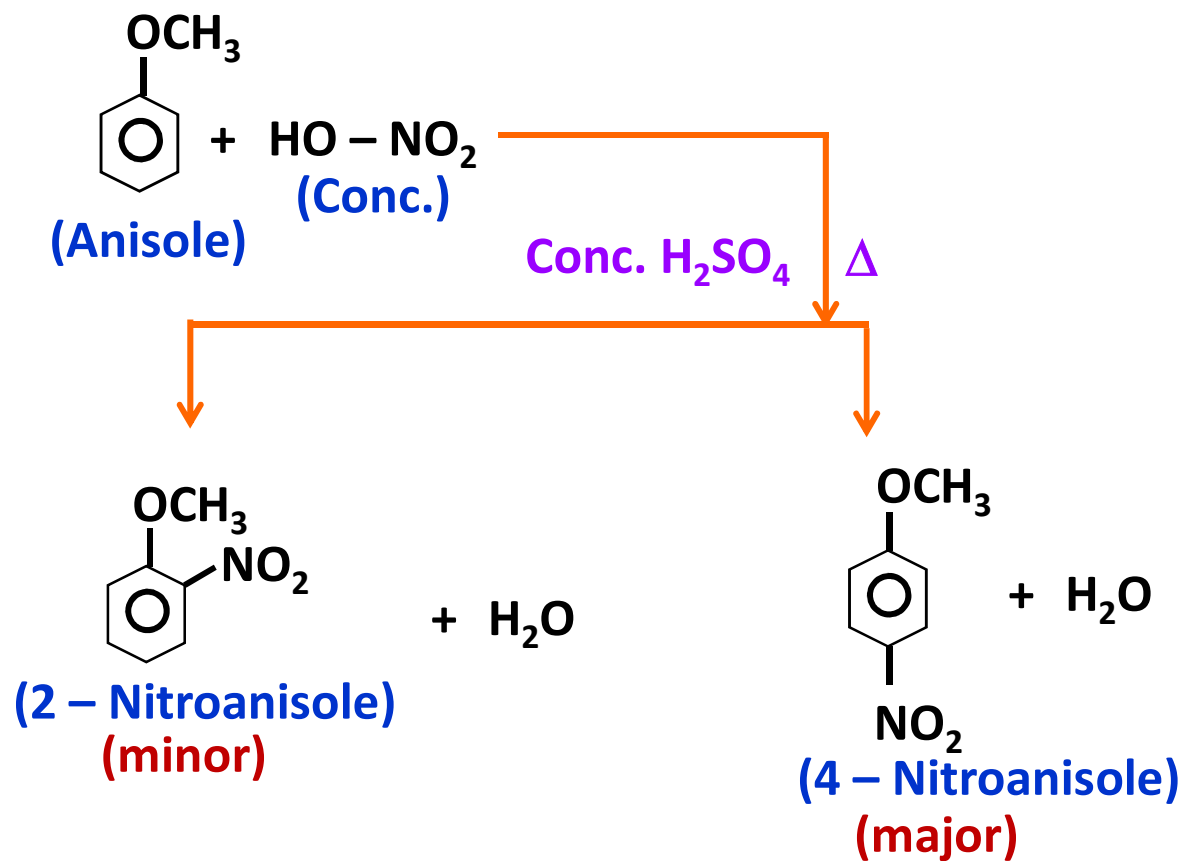












MCQs

1. Anisole when treated with Br_2 in acetic acid gives,

a) o – bromoanisole

b) m – bromoanisole

c) p – bromoanisole

 d) Both a & c

2. Anisole when heated with acetyl chloride in presence of anhydrous AlCl_3 ...

a) 2 – methoxyacetophenone

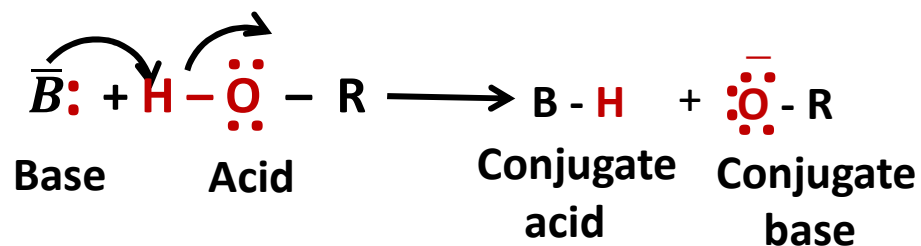
b) 3 – methoxyacetophenone

c) 4 – methoxyacetophenone

d)  Both a & c

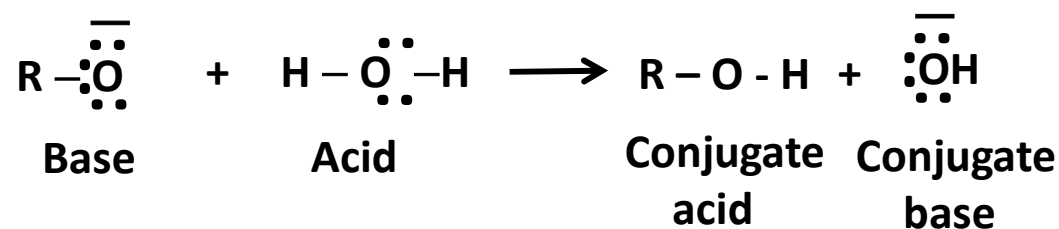
Acidic nature of Alcohols , Phenols & Ethers

The reactions show that alcohols and phenols are acidic in nature. In fact, alcohols and phenols are brownsted acids i.e., they can donate a proton to a stronger base (B:).



Alcohols are however, weaker acids than water.

`This can be illustrated by the reaction of water with an alkoxide.



This reaction shows that water is a better proton donor (i.e., stronger acid) than alcohol.

Also, in the above reaction, we note that alkoxides are strong bases (sodium ethoxide is a stronger base than sodium hydroxide).



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