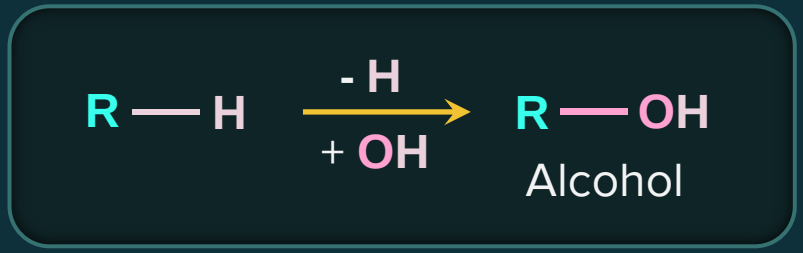
Welcome to

Aakash + BYJU'S LIVE

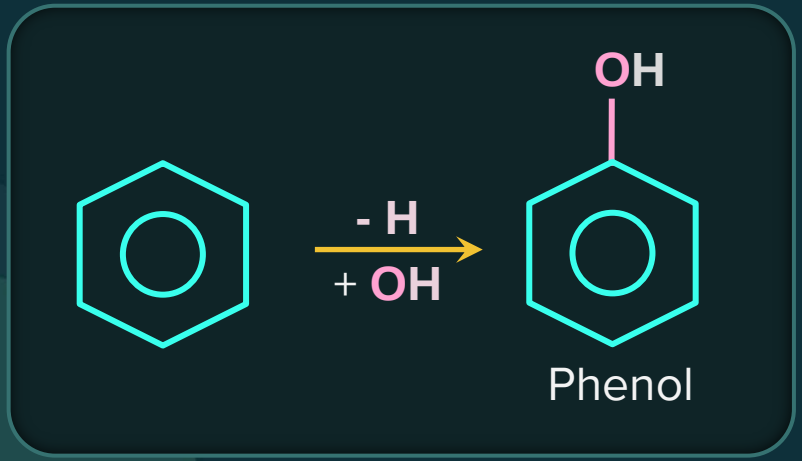
Alcohols, Phenols, & Ethers

Alcohol and Phenol

Replacement of **H** by **OH** at alkyl carbon gives **alcohol**

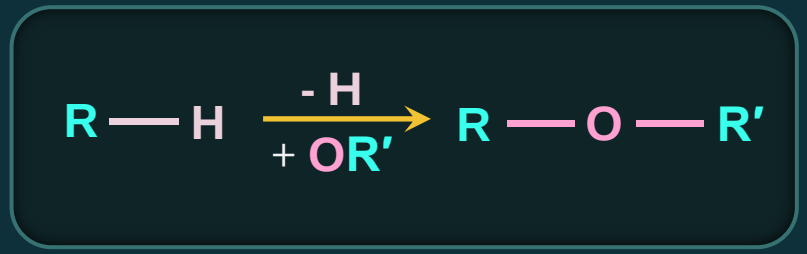


Replacement of **H** by **OH** at one carbon of benzene ring gives **alcohol**

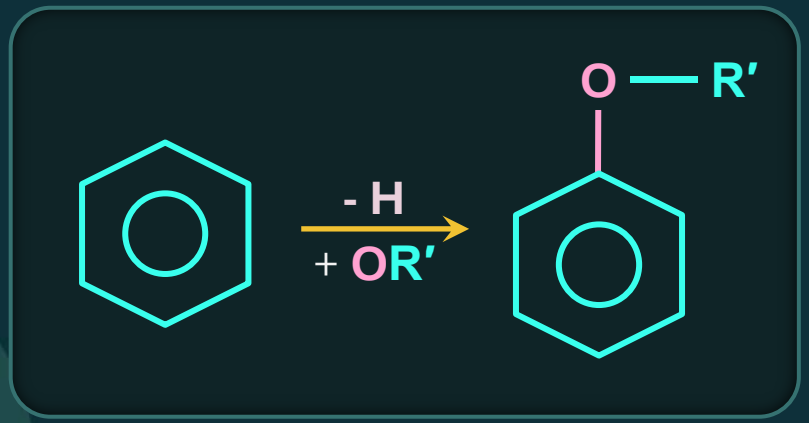


Alkyl and Aryl Ethers

Replacement of **H** by **OR** at alkyl carbon gives **alkyl ethers**



Replacement of **H** by **OR** at one carbon of benzene ring gives **aryl ethers**



Classification of alcohols and phenols

- Based on number of –OH groups
- Based on hybridisation of ‘C’ in C–OH bond

Classification of Alcohols

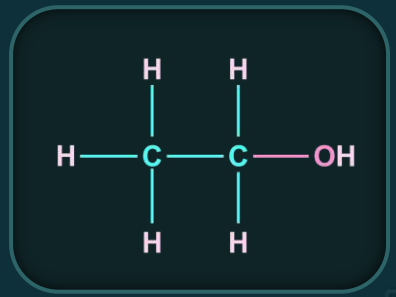
Basically, alcohols are divided into two classes:
1) Monohydric alcohol
2) Polyhydric alcohol.
Under polyhydric alcohol comes dihydric and trihydric alcohol.

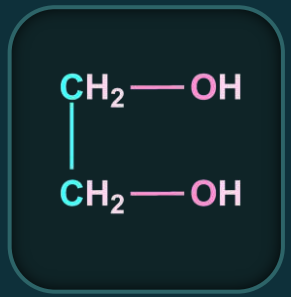
Based on number of -OH groups

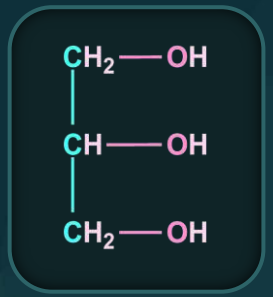
1 — Monohydric

2 — Dihydric

3 — Trihydric



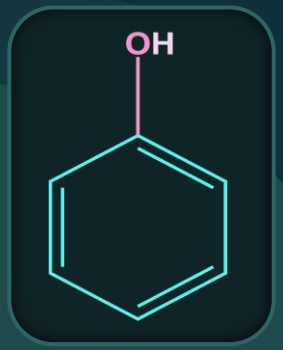


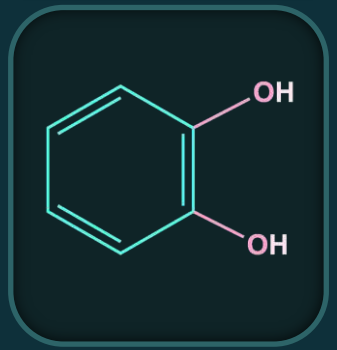


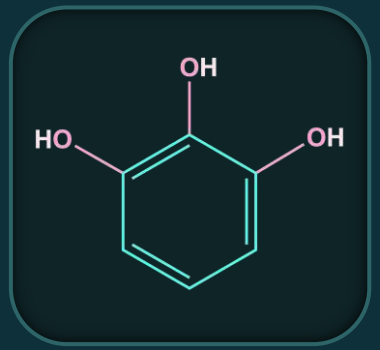
Classification of Phenols

Based on number of -OH groups

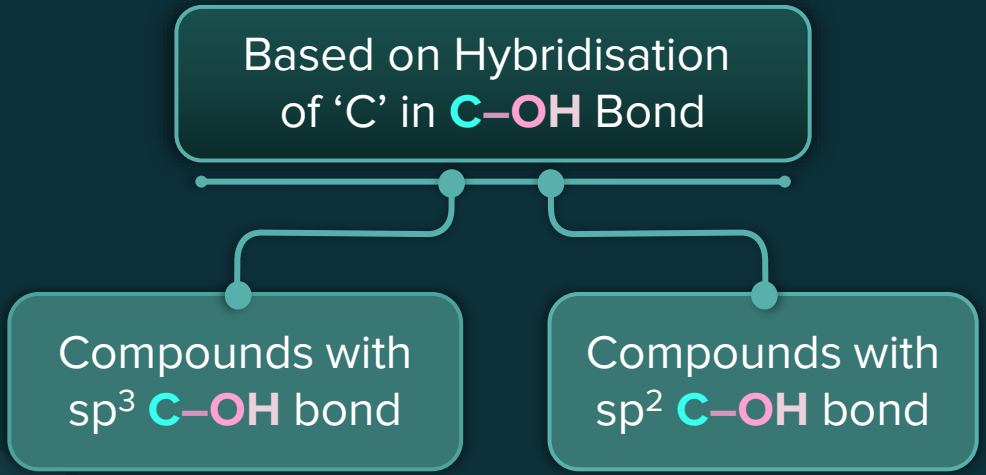
- 1 — Monohydric
- 2 — Dihydric
- 3 — Trihydric







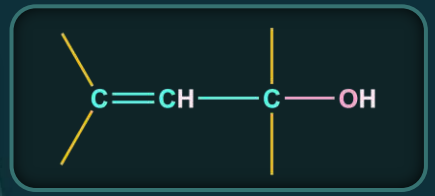
Classification of Alcohols and Phenols



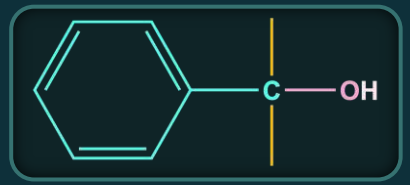
Alcohols

Compound Containing
sp^3 C–OH Bond

- Alkyl alcohol
  - 1°
  - 2°
  - 3°
- Allylic alcohol



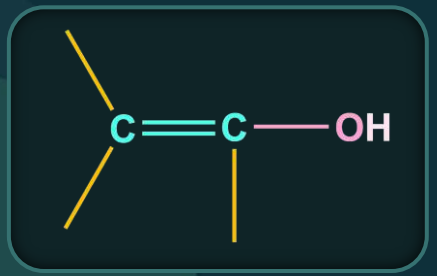
- Benzylic alcohol



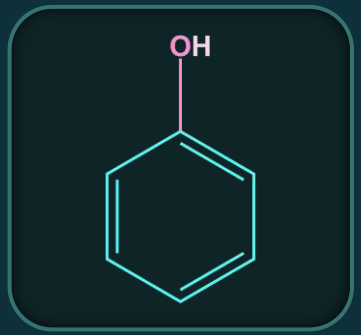
Classification of Alcohols and Phenols

Compounds Containing
sp^2 C–OH Bond

- Vinylic alcohols



- Phenol



Symmetrical And Unsymmetrical Ethers

Ethers

Symmetrical

Unsymmetrical

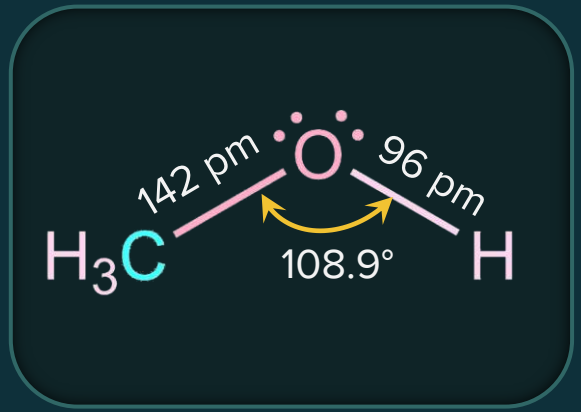
Alkyl or aryl groups attached to either side of the oxygen atom are **same**.

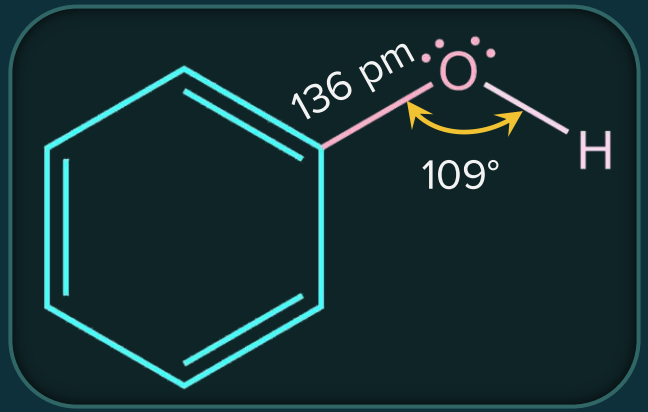
Alkyl or aryl groups attached to either side of the oxygen atom are **different**.

Example: $C_2H_5OC_2H_5$

Example: $C_2H_5OCH_3$

Structure of Alcohol & Phenol



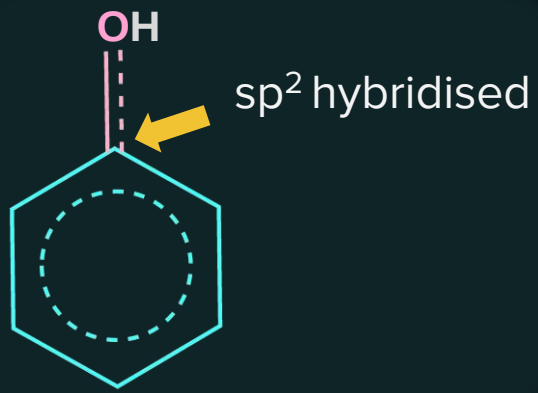


The C-O-H bond angle in alcohols is **slightly less** than the tetrahedral angle (109° 28′)

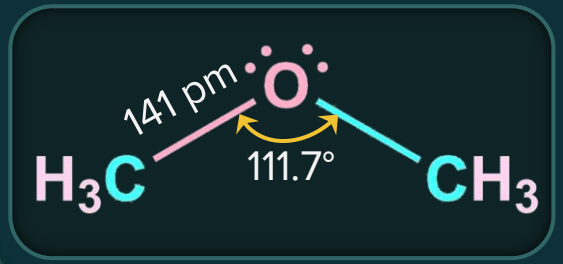
It is due to **repulsion** between the unshared electron pairs of oxygen.

01 **Partial double bond character**

02 Due to **sp^2 hybridised carbon** to which oxygen is attached.

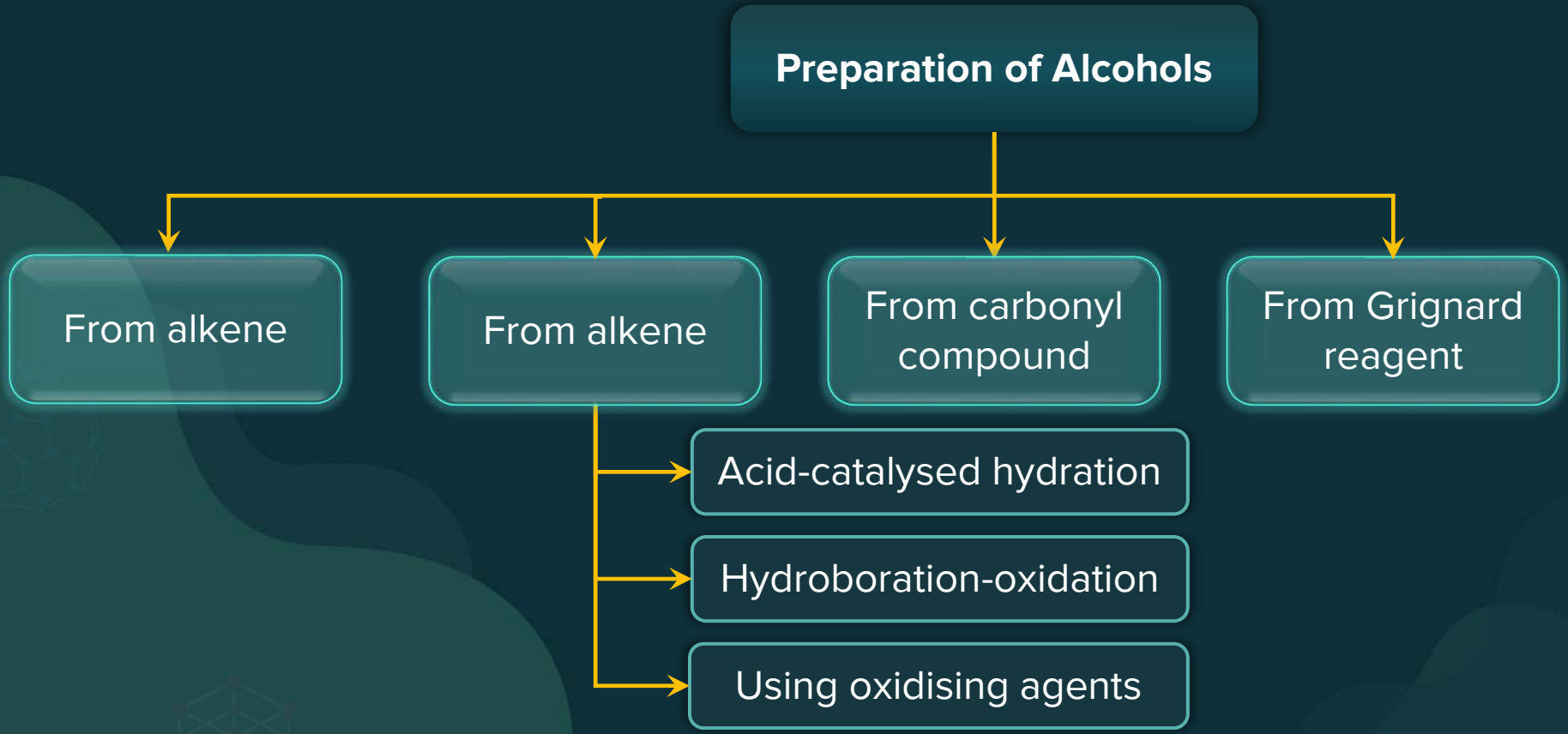


Structure of Ether



The bond angle is **slightly greater** than the tetrahedral angle due to the repulsive interactions between two bulky (-R) groups.

The **C–O bond length** (**141 pm**) is almost the **same** as in alcohols.


Preparation of Alcohols
From alkene
From alkene
From carbonyl compound
From Grignard reagent
Acid-catalysed hydration
Hydroboration-oxidation
Using oxidising agents

Preparation of Alcohols from Alkane

Oxidation of **methane**

$$2CH_4 + O_2 \xrightarrow{\text{Cu / 523 K / 1 atm}} 2CH_3OH$$

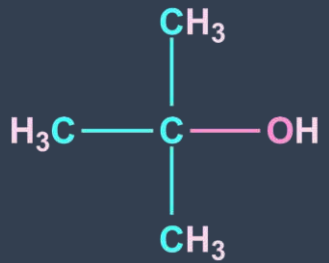
Methanol

Oxidation of **2-Methylpropane**

$(CH_3)_3CH$

2-Methylpropane

$\xrightarrow[\text{Oxidation}]{KMnO_4}$



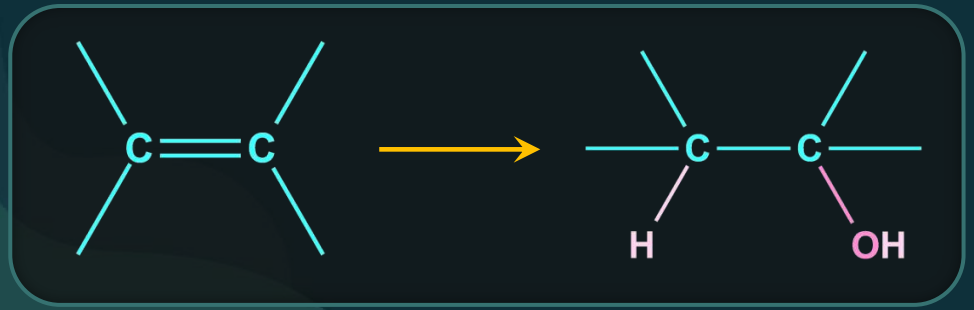
2-Methylpropan-2-ol

Acid-Catalysed Hydration of Alkenes

Alkenes react with water in the presence of an acid catalyst to yield **alcohols**.

In case of unsymmetrical alkenes, the addition of water takes place in accordance with **Markovnikov's rule**.

General reaction



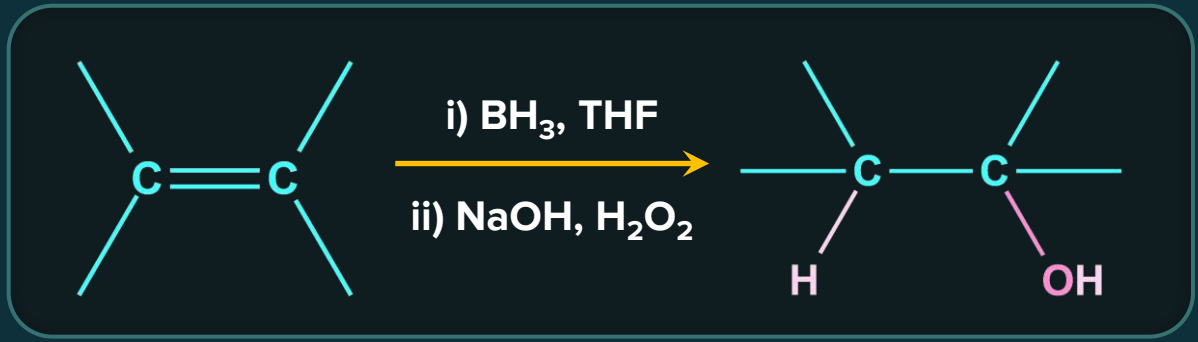
Reagent used — **dil. H_2SO_4**

Note

Acid-catalysed hydration of alkenes is **reversible** and the mechanism for the **acid-catalysed hydration** of an alkene is simply the **reverse** of that for the **dehydration** of an alcohol.

Hydroboration-Oxidation

General reaction



Hydroboration–oxidation reactions are **stereospecific.**

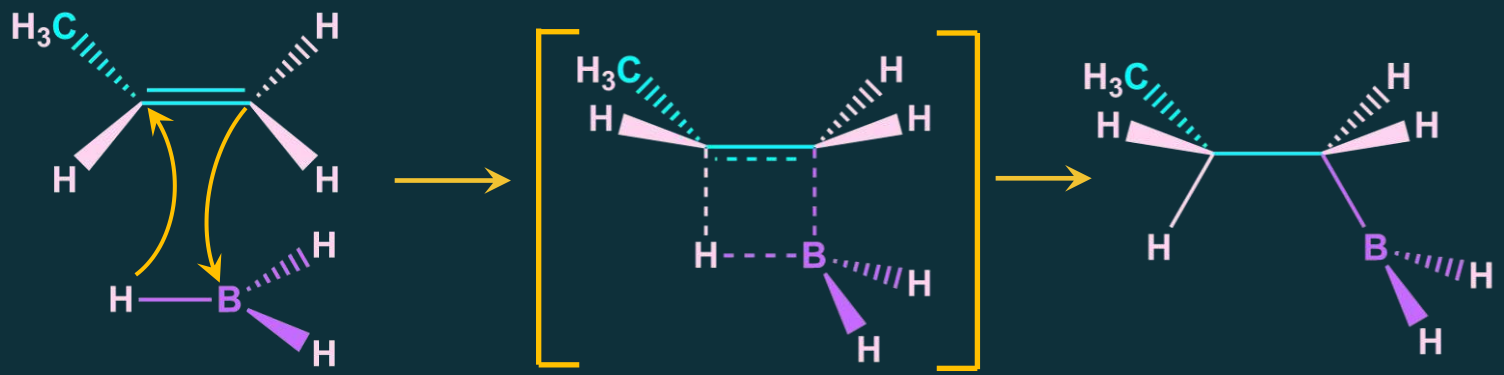
The net addition of H and OH is **syn.**

Stereochemistry of Hydroboration-Oxidation

If **chirality centres** are formed, their configuration depends on the **stereochemistry** of the **starting alkene.**

Mechanism

Step 1

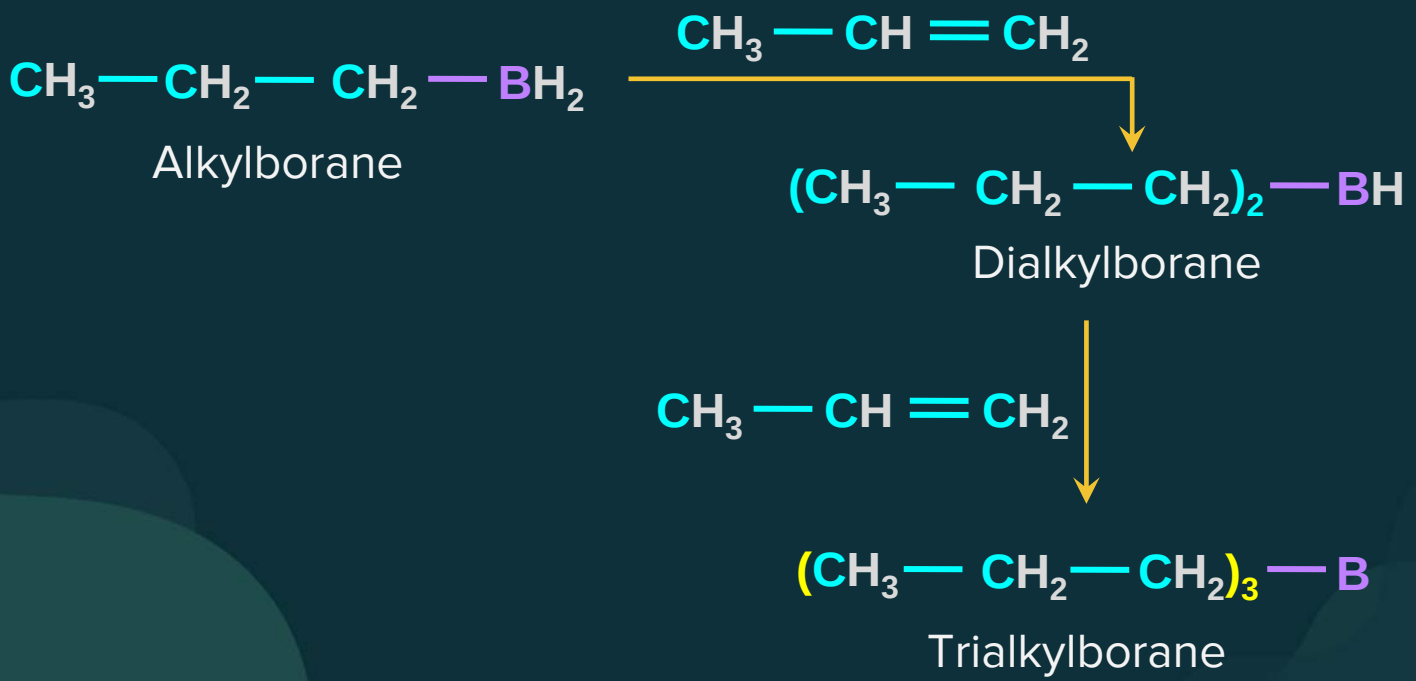


Four-atom concerted **T.S.**

Syn additon of H and B

Mechanism

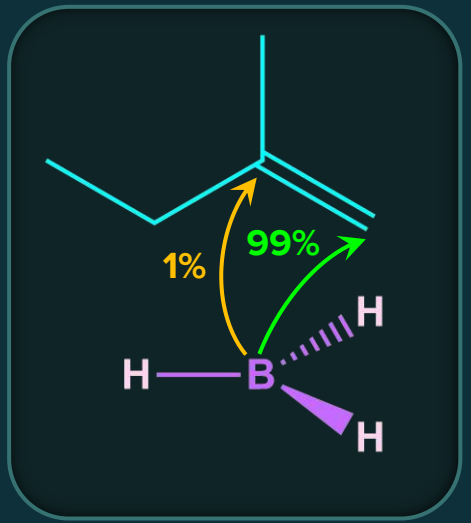
Step 2

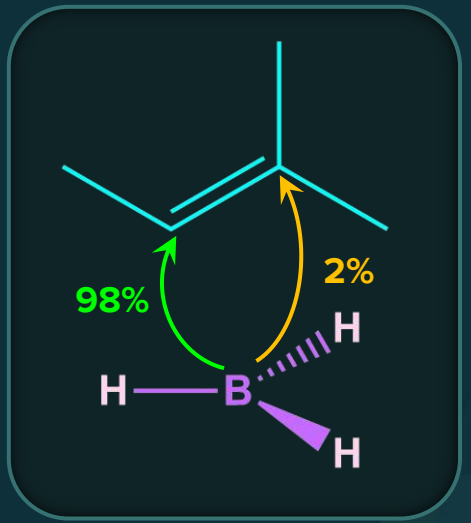


Hydroboration

Hydroboration is regioselective and it is **anti-Markovnikov's** addition.

The hydrogen atom gets attached to the carbon atom with **fewer hydrogen atoms.**



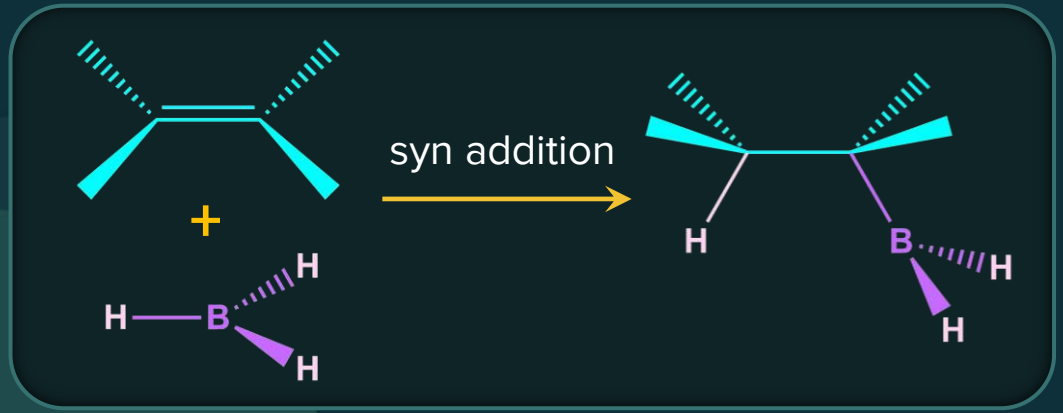


Hydroboration

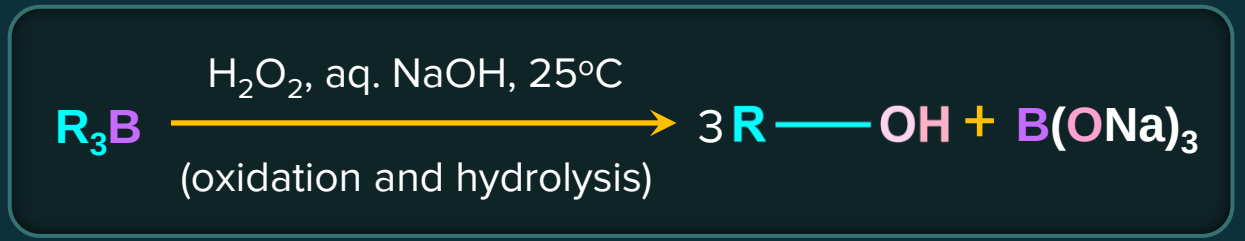
Observation:	Reason:
Boron gets attached to the **less substituted carbon** atom of the double bond.	**Steric factors**: The bulky boron-containing group can approach the less substituted carbon atom more easily.

Stereochemistry of Hydroboration

The transition state for hydroboration requires that the boron atom and the hydrogen atom be added to the **same face of the double bond.**



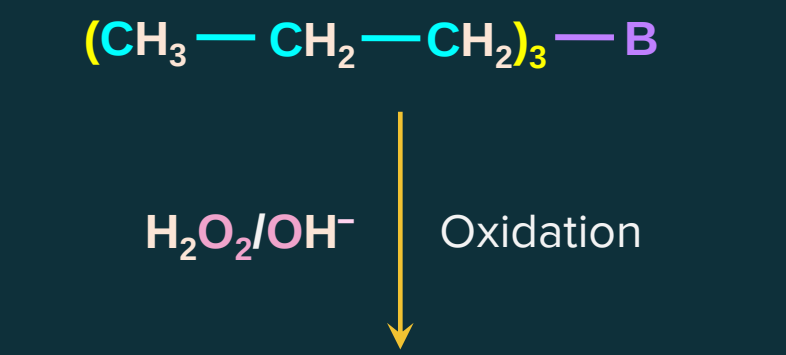
Oxidation and Hydrolysis of Alkylboranes



The oxidation and hydrolysis take place with **retention of configuration**

at the carbon initially bearing boron and ultimately bearing the **hydroxyl group**

Mechanism

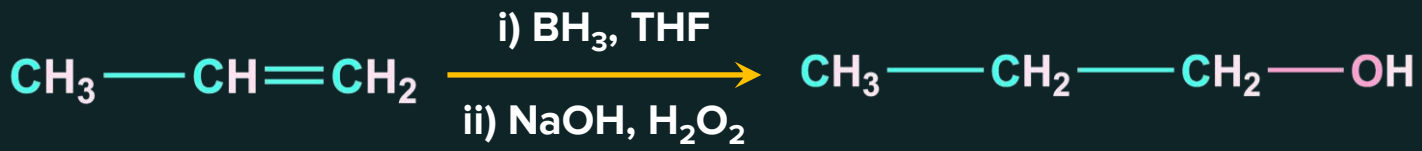


Regiochemistry of Hydroboration–Oxidation

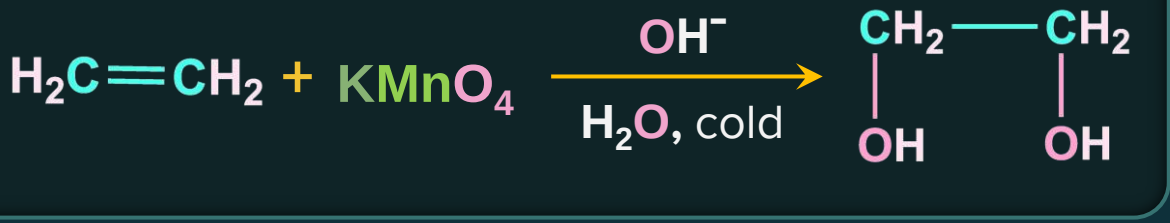
Hydroboration–oxidation reactions are **regioselective.**

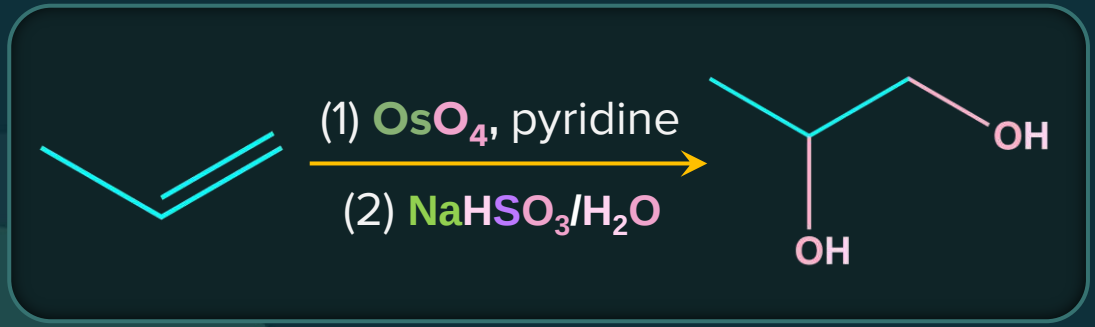
The net result of hydroboration–oxidation is **anti-Markovnikov** addition of water to an alkene.

Example

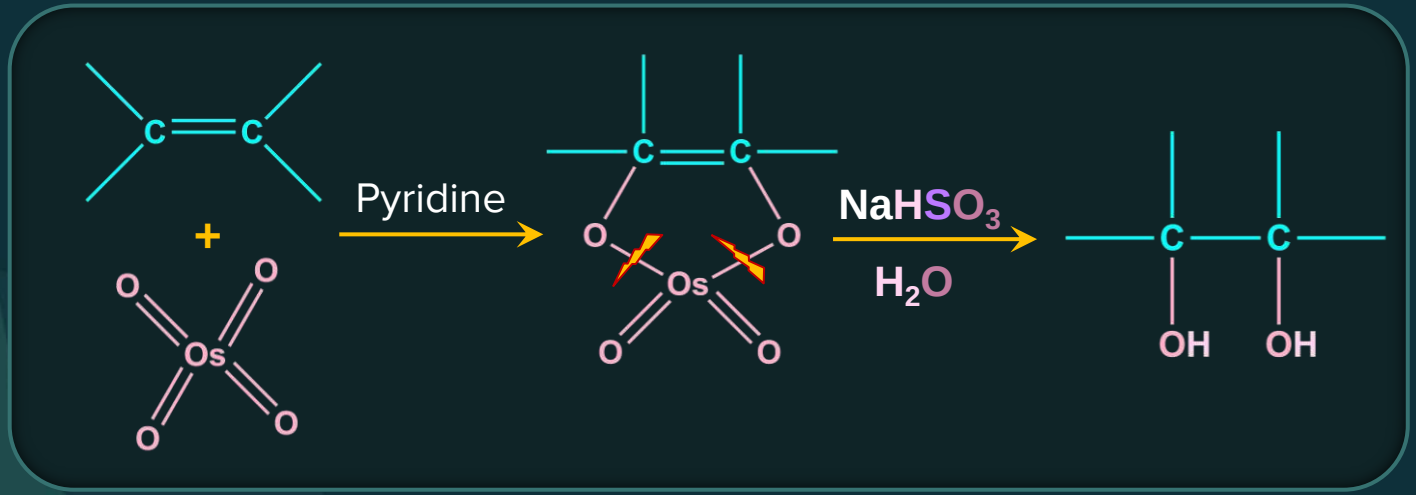


Preparation of Alcohols from Alkenes





Mechanism



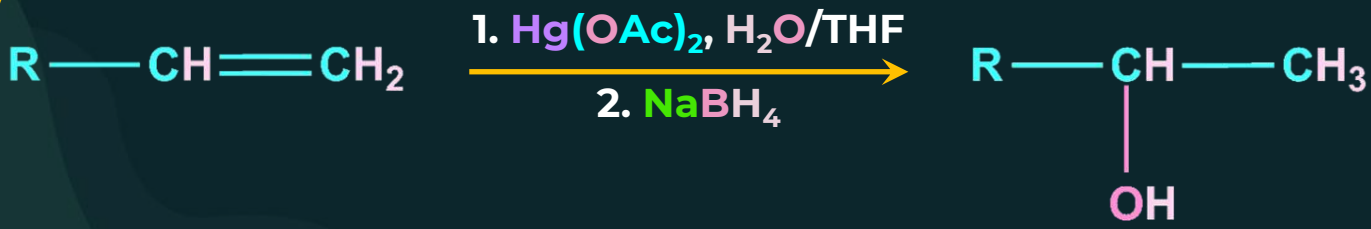
Mechanism

Mechanism for the formation of a **1,2-diol** by osmium tetroxide involves

a cyclic intermediate that results in **syn addition** of the oxygen atoms

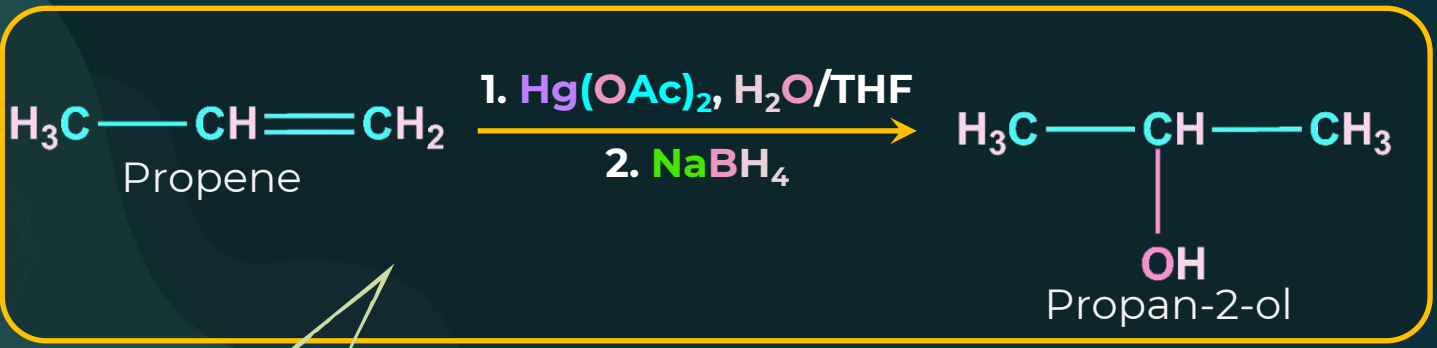
Oxymercuration-Demercuration

General Reaction



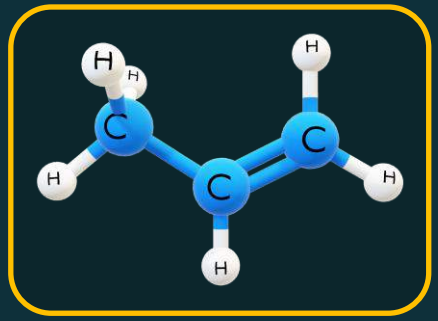
Oxymercuration-Demercuration

Example



Industrial method to convert alkene to alcohol

Oxymercuration-Demercuration



If the reaction involves **unsymmetrical alkene**, then addition of water will occur in

Markovnikov's manner

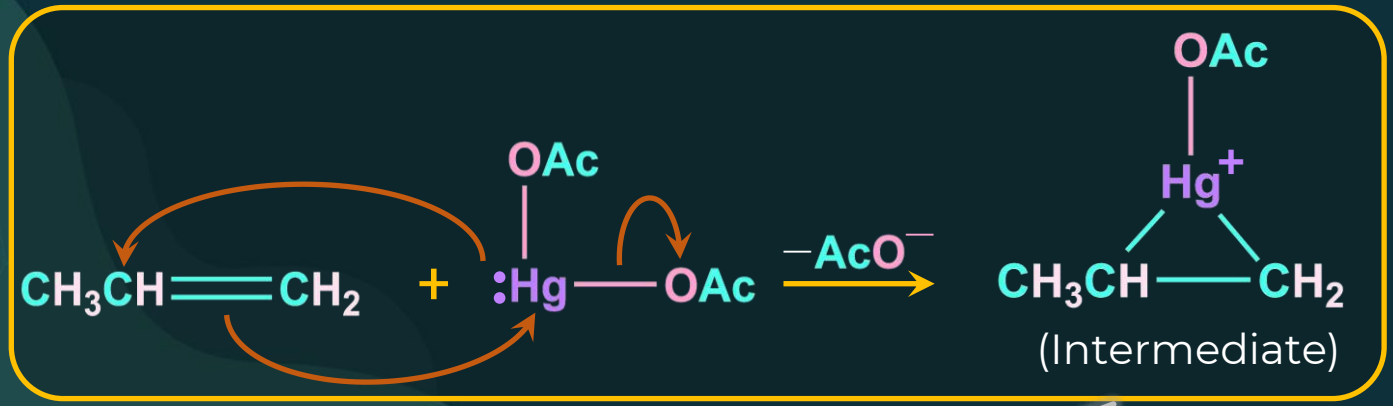
Steps Involved in Oxymercuration-Demercuration Reaction

Step 1	Oxymercuration
Step 2	Demercuration

Steps Involved in Oxymercuration-Demercuration Reaction

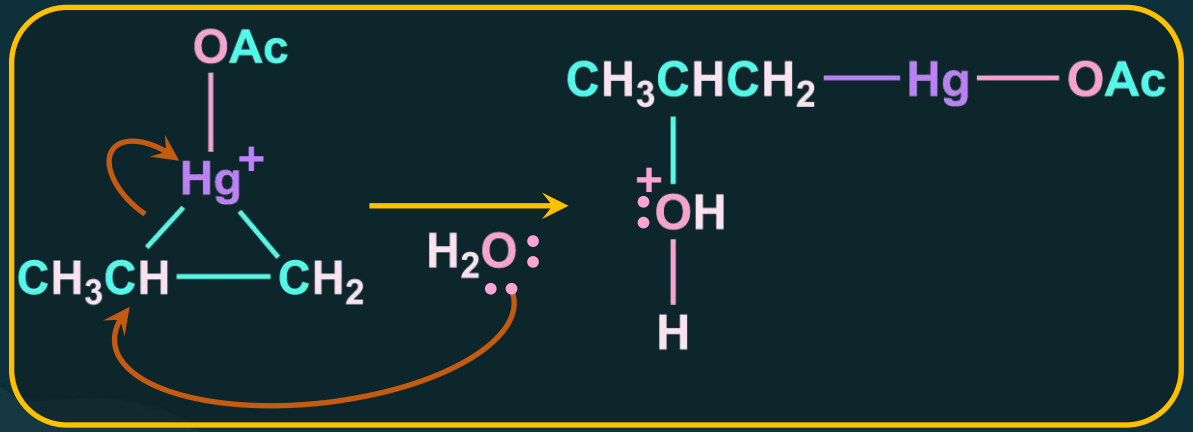
Step 1

Oxymercuration

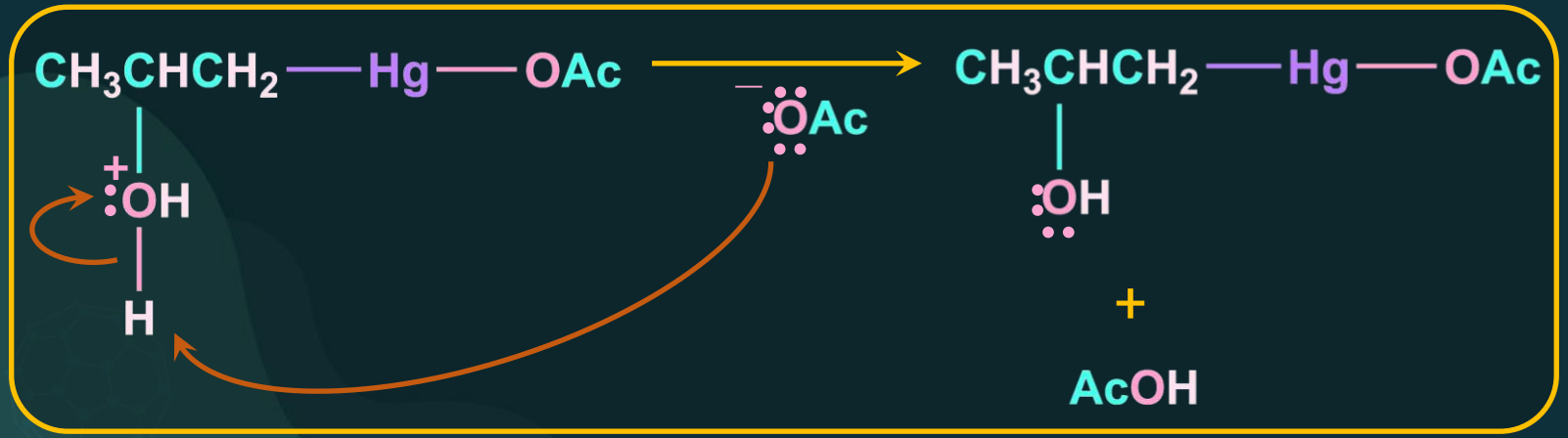


Cyclic mercurinium ion

Steps Involved in Oxymercuration-Demercuration Reaction



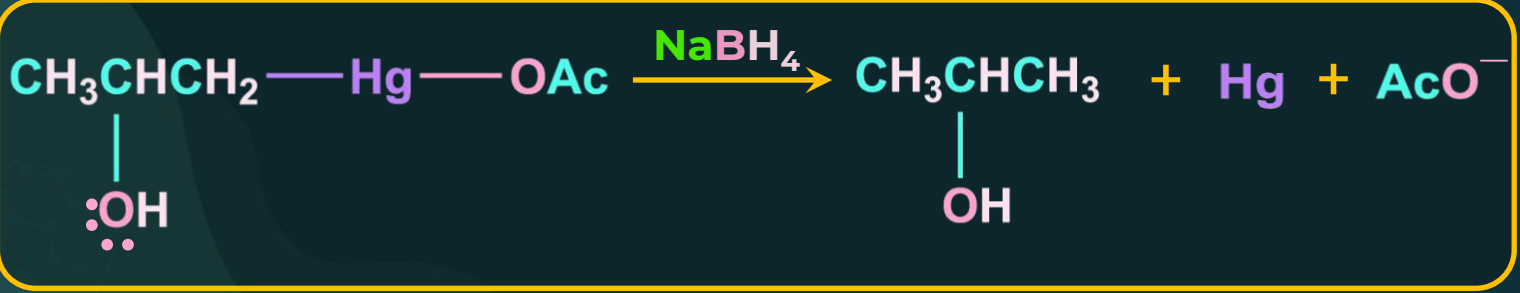
Steps Involved in Oxymercuration-Demercuration Reaction



Steps Involved in Oxymercuration-Demercuration Reaction

Step 2

Demercuration



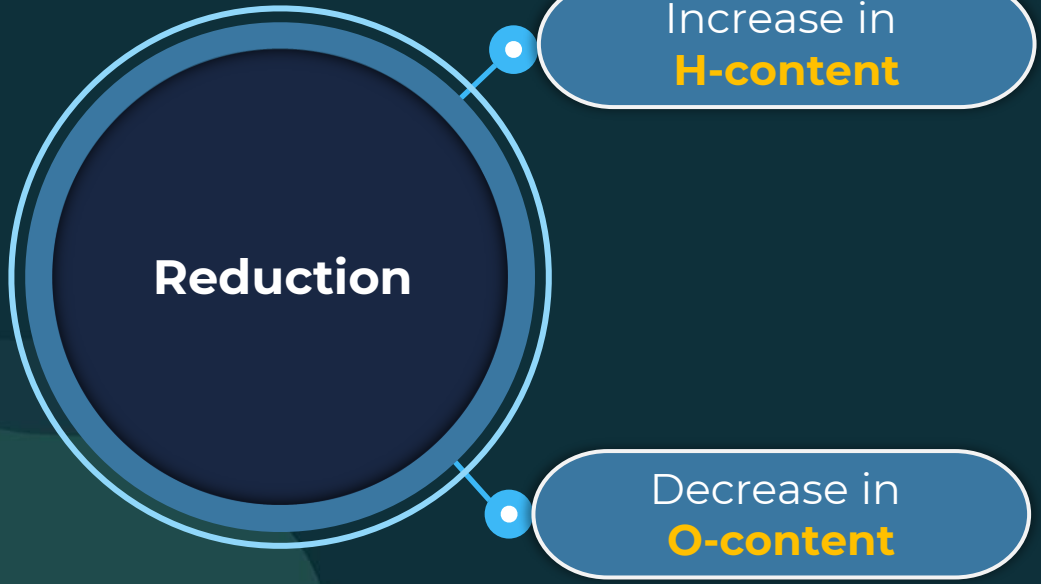
Note

Cyclic mercurinium ion is formed as an intermediate

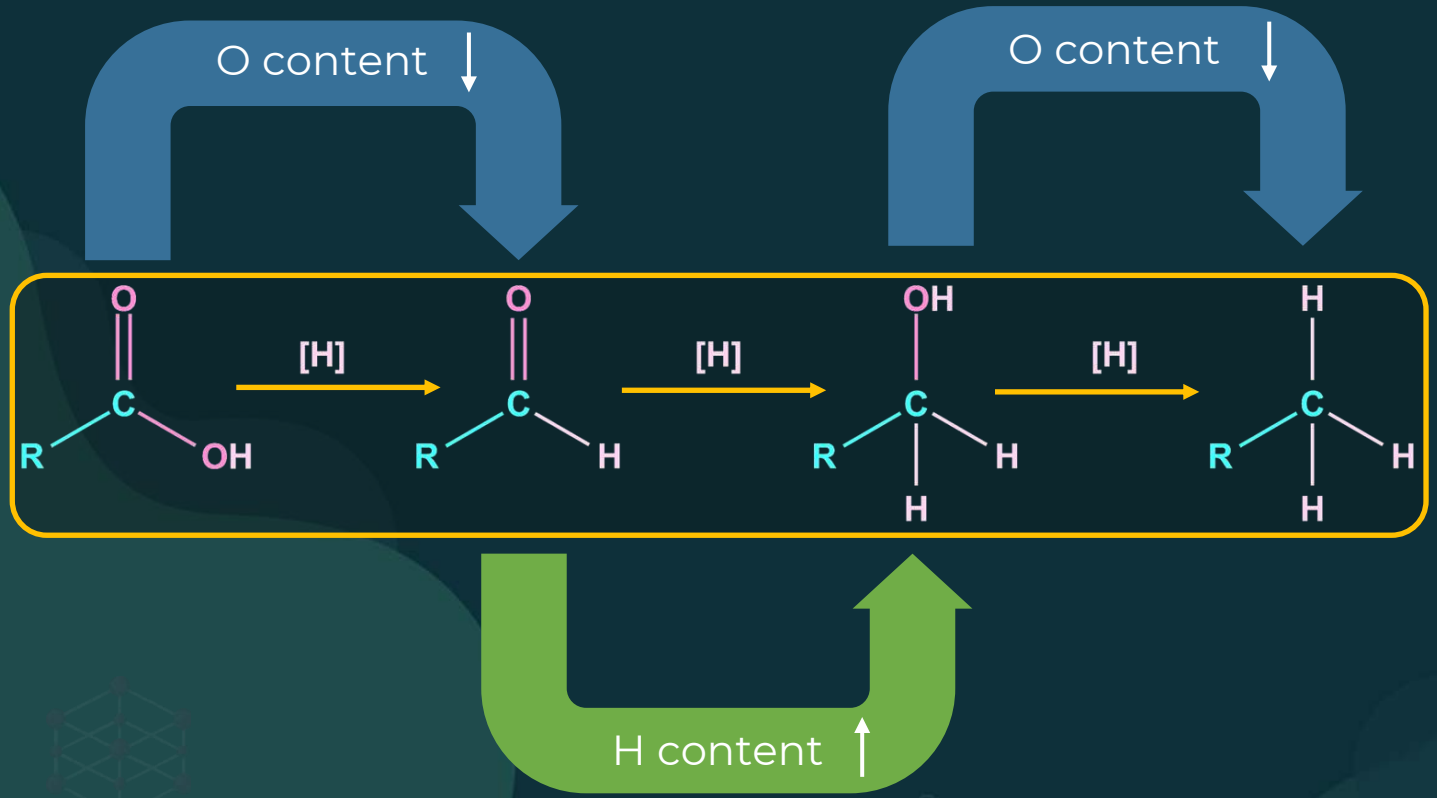
Non-classical carbocation

Reduction in Organic Compounds

In general

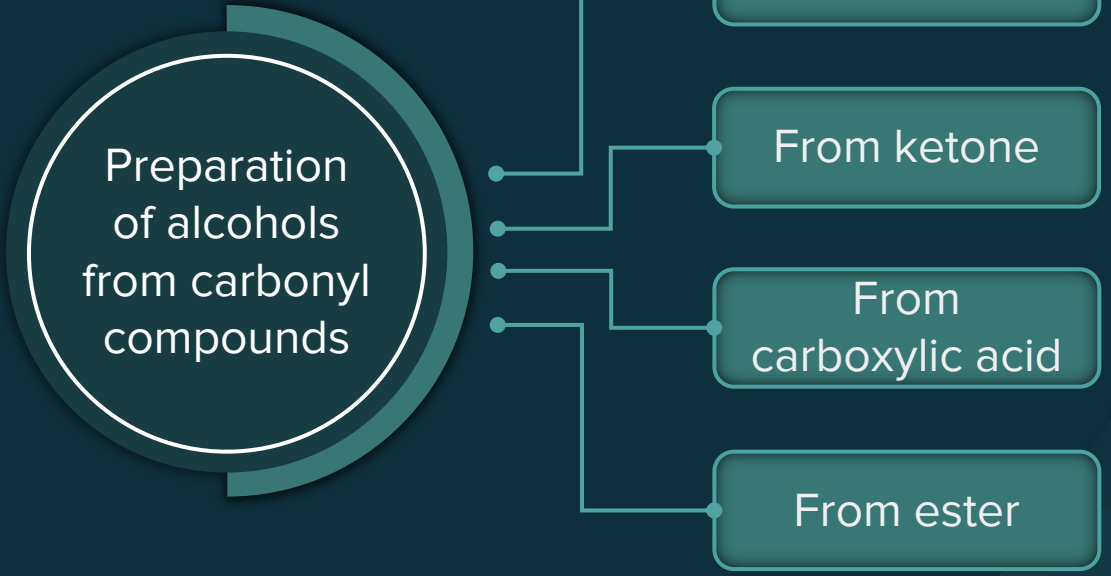


Reduction in Carbonyl Compounds

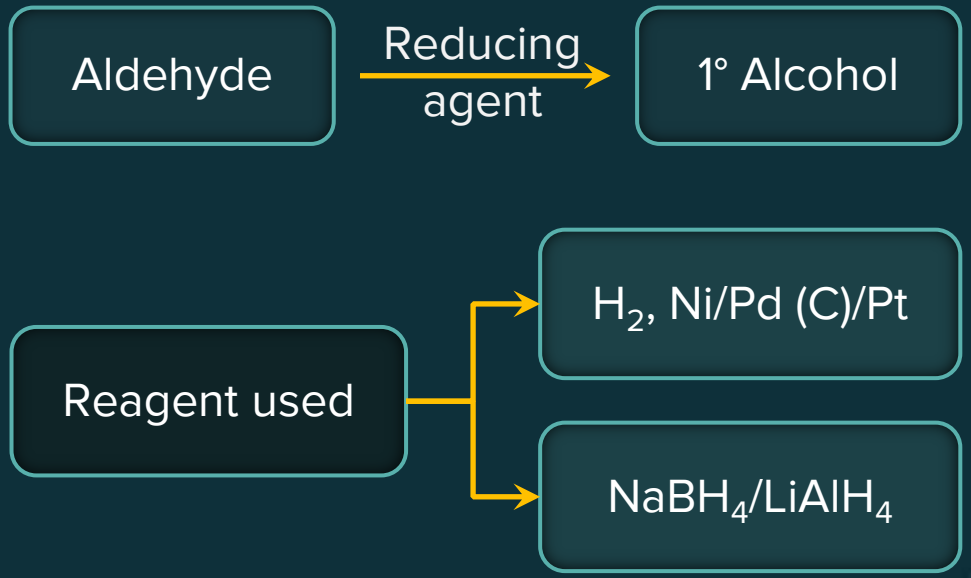


Preparation of Alcohols from Carbonyl Compounds

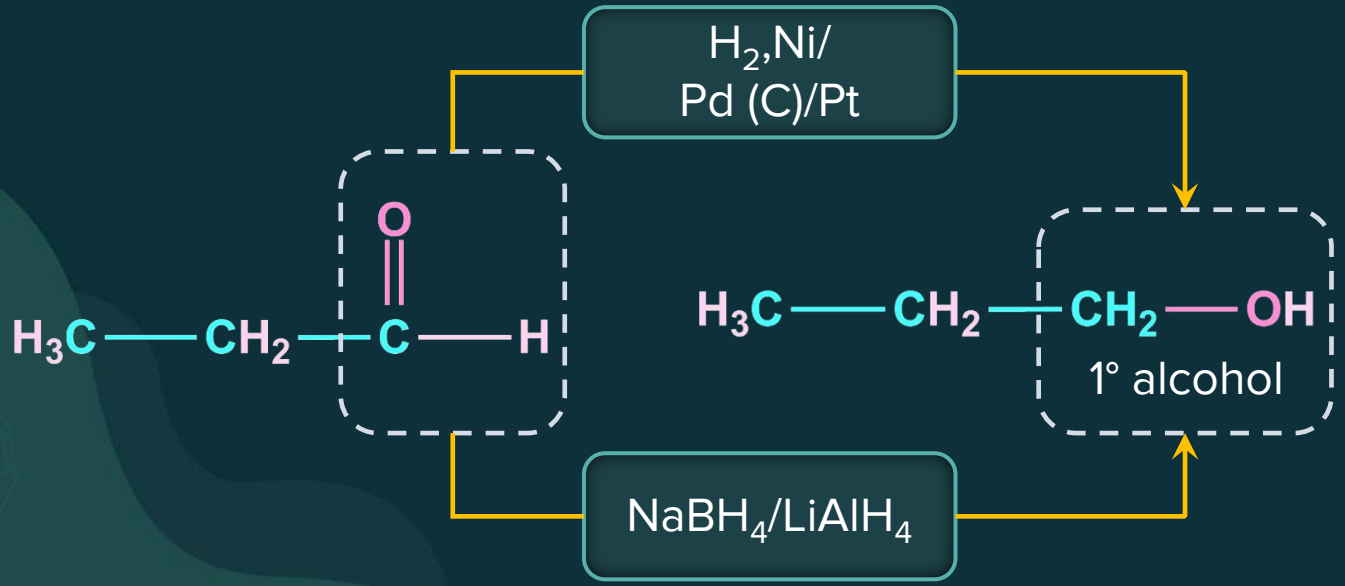
Alcohols can be prepared by **reduction of carbonyl compounds**.



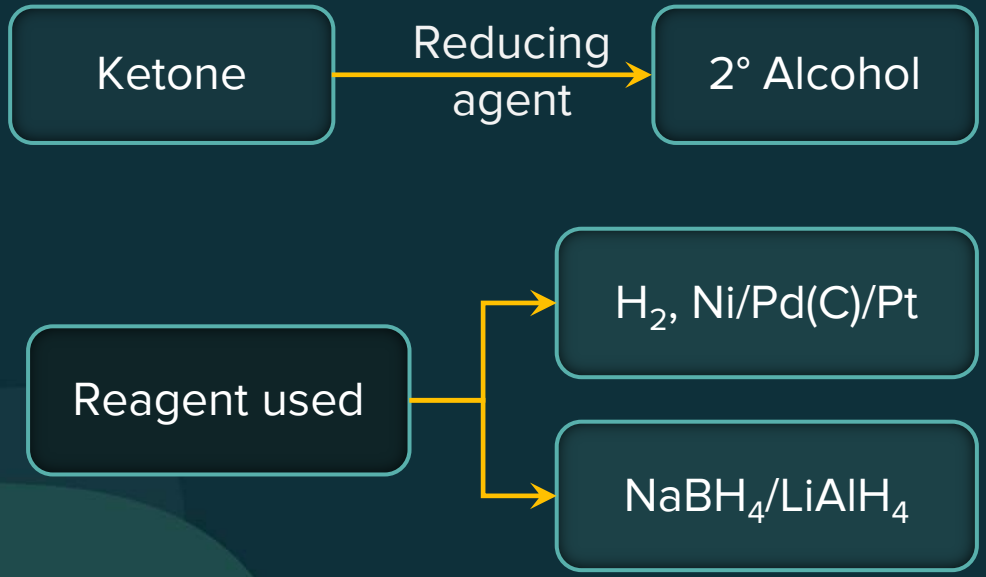
Reduction of Aldehyde



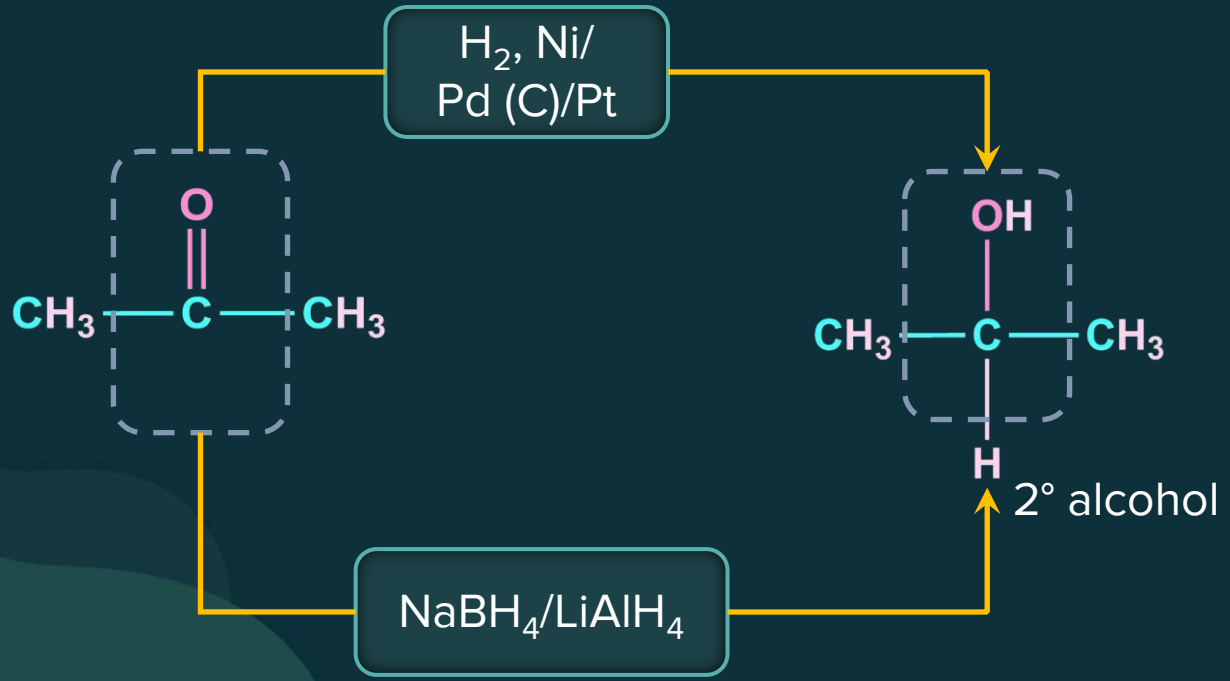
Reduction of Aldehyde



Reduction of Ketone



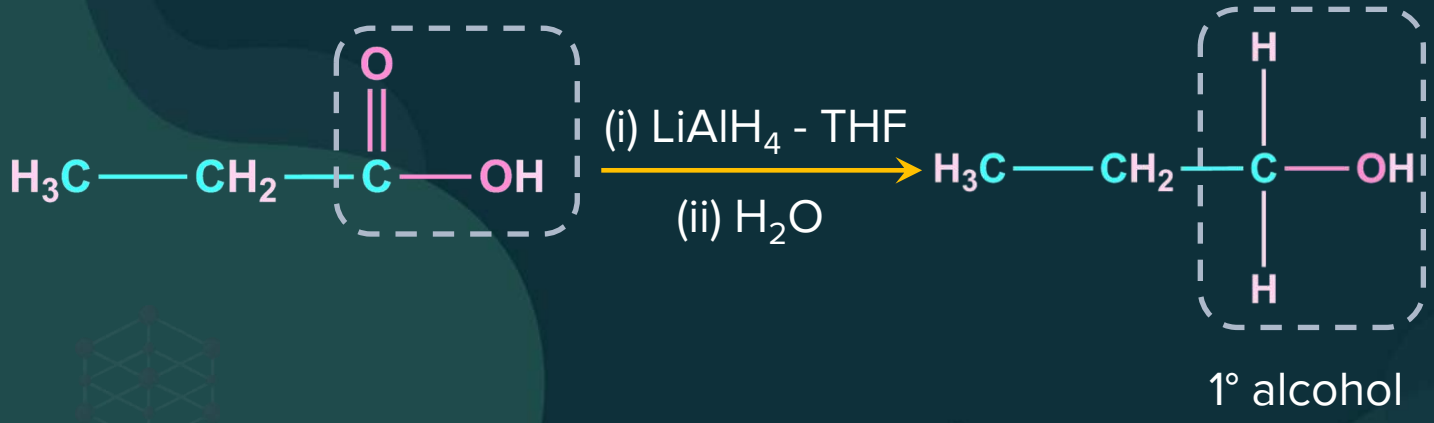
Reduction of Ketone



Reduction of Carboxylic Acid

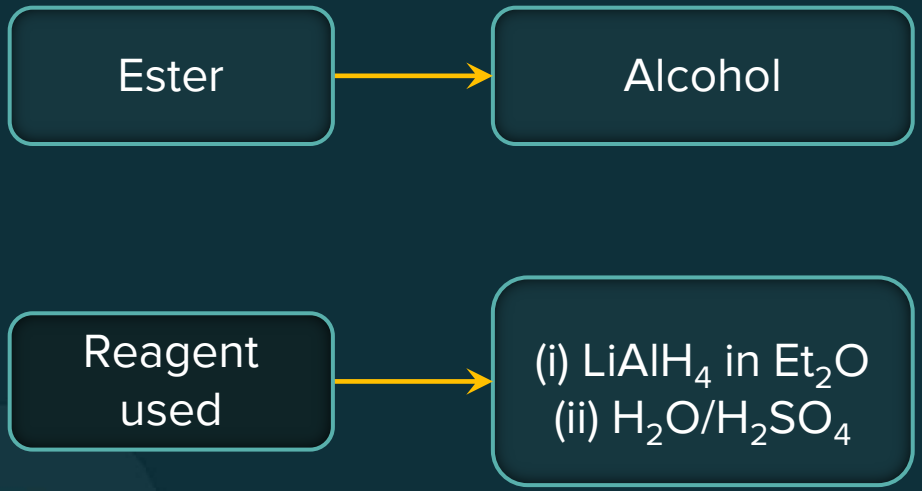
Carboxylic acid → (Reducing agent) → 1° Alcohol

Reagent used → (i) $LiAlH_4$ - THF, (ii) H_2O

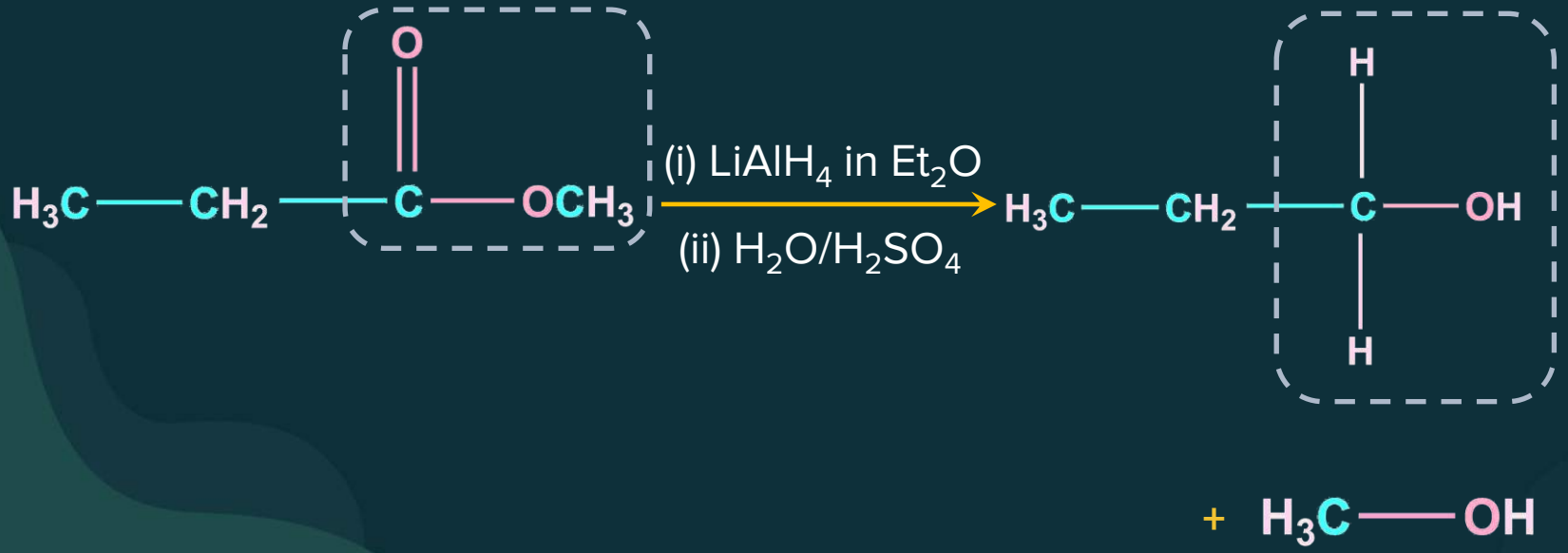


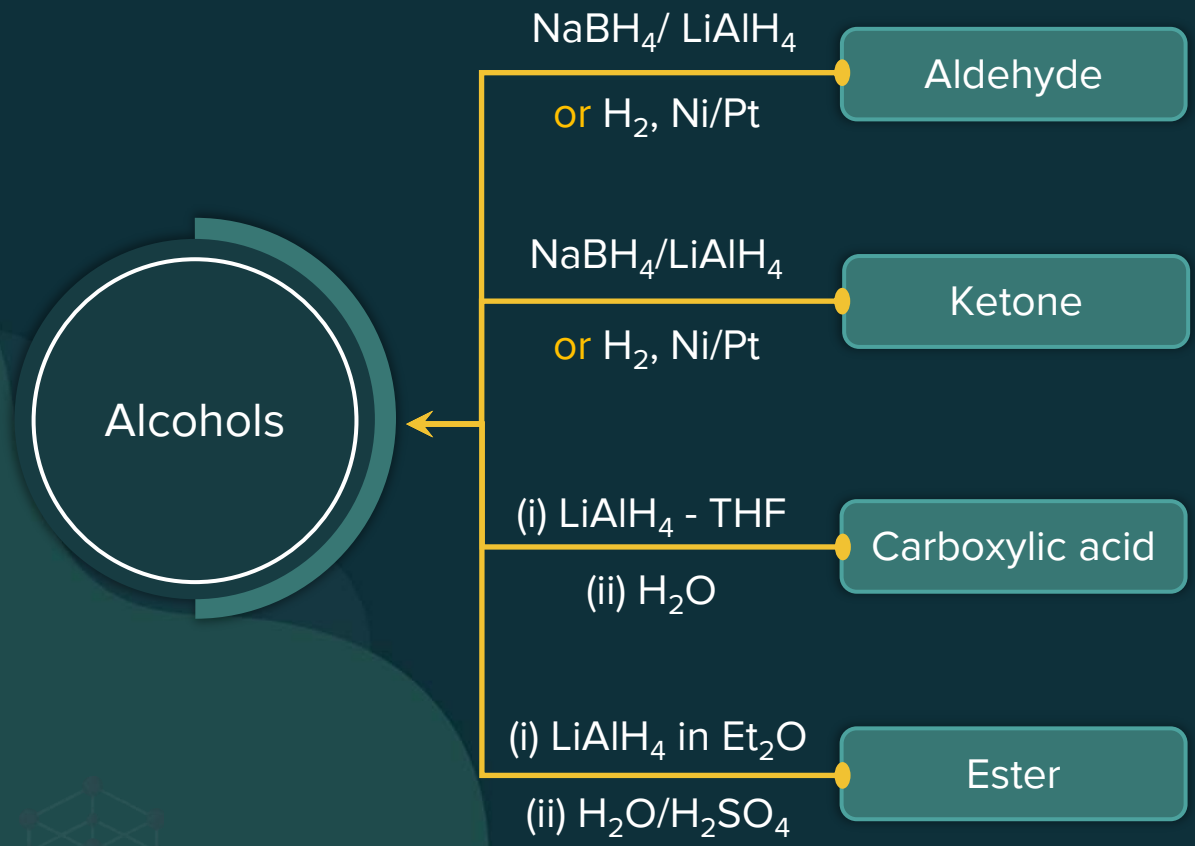
1° alcohol

Reduction of Ester

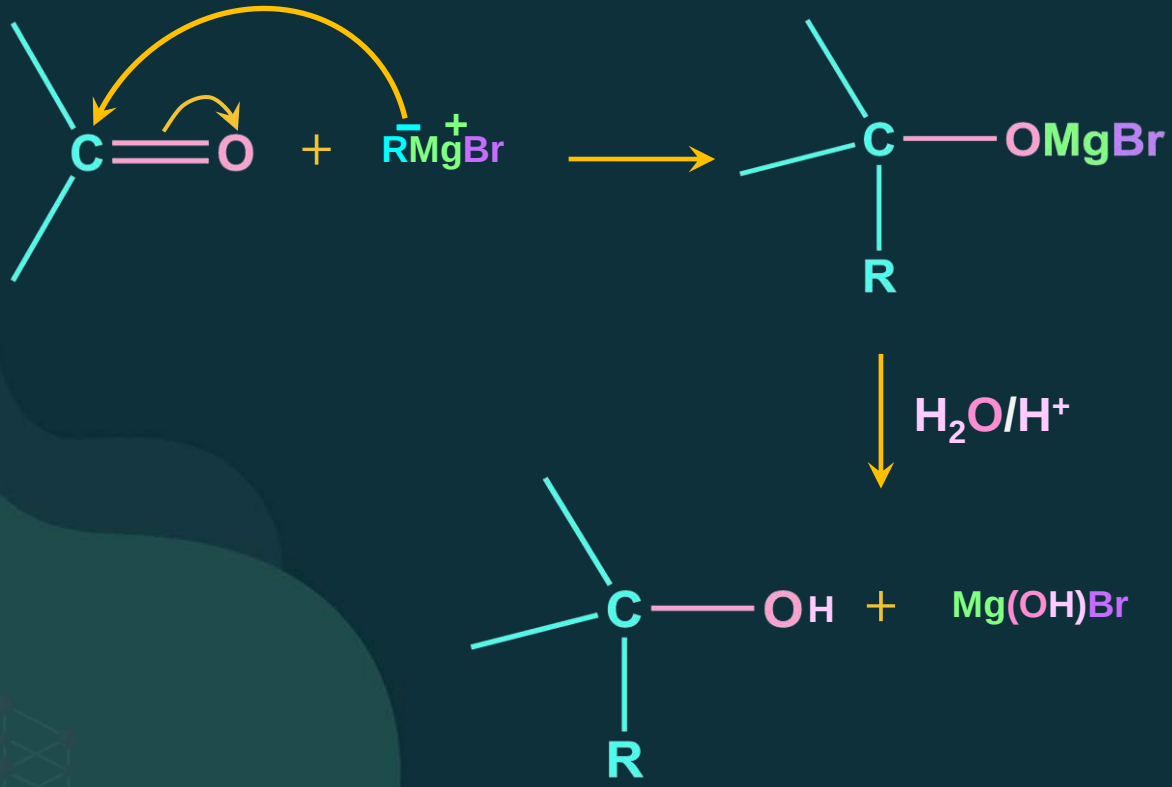


Reduction of Ester



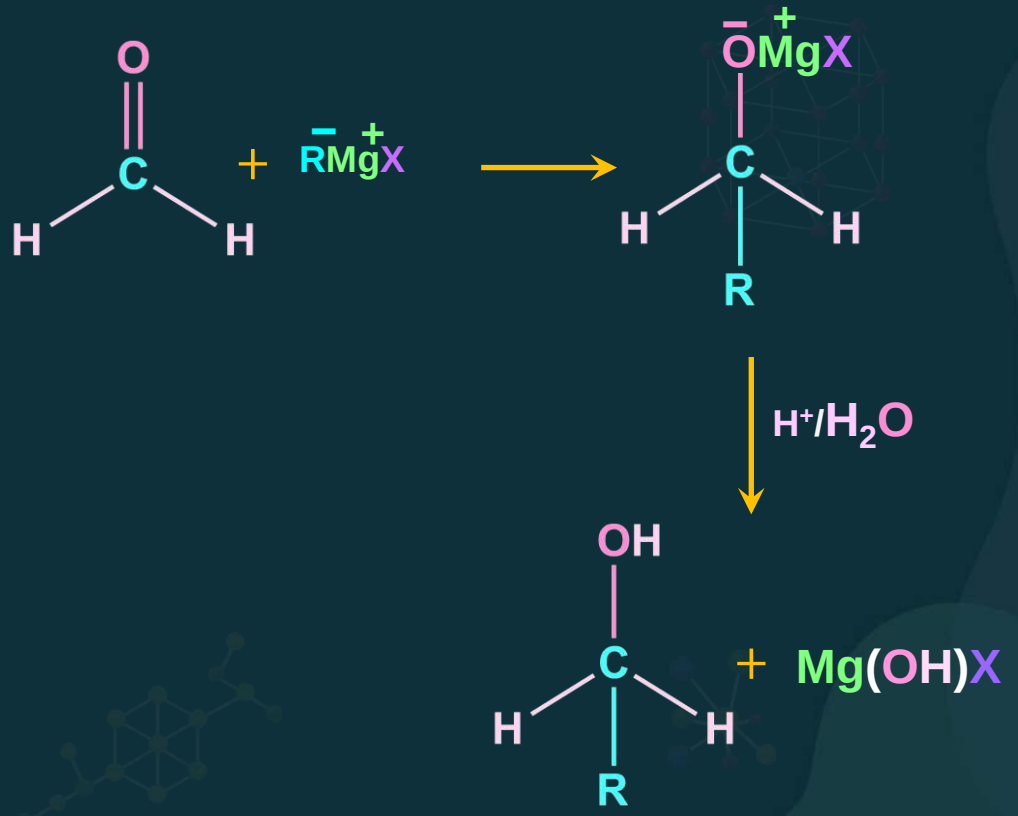

Alcohols
$NaBH_4$/ $LiAlH_4$
or H_2, Ni/Pt
Aldehyde
$NaBH_4$/$LiAlH_4$
or H_2, Ni/Pt
Ketone
(i) $LiAlH_4$ - THF
(ii) H_2O
Carboxylic acid
(i) $LiAlH_4$ in Et_2O
(ii) H_2O/H_2SO_4
Ester

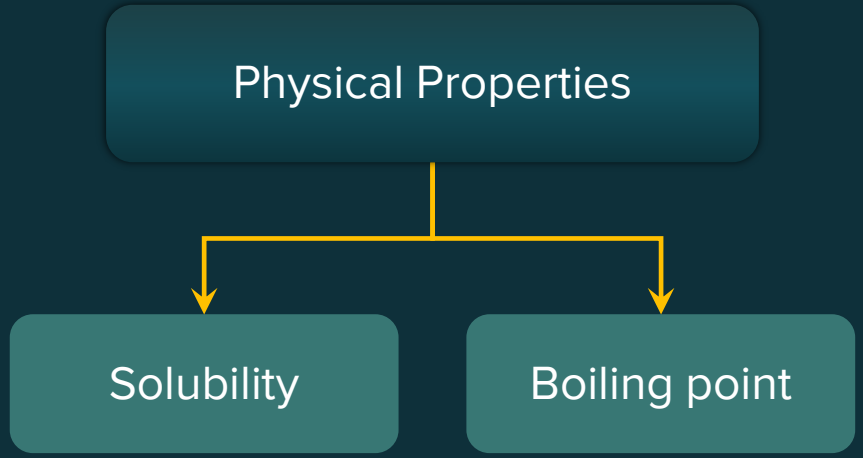
Addition of Grignard Reagent



Example

Reaction of Grignard reagent with formaldehyde




Physical Properties
Solubility
Boiling point

Solubility

Miscible in all proportions

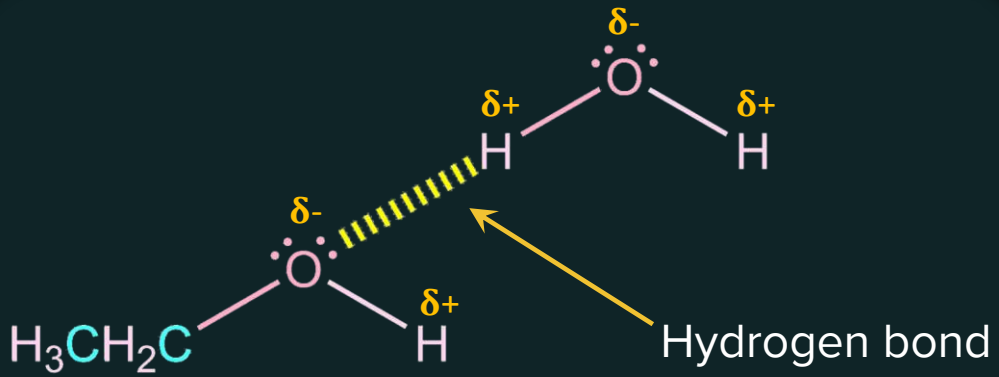
- Methanol and water
- Ethanol and water
- Propanol and water

1

In these cases, the alkyl groups of the alcohols are **relatively small,** and the molecules **resemble water** more than they resemble an alkane.

Solubility

Molecules are capable of forming strong hydrogen bonds with each other.

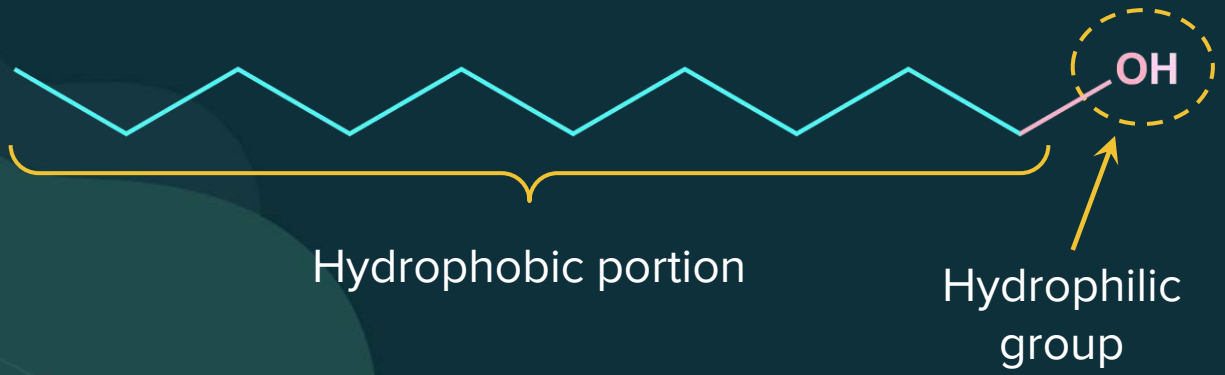


If the carbon chain of an alcohol is **long**, the alcohol is **much less soluble** in water.

Decyl alcohol with a chain of 10 carbon atoms, is **very slightly soluble** in water.

Solubility

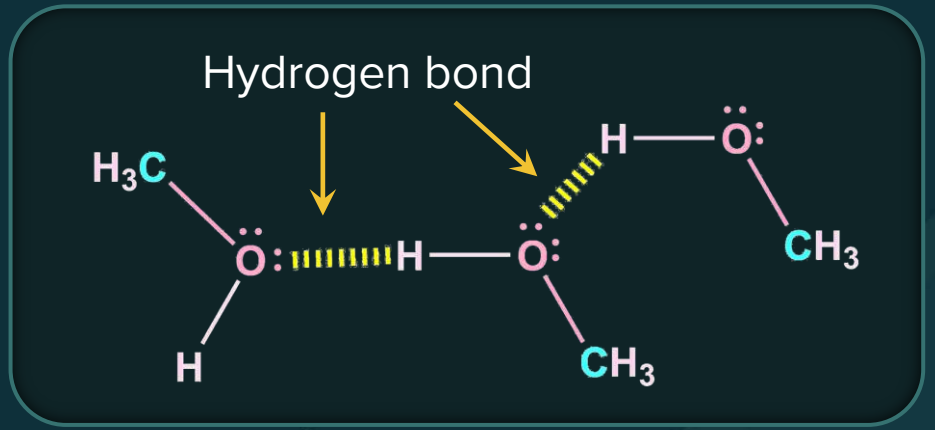
Decyl alcohol **resembles an alkane** more than it does water.

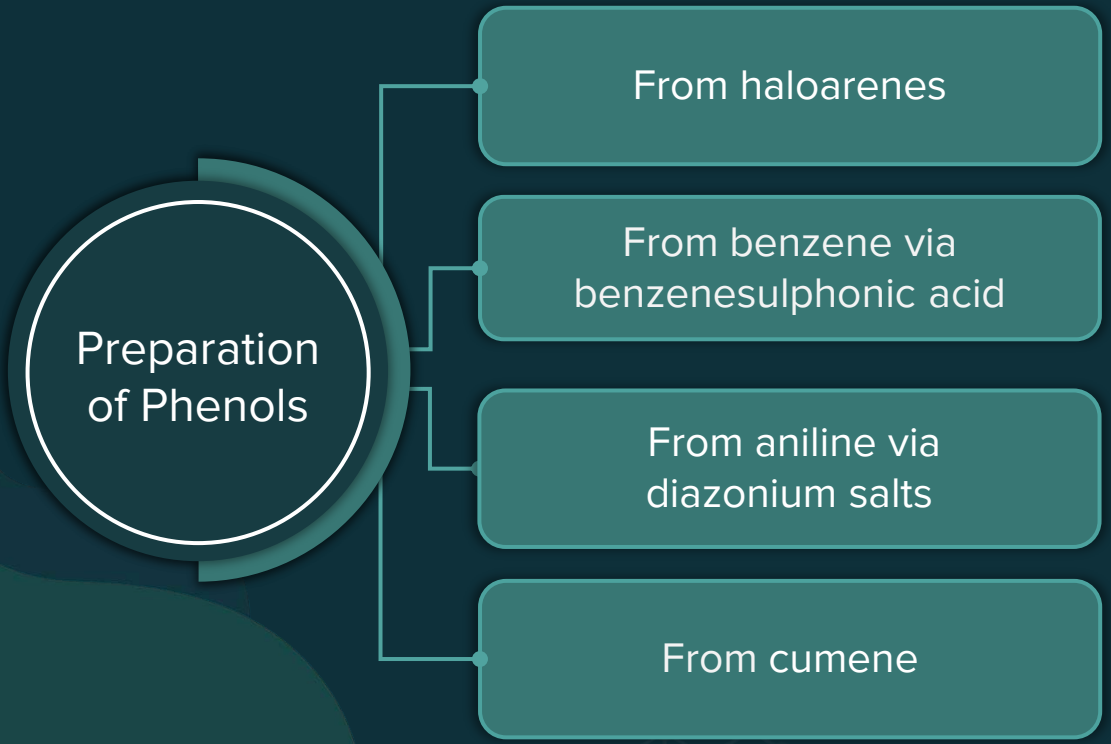


Boiling Point

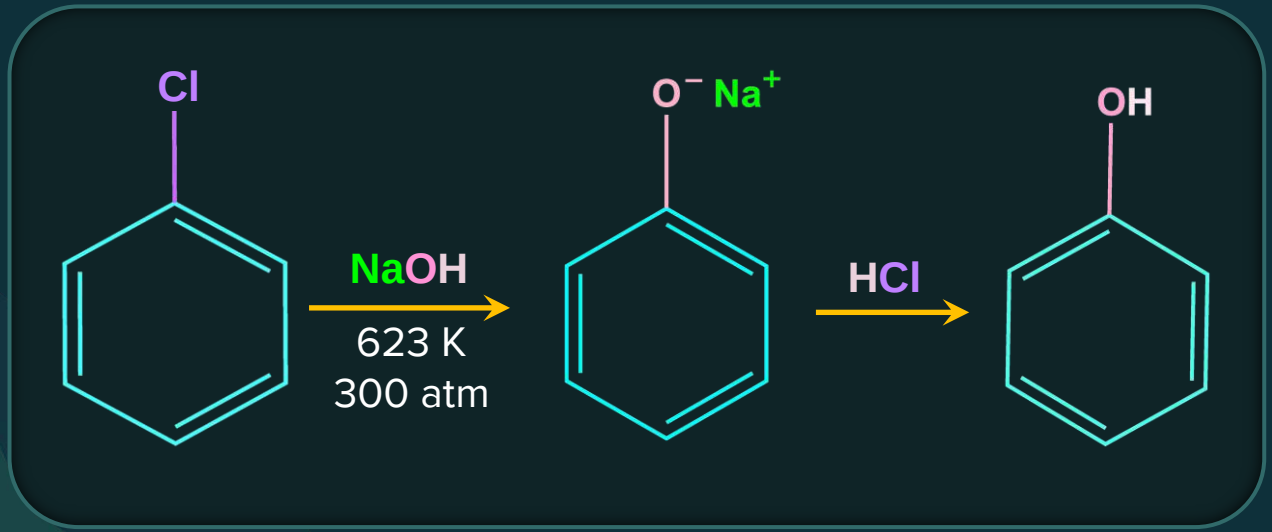
Alcohol molecules can associate with each other through **hydrogen bonding**, whereas those of **ethers and hydrocarbons cannot.**

Alcohols have **much higher** boiling points than ethers and hydrocarbons of comparable molar mass.



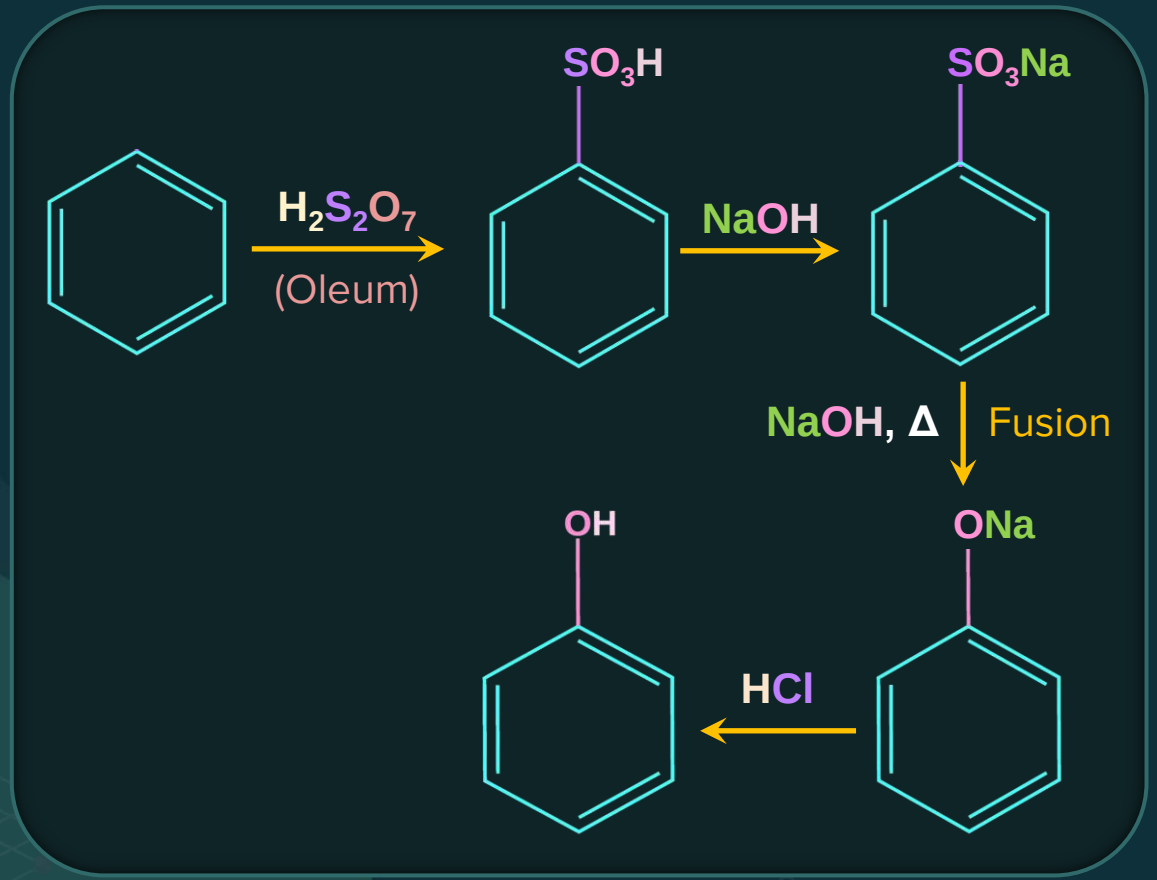

Preparation of Phenols
From haloarenes
From benzene via benzenesulphonic acid
From aniline via diazonium salts
From cumene

Dow Process

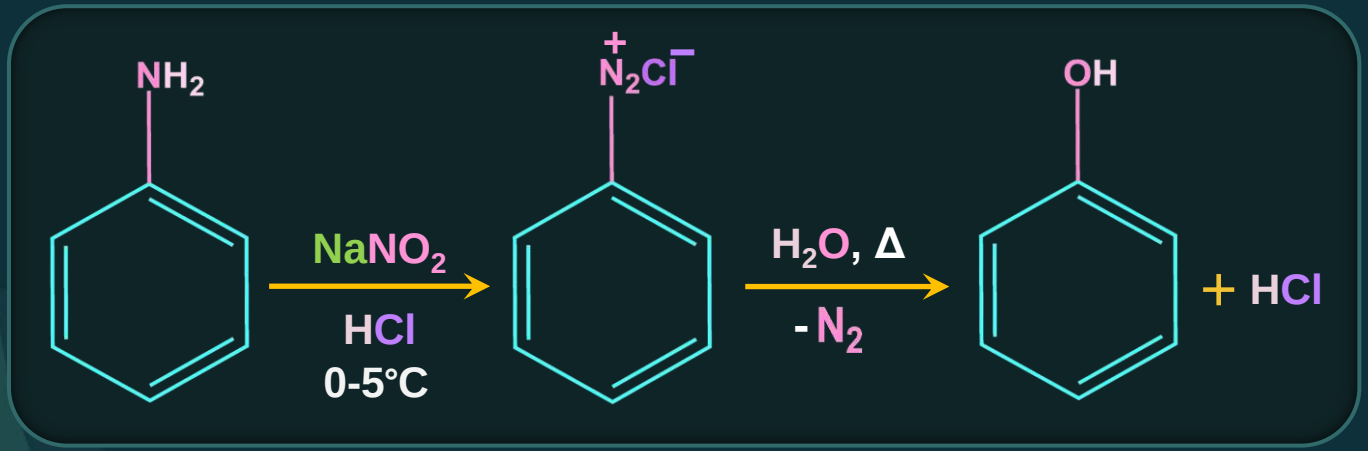


Dow's process is a method to prepare phenol. The reactant **chlorobenzene** is heated with aqueous sodium hydroxide at temperatures **623K** and **300atm** to get **sodium phenoxide ion**. Then in the next step sodium phenoxide ion is treated with dilute HCl which gives the final product as phenol.

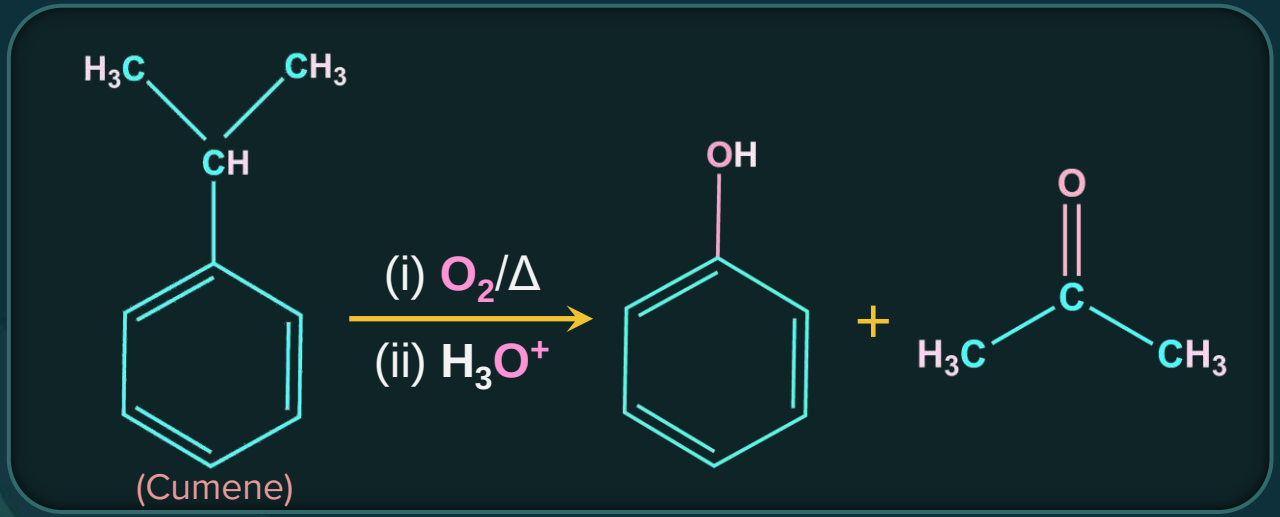
Phenol from Benzene via Benzenesulphonic Acid



Phenols from Aniline via Diazonium Salts



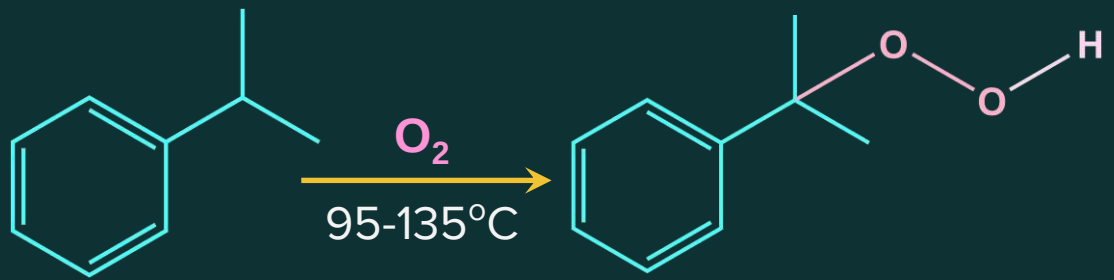
Phenols from Cumene



Mechanism

Step 1

Formation of cumene hydroperoxide

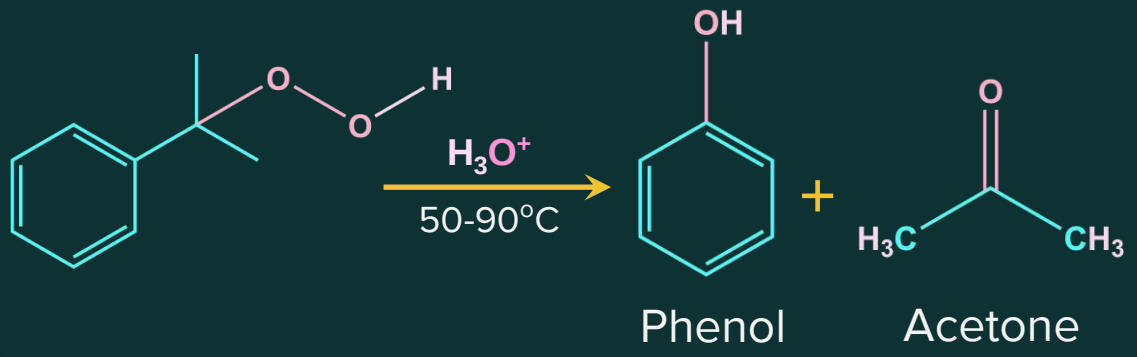


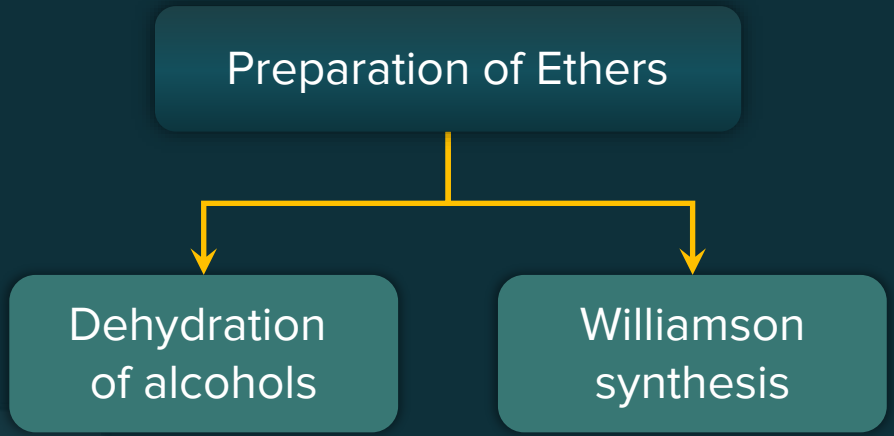
Cumene hydroperoxide

Mechanism

Step 2

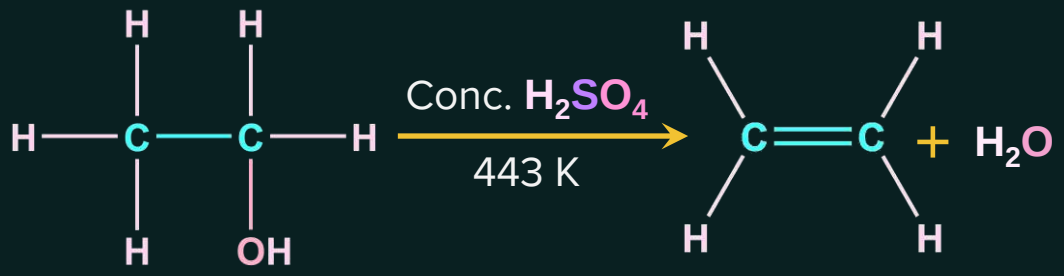
Treatment with acid




Preparation of Ethers
Dehydration of alcohols
Williamson synthesis

Recall

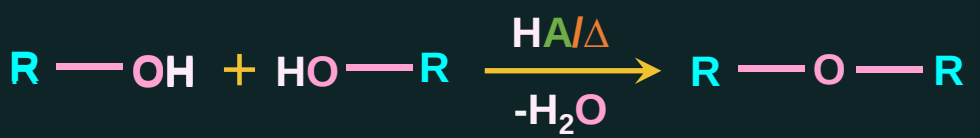
Alcohols can **dehydrate** to form **alkenes**.



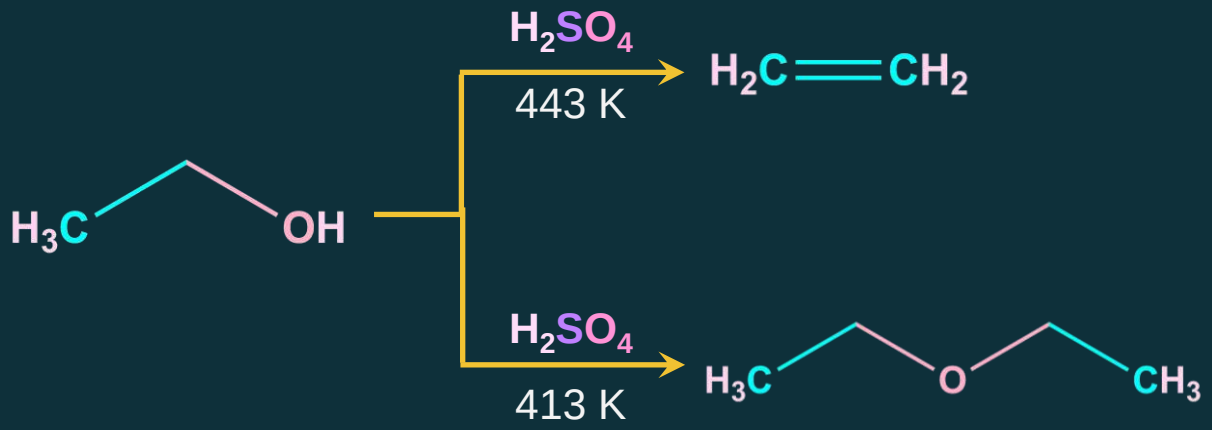
Dehydration of Alcohols

Primary alcohols can also dehydrate to form ethers.

Dehydration to form an ether usually takes place at a **lower temperature** than dehydration to the alkene.



Preparation of Ethers

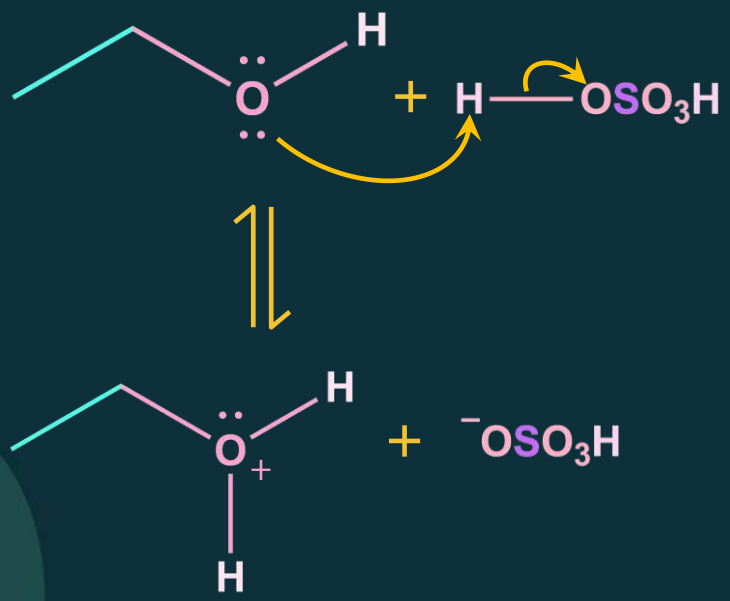


Preparation of Ethers

The formation of an ether by intermolecular dehydration of alcohols occurs by an **S_N2 mechanism.**

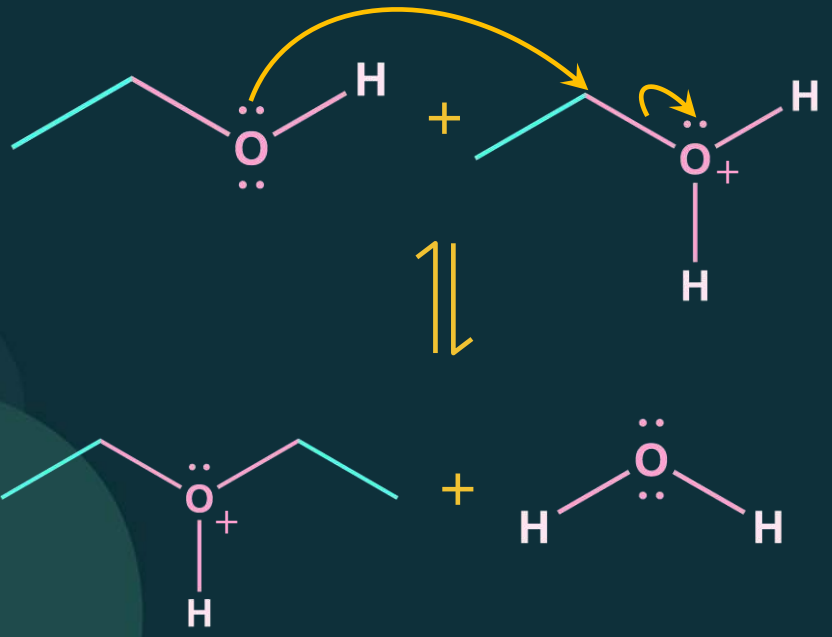
Mechanism

Step 1 Protonation of alcohol



Mechanism

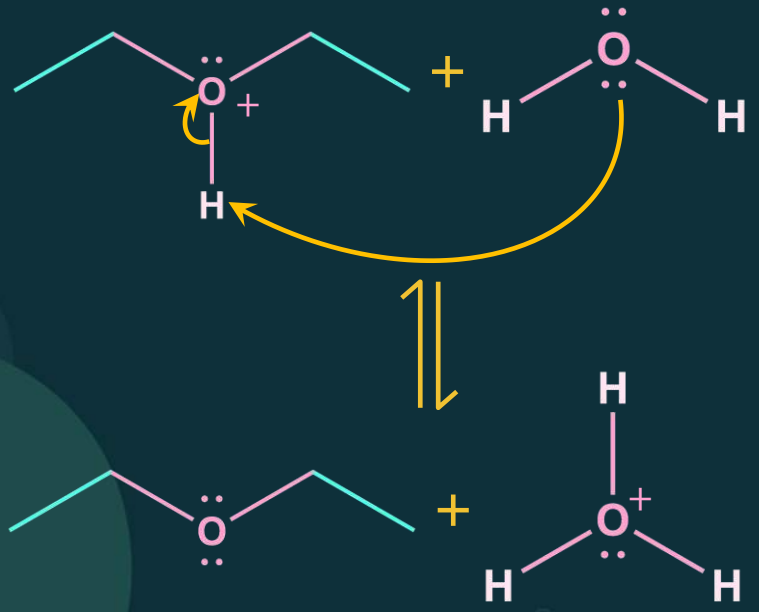
Step 2 Attack of Nucleophile



Mechanism

Step 3

Deprotonation



Limitations of Intermolecular Dehydrations

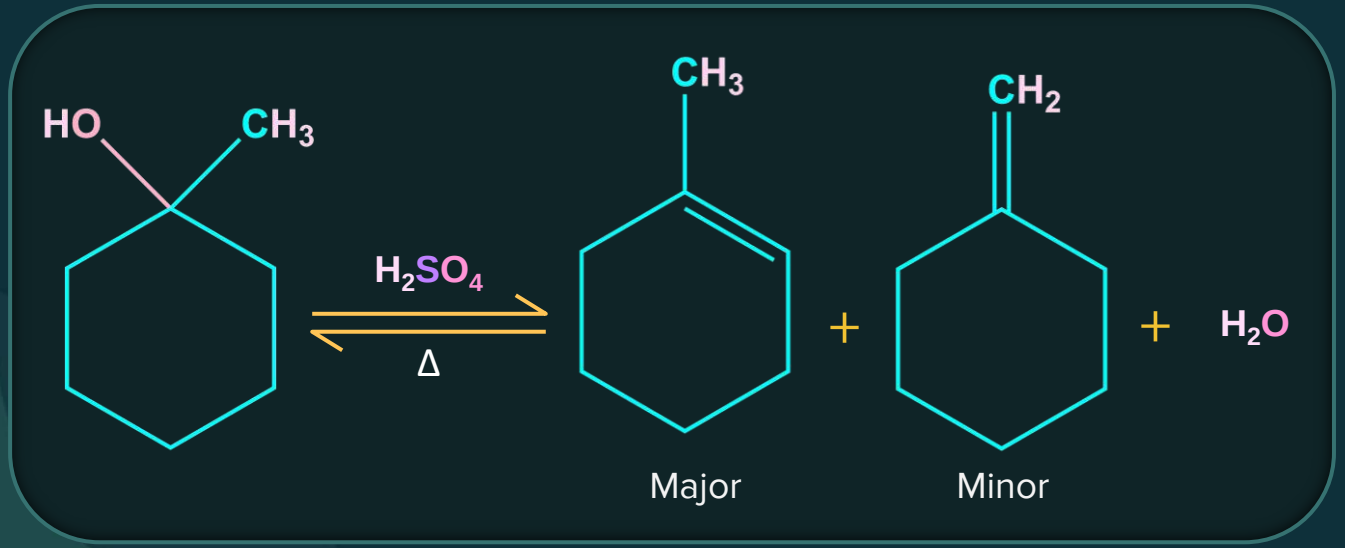
01

Synthesis of ethers using **secondary alcohol** is usually unsuccessful because **alkenes are formed very easily**.

02

Synthesis of ethers with **tertiary alkyl** groups lead **exclusively to the formation of alkenes**.

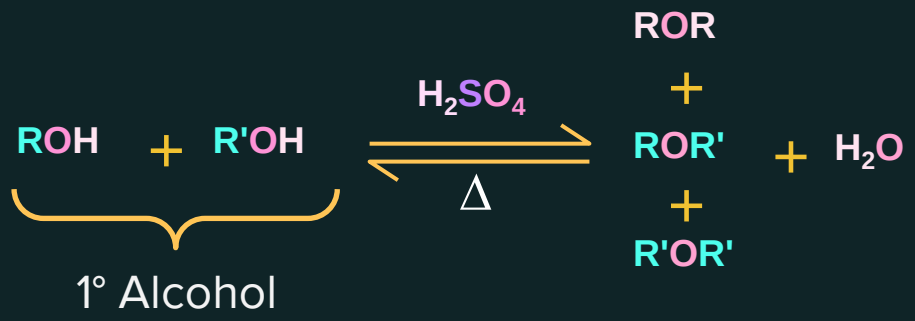
Limitations of Intermolecular Dehydrations



Limitations of Intermolecular Dehydrations

03

Not useful for the preparation of **unsymmetrical ethers** from primary alcohols because the reaction leads to a mixture of products.



Williamson Synthesis of Ethers

Synthesis of symmetrical and unsymmetrical ethers by a **nucleophilic substitution** reaction.

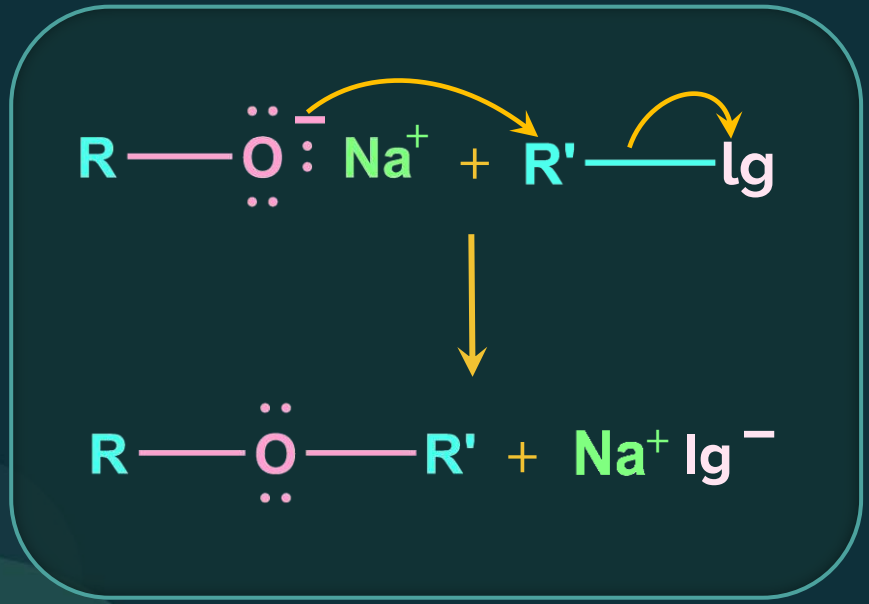
General reaction

Williamson Synthesis of Ethers

The **alkoxide ion** reacts with the substrate via **S_N2 mechanism.**

The substrate must be **unhindered** (1° or 2° alkyl halides) and bear a **good leaving group**.

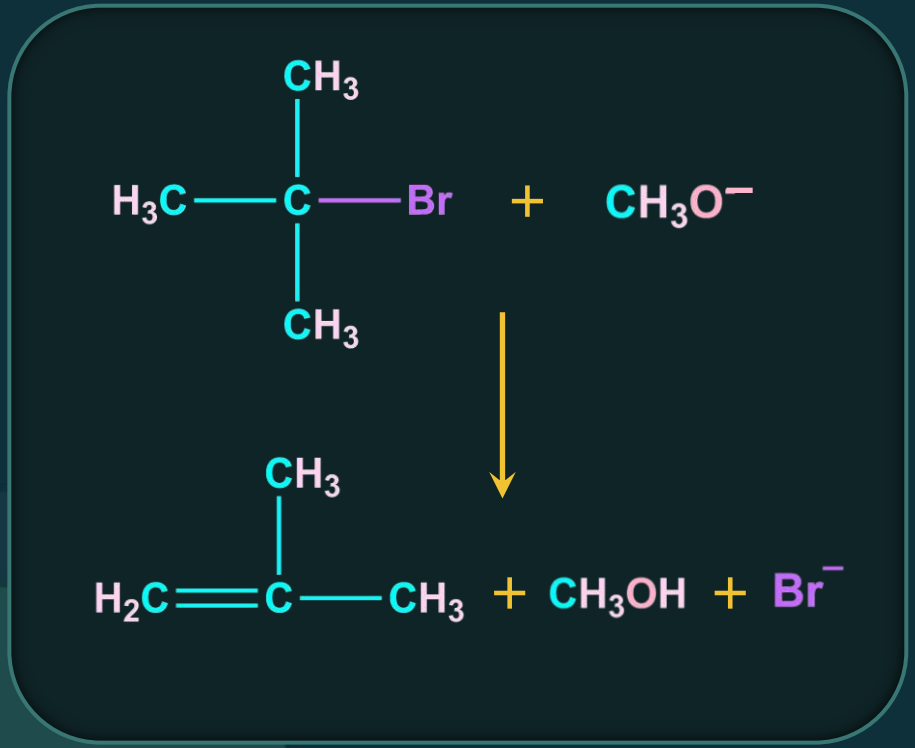
Mechanism



Williamson Synthesis of Ethers

If **tert-butyl halide** and **methoxide ion** are used as reactants, it would result in an **elimination product** and little or **no ether.**

This is because reaction of a **tertiary alkyl halide** under S_N2/E2 condition forms primarily the **elimination product.**


CH3
H3C
C
Br
+
CH3O−
CH3
CH3
H2C
C
CH3
+
CH3OH
+
Br−

Williamson Synthesis of Ethers

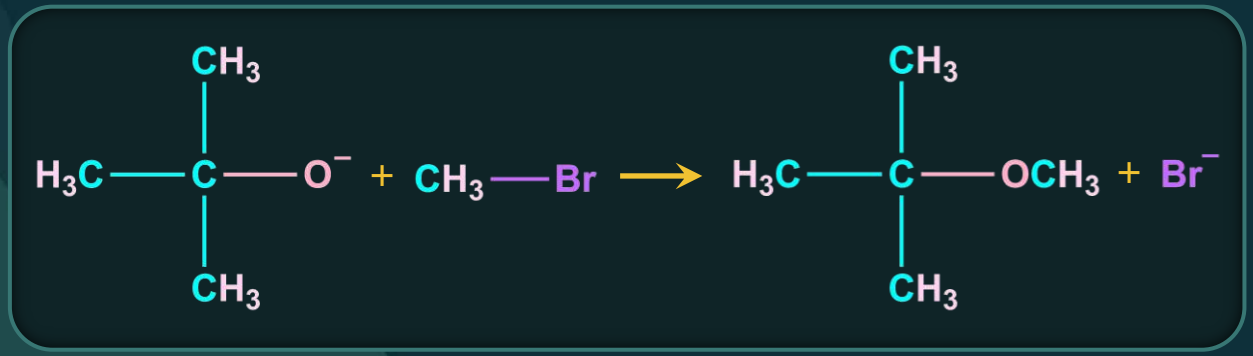
In carrying out a Williamson synthesis of ether:

Less hindered alkyl group should be provided by the **alkyl halide.**

More hindered alkyl group should come from the **alkoxide.**

Williamson Synthesis of Ethers

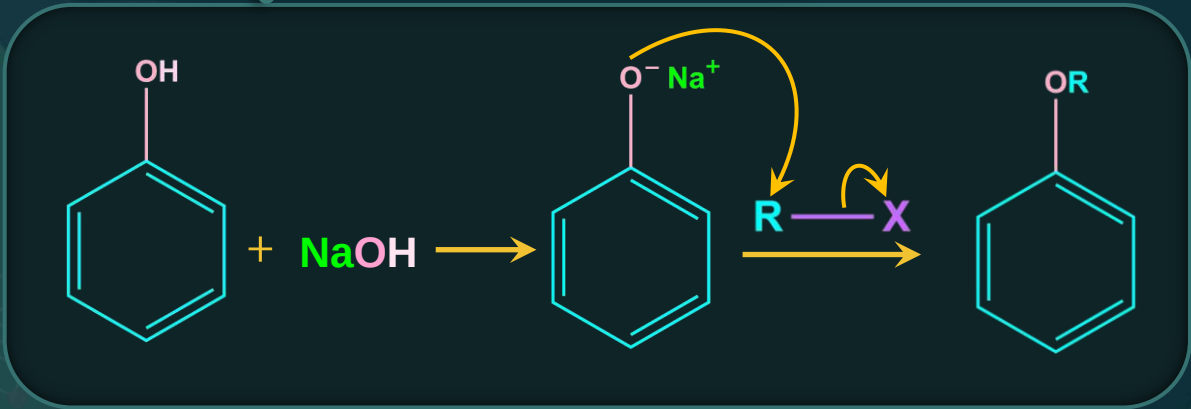
To synthesise tert-Butyl methyl ether, the starting materials **should** be a **methyl halide** and **tert-Butoxide ion**.



Williamson Synthesis of Ethers

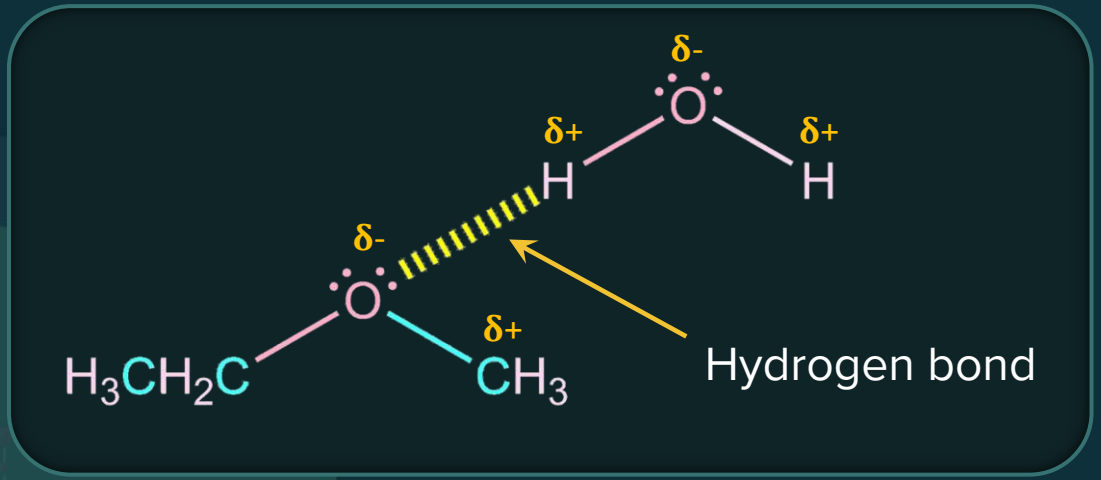
To prepare alkyl phenyl ether

Phenoxide ion is treated with alkyl halide



Solubility

Ethers are **soluble in water** because they form **H-bond** and have solubilities **comparable to alcohols** of similar molar mass.

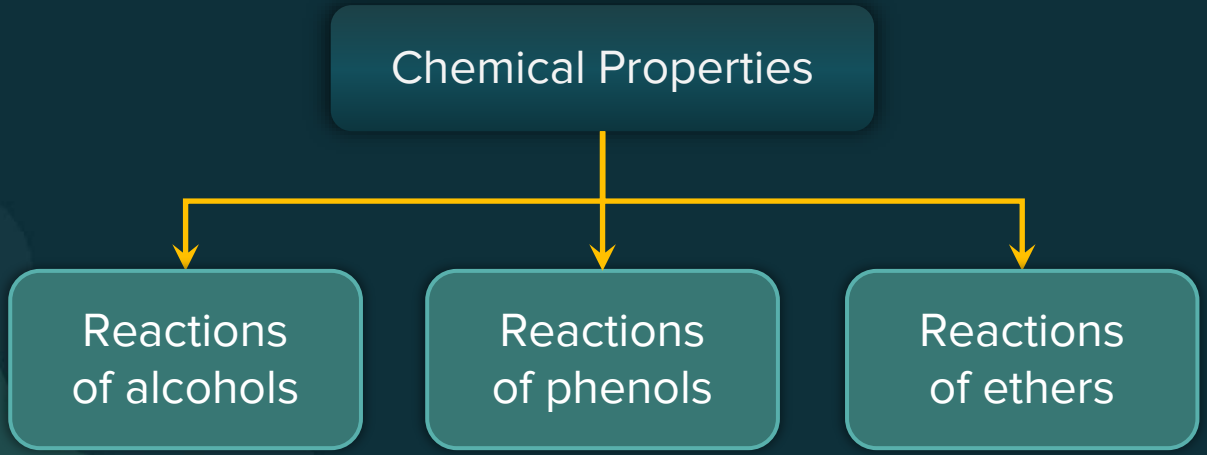


Boiling Point

Ethers have boiling point that are roughly **comparable** with those of hydrocarbons of the **similar molar mass** (M.M.)

B.P. of Diethyl ether (M.M. = 74 g mol^{-1})	=	34.6°C
B.P. of Pentane (M.M. = 72 g mol^{-1})	=	36°C

Molar mass ↑ → Boiling points of alcohols ↑


Chemical Properties
Reactions of alcohols
Reactions of phenols
Reactions of ethers

Alcohol as an Electrophile

Polarisation of the **C — O** bond makes the carbon atom partially positive, and if it were not for the fact that OH^- is a poor leaving group, this **carbon** would be susceptible to **nucleophilic** attack.

Alcohol as an Electrophile

The **hydroxyl** group can be converted to a good **leaving group,** so as to allow **substitution** or **elimination** reactions.

Once the alcohol is converted to a good leaving group, **substitution reactions** become possible (S_N2 or S_N1, depending on the class of alcohol).

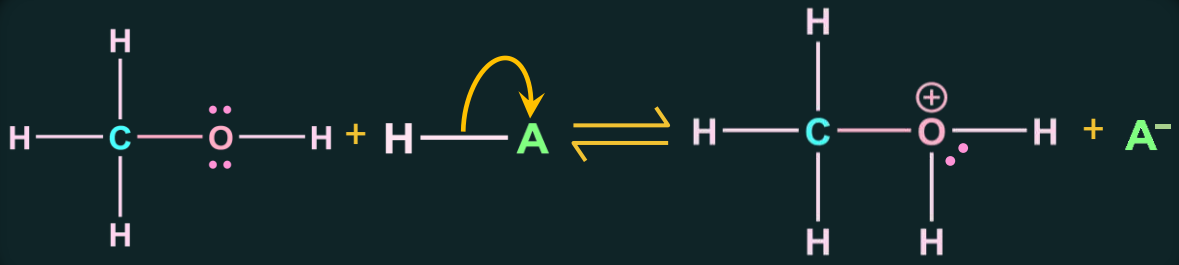
Hydroxyl group can be converted to a **good leaving group by**

- Protonation of alcohol
- Conversion of alcohols into alkyl halides
- Conversion to a sulphonate ester derivative

Protonation of Alcohols

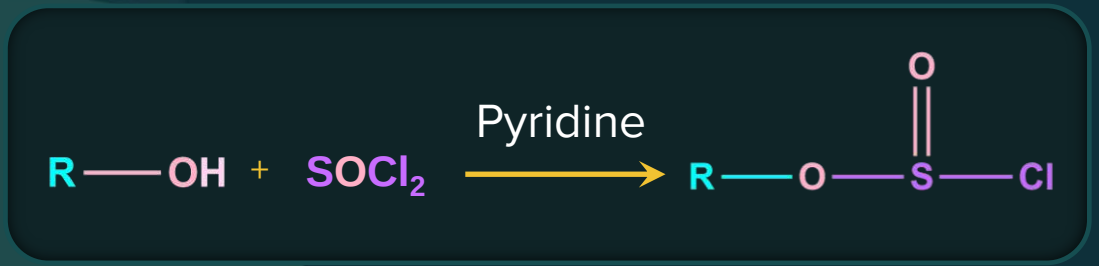
1

Protonation of an alcohol converts a poor leaving group (OH^-) into a good leaving group (H_2O).



Conversion of Alcohols into Alkyl Halides

2 With PBr_3 and $SOCl_2$, an alcohol **converts** a **poor leaving group** (OH^-) into a **good leaving group** (Br^- or Cl^-).

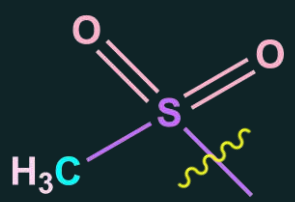


Conversion to a Sulphonate Ester Derivative

The hydroxyl group of an alcohol can be converted into a **good leaving group** by the conversion to a sulphonate ester derivative.

where **R** = **-Ms, -Ts, -Tf**

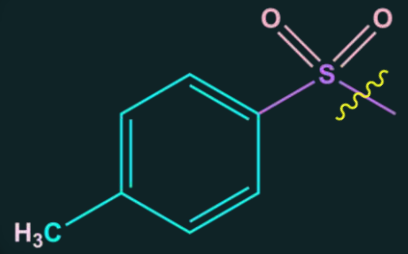
Conversion to a Sulphonate Ester Derivative



or **Ms –**

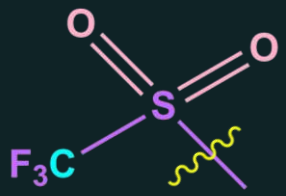
or **$MeSO_2$ –**

The mesyl group



or **Ts –**

The tosyl group



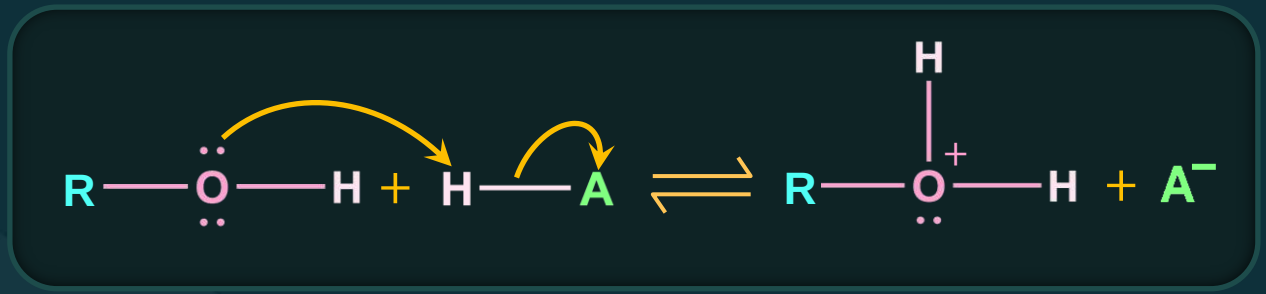
or **CF_3SO_2 –**

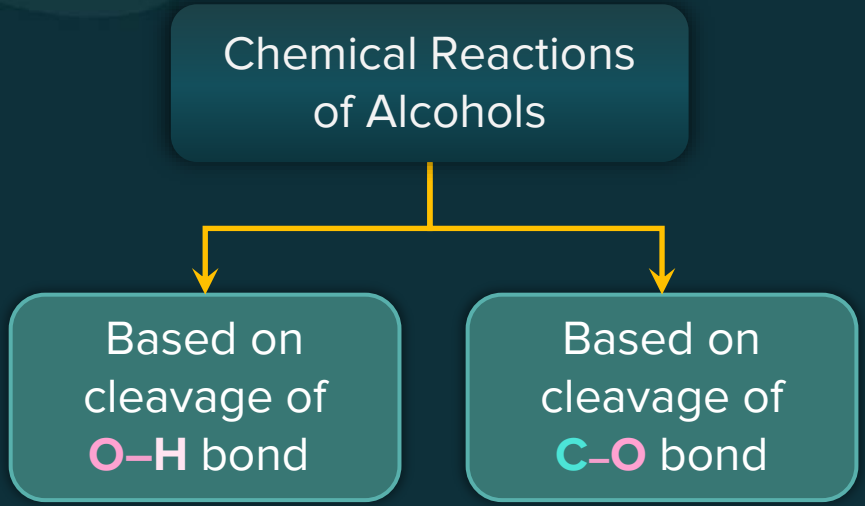
or **Tf –**

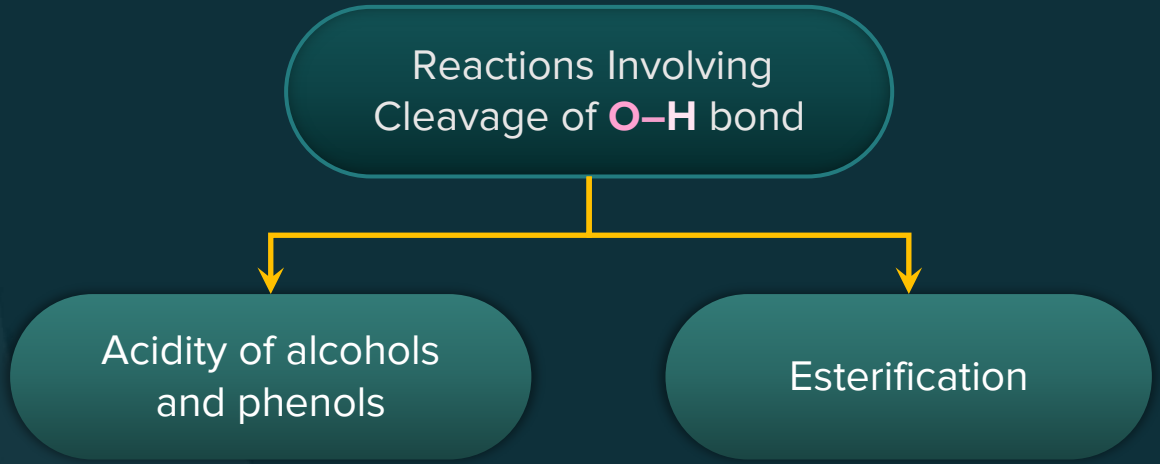
The trifyl group

Alcohol as Nucleophile

The **oxygen** atom of the hydroxyl group is **nucleophilic** in nature.




Chemical Reactions of Alcohols
Based on cleavage of O–H bond
Based on cleavage of C–O bond


Reactions Involving
Cleavage of O–H bond
Acidity of alcohols
and phenols
Esterification

Acidity of Alcohols and Phenols

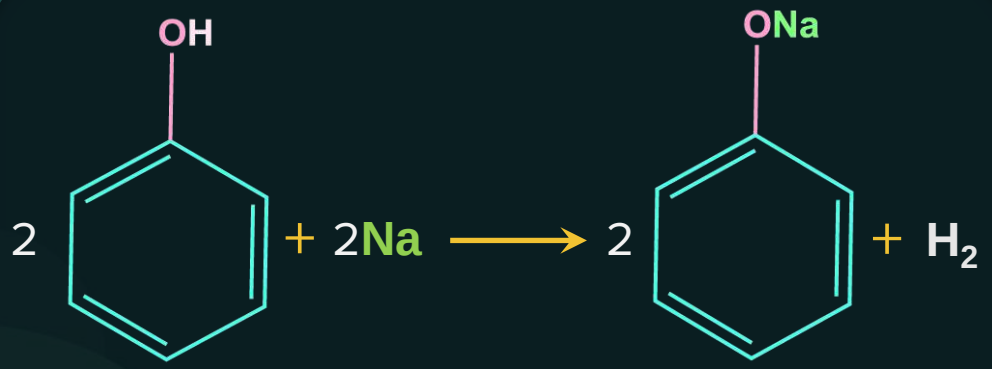
Reaction with **metals**

Alcohols and phenols release H_2 gas on reaction with sodium, potassium, or other alkali metals.

This reflects the **presence** of **acidic** hydrogen.

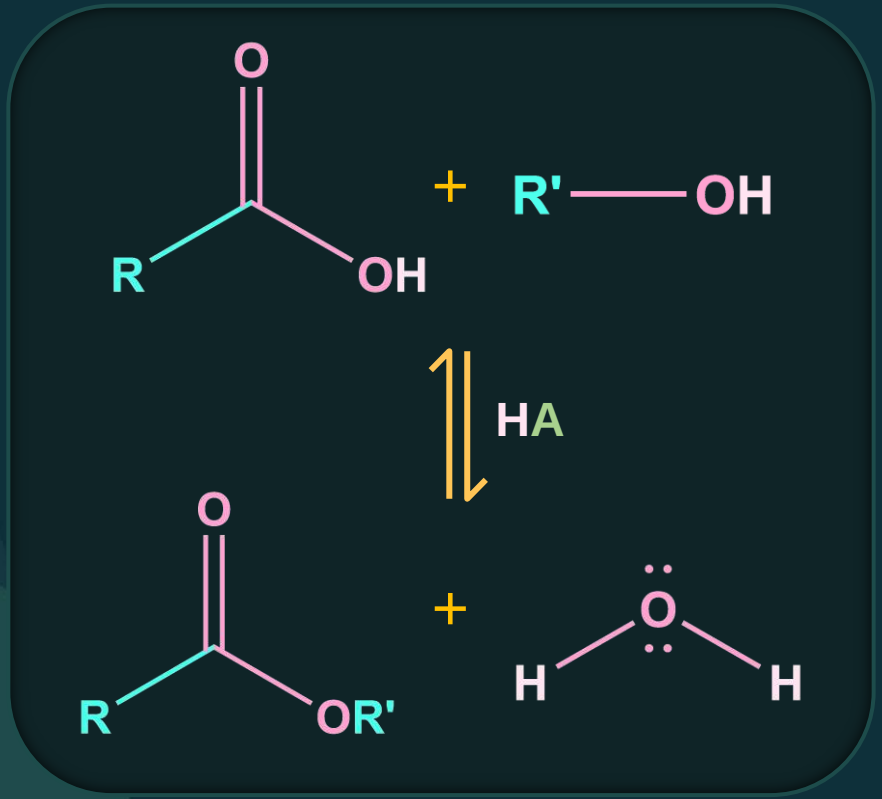
Acidity of Alcohols and Phenols

$$2ROH + 2Na \longrightarrow 2RONa + H_2$$



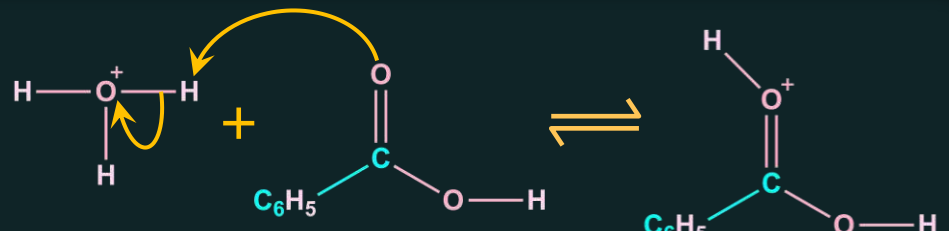
Esterification

General reaction

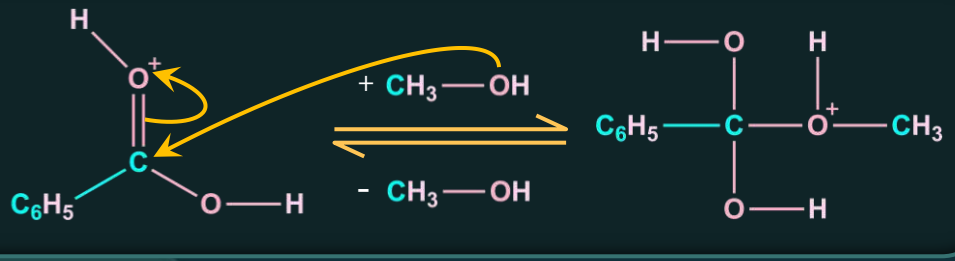


Mechanism

Step 1

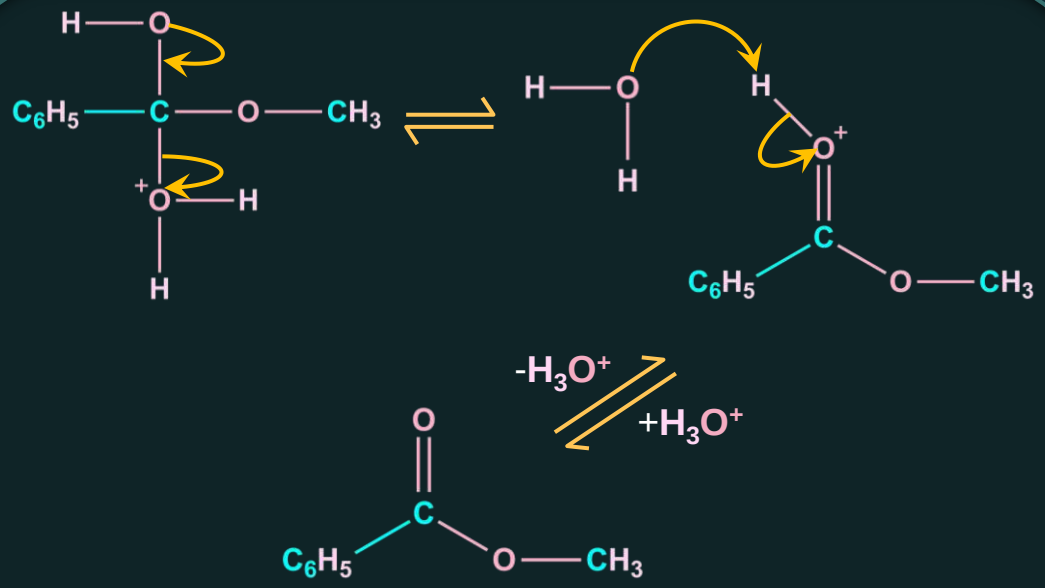


Step 2



Mechanism

Step 3



Acid-Catalysed Esterification

Esterification proceeds **very slowly** in the absence of strong acids.

When an acid and an alcohol react with a small amount of **conc. H_2SO_4 or HCl,** they reach equilibrium within few hours.

Acid-Catalysed Esterification

Yield of esterification can be **increased by**

1. The use of an **excess** of either carboxylic acid or the alcohol.
2. By **removing water** from the reaction mixture as it is formed

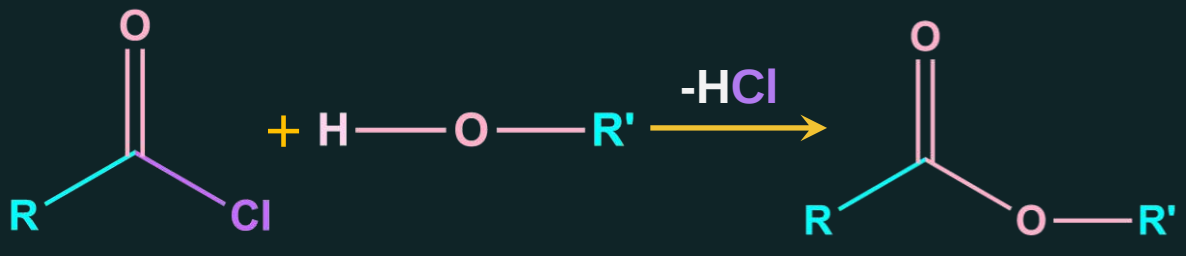
Steric Factors

Tertiary alcohols react so slowly in acid-catalysed esterifications that they usually undergo **elimination instead**.

However, they can be safely converted to esters by using **acyl chlorides and anhydrides**

Esters from Acyl Chlorides

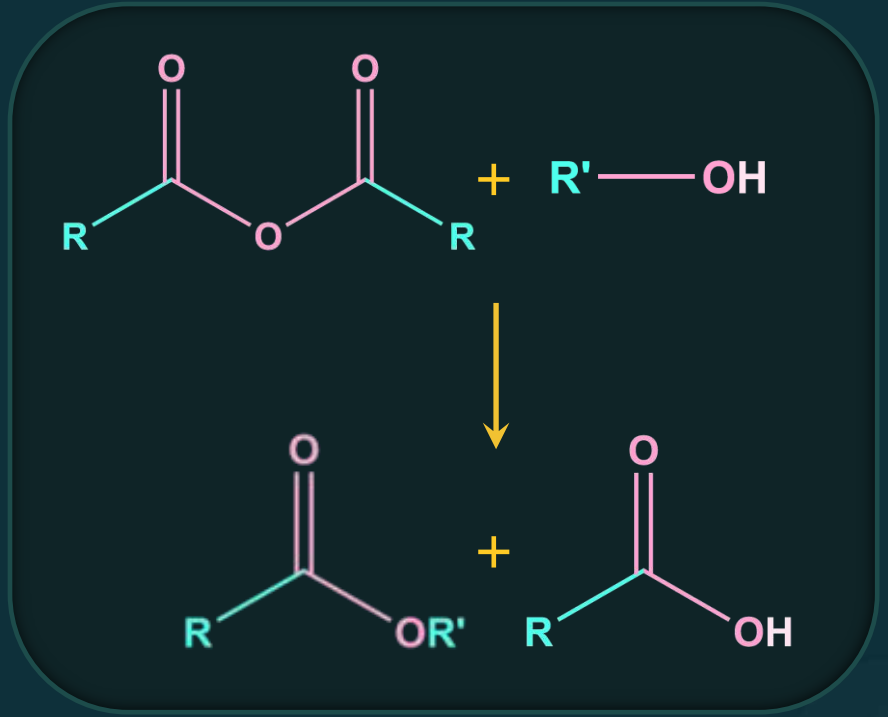
General reaction



Pyridine is often added to the reaction mixture to react with the HCl that forms.

Esters from Carboxylic Acid Anhydride

General reaction



Note

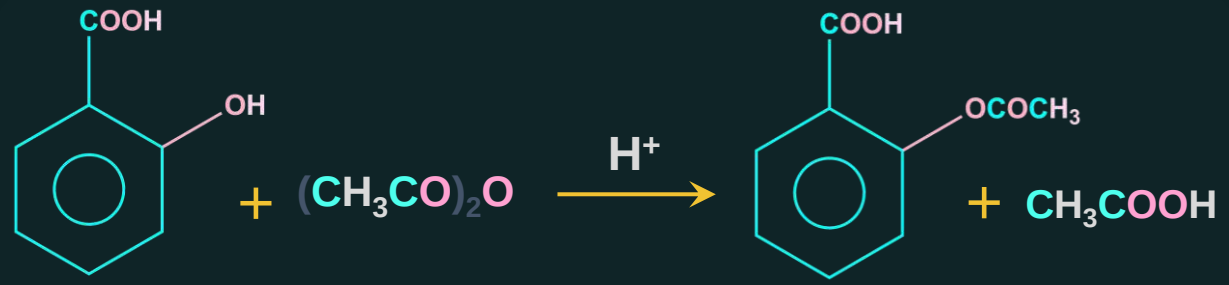
Ester synthesis is **best** accomplished by the reaction of an alcohol with an **acyl chloride** or **acid anhydride.**

Esters from Acyl Chloride or Anhydride

These reagents **avoid** the use of a strong acids, which is normal for acid-catalysed esterification.

A strong acid may cause **side reactions** depending on what other functional groups are present.

Application

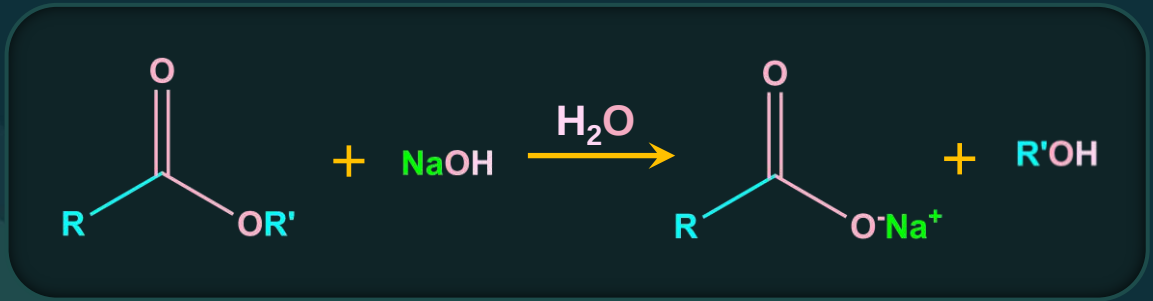


Salicylic acid

Acetylsalicylic acid
(**Aspirin**)

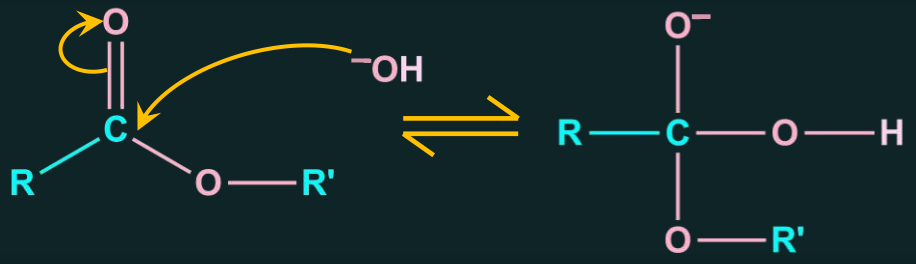
Saponification

Refluxing an ester with aqueous sodium hydroxide, produces an alcohol and the sodium salt of the acid

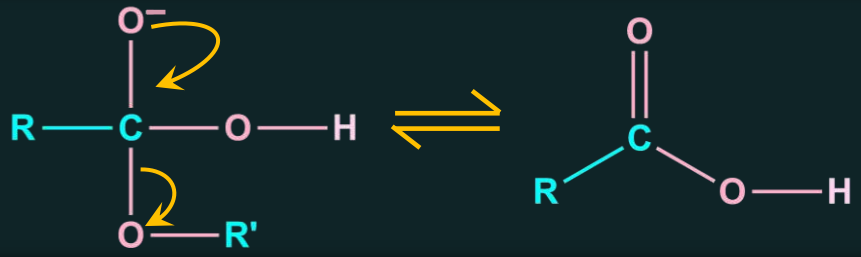


Mechanism

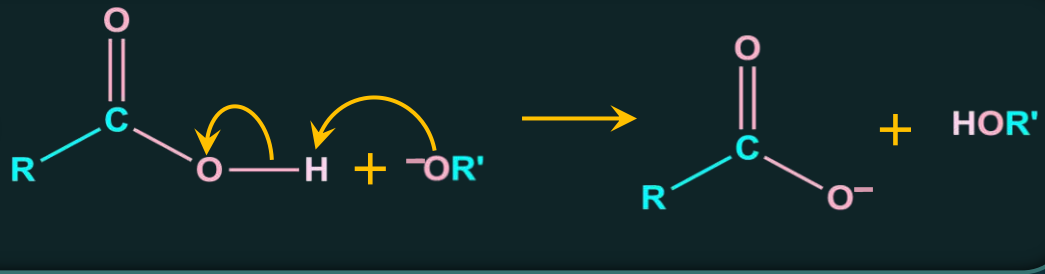
Step 1



Step 2



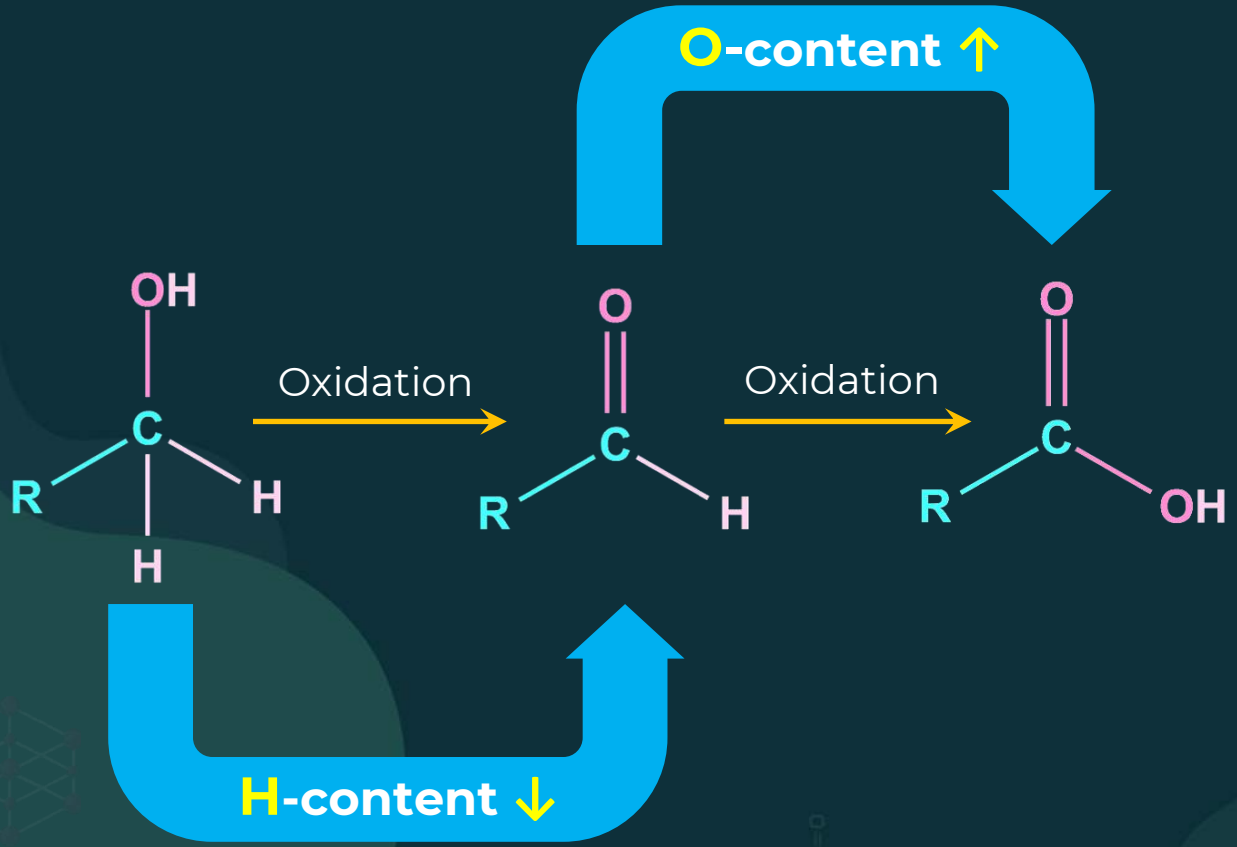
Step 3



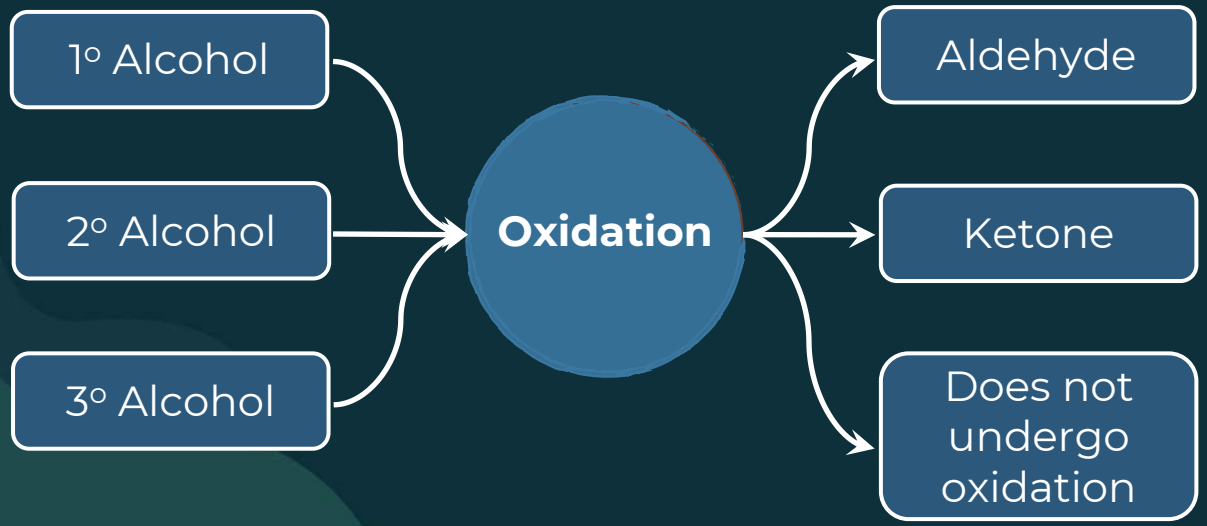
Note

Base-promoted hydrolysis of an ester, as a result, is an essentially **irreversible** reaction.

Oxidation of Alcohols



Oxidation of Alcohols



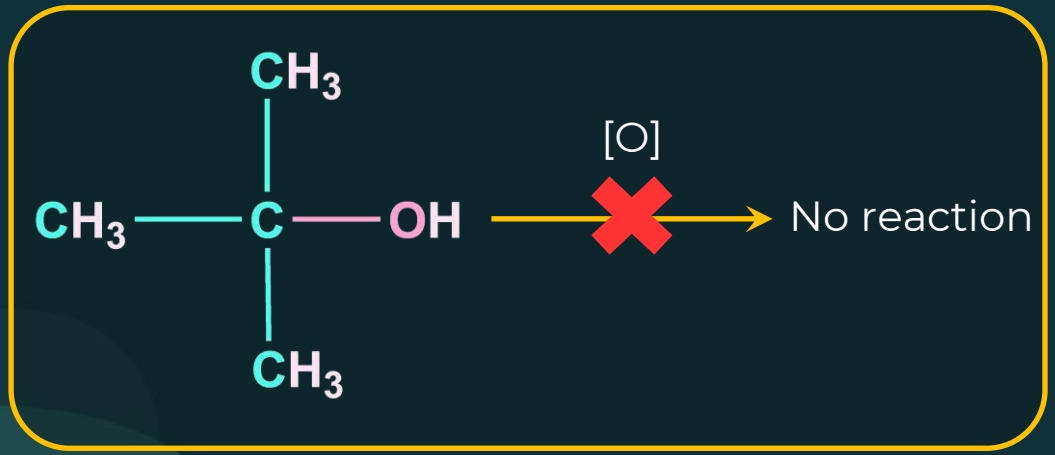
Note

3° alcohols can be oxidised at **high temperatures using $KMnO_4$** (drastic conditions).

But a **mixture of carboxylic acids** is obtained.

Oxidation of Alcohols

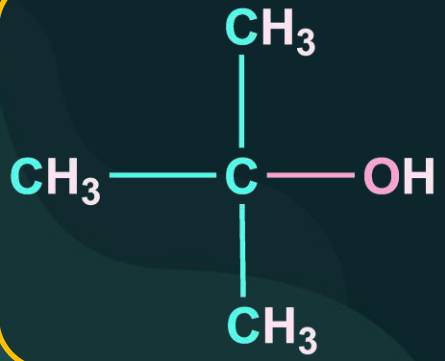
Example



Tertiary alcohol can not undergo oxidation under normal conditions, it breaks into smaller molecules of carboxylic acid when treated with very strong oxidizing agents.

Oxidation of Alcohols

Example



$KMnO_4$

High temperature

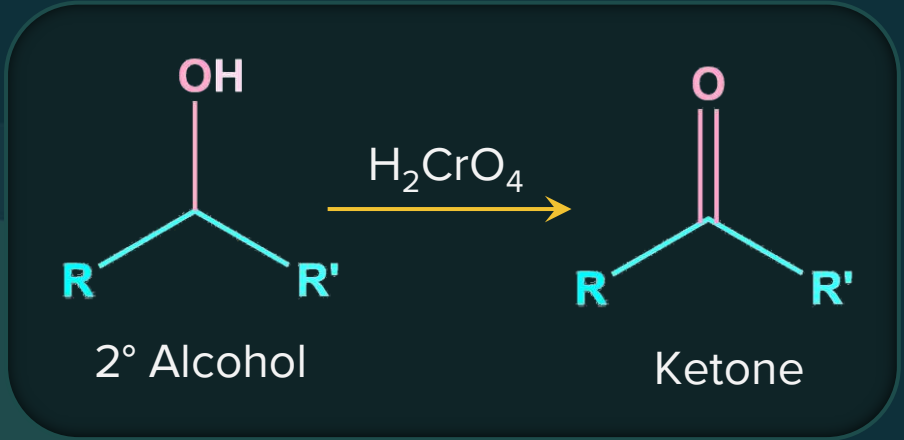
Mixture of low membered **carboxylic acid**

Oxidation of 1° Alcohols to Carboxylic Acids

Primary alcohols can be oxidised to **carboxylic acids** by potassium permanganate **($KMnO_4$)** or chromic acid **(H_2CrO_4)**.

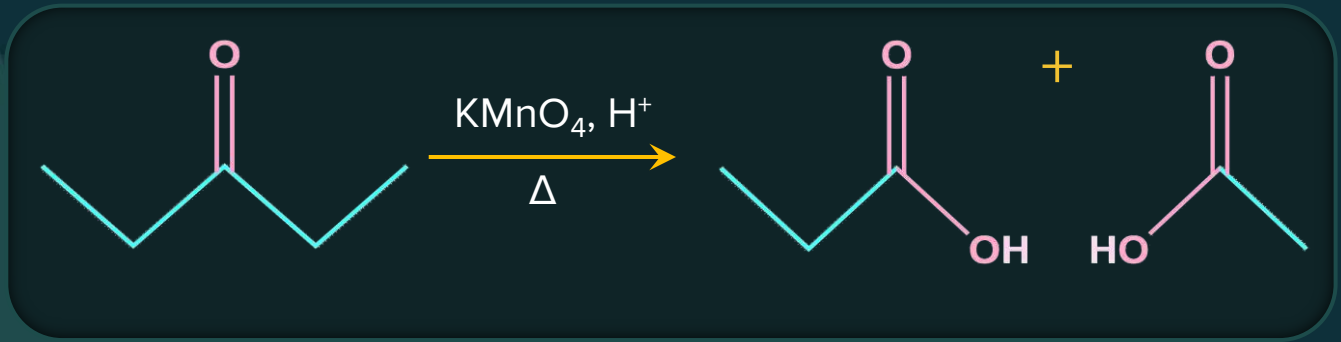
Oxidation of 2° Alcohols to Ketone

Both **$KMnO_4$** and **H_2CrO_4** can also be used to oxidise a **secondary alcohol** to a **ketone.**



Acidic $KMnO_4$ & $K_2Cr_2O_7$ as Oxidising Agents

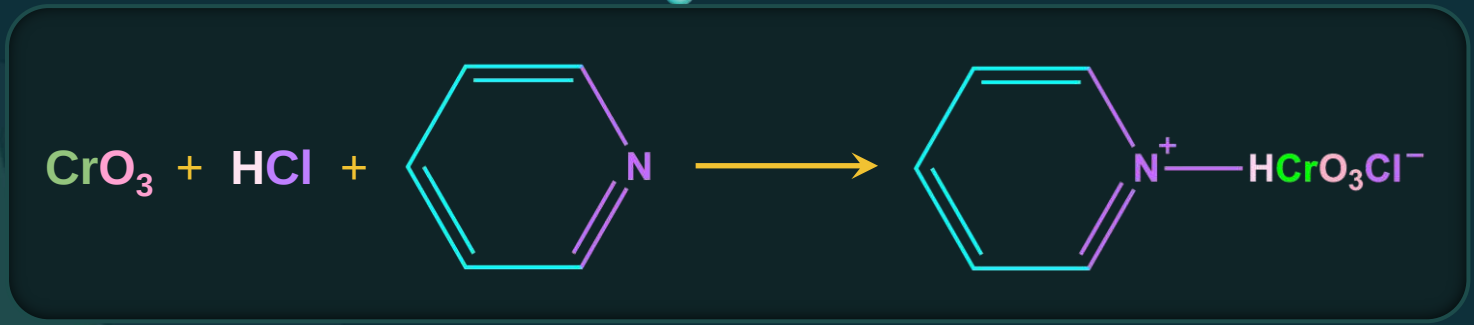
Ketones are difficult to oxidise. They are oxidised only on heating with a **strong oxidising agent**.



Cleavage of C–C bonds takes place and a mixture of **carboxylic acids** containing **lesser number** of carbon atoms is formed.

Oxidation of Primary Alcohols

An excellent reagent for converting a primary alcohol into an aldehyde is **pyridinium chlorochromate (PCC)**.

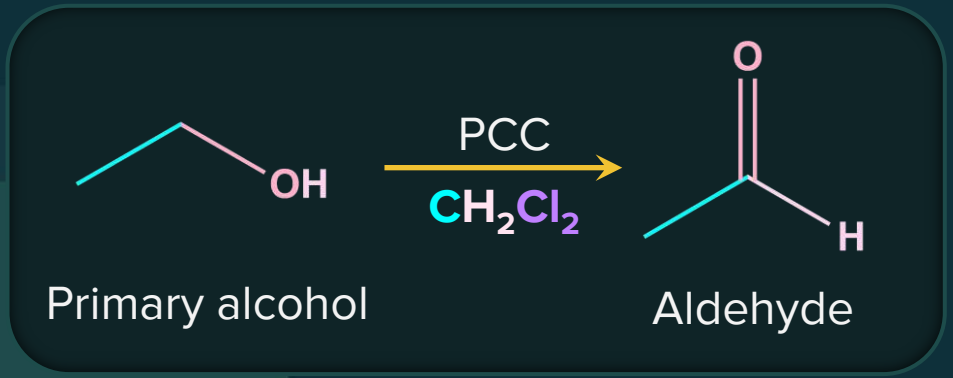


Pyridinium chlorochromate (PCC)

PCC is formed when **CrO_3 is dissolved in HCl** and then treated with **pyridine**.

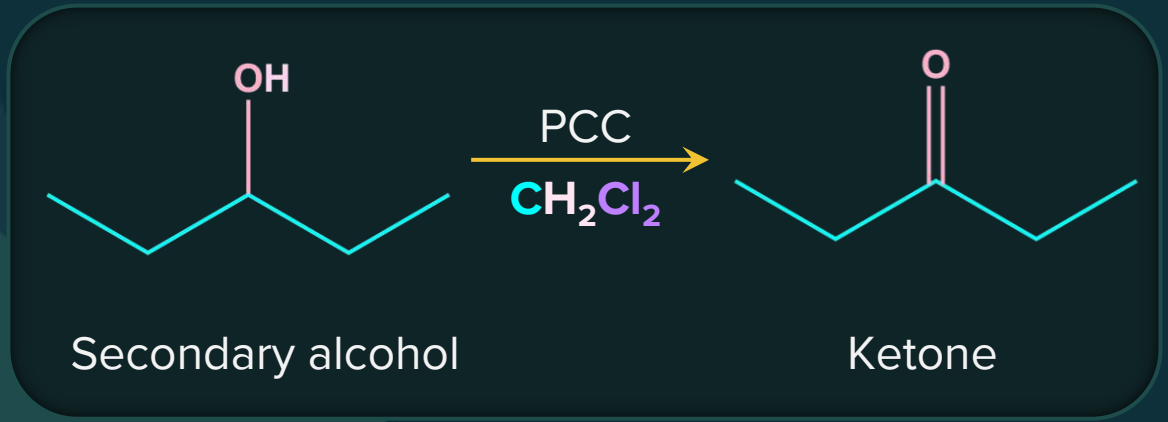
PCC

PCC, when dissolved in methylene chloride (CH_2Cl_2), will oxidise a primary alcohol to an **aldehyde,** and stop at that stage.



PCC

PCC will also oxidise a secondary alcohol to a **ketone**.



PCC

PCC **does not** attack double bonds.

Oxidation of 2º Alcohols

Oxidation of 2° alcohols usually **stops at the ketone stage** because further oxidation requires the breaking of a **C–C** bond.

Jones Reagent

Chromic acid is usually prepared by adding Cr(VI) oxide (CrO_3) or sodium dichromate ($Na_2Cr_2O_7$) to **aqueous sulfuric acid.**

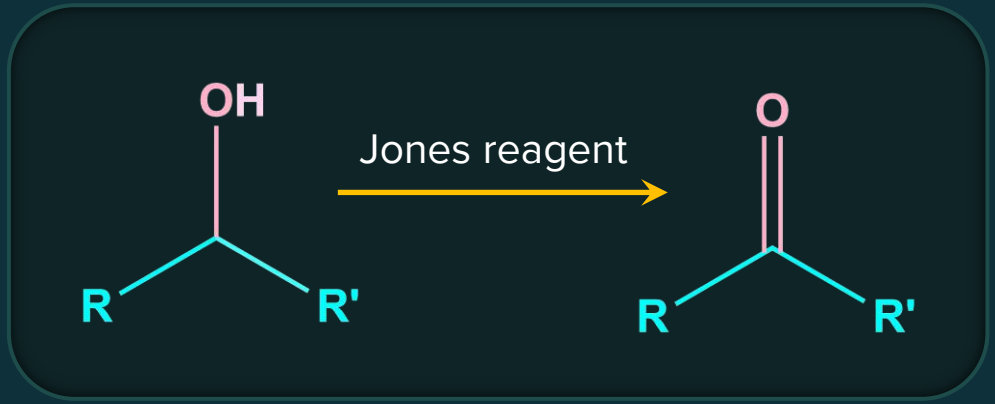
The mixture is known as **Jones reagent**

Jones Reagent

Oxidations of secondary alcohols are generally carried out by adding **Jones reagent** to a solution of the alcohol in acetone or acetic acid.

This procedure **rarely affects double bonds** present in the molecule.

Jones Reagent



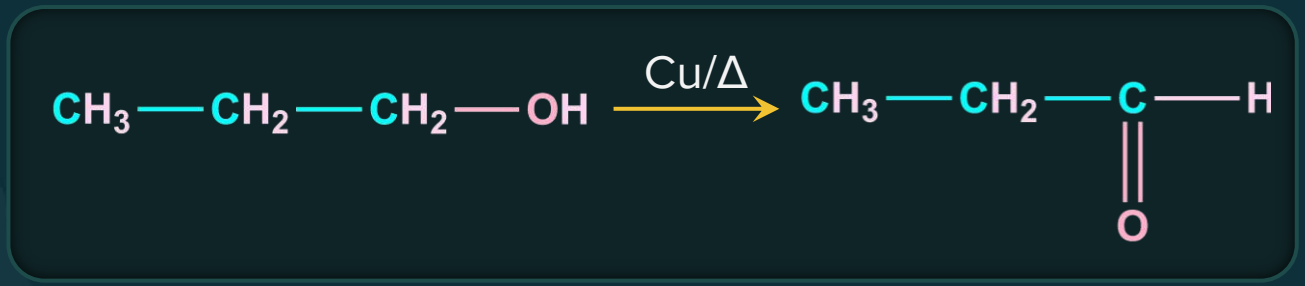
Oxidation

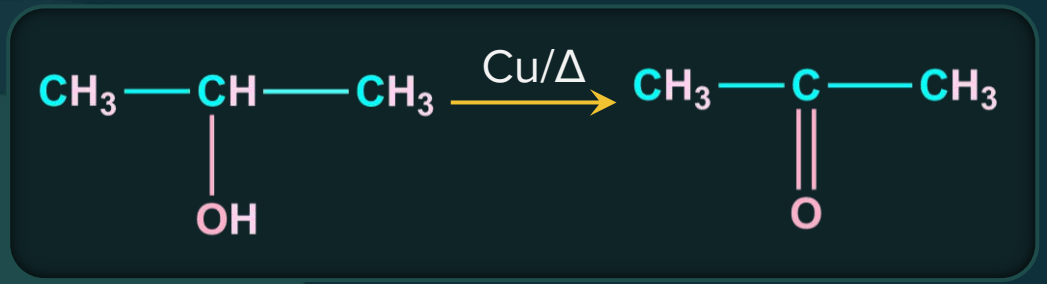
When the vapours of a primary or a secondary alcohol are passed over **heated copper** at 573 K

Dehydrogenation takes place and an **aldehyde or a ketone is formed,** while tertiary alcohols undergo **dehydration**

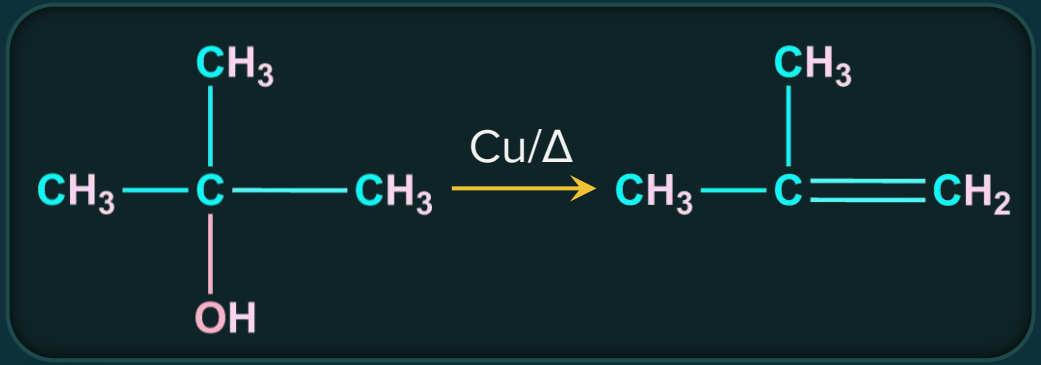
Oxidation

Dehydrogenation

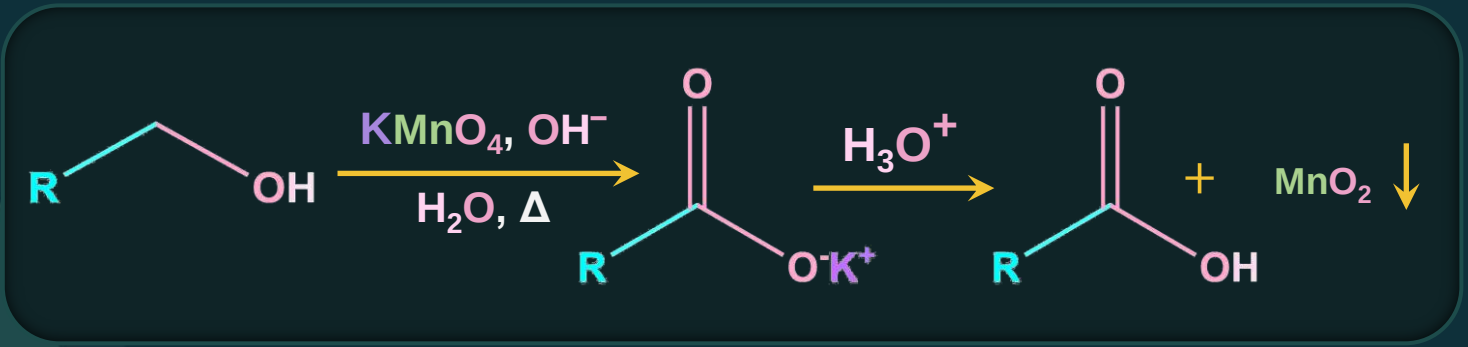




Dehydration

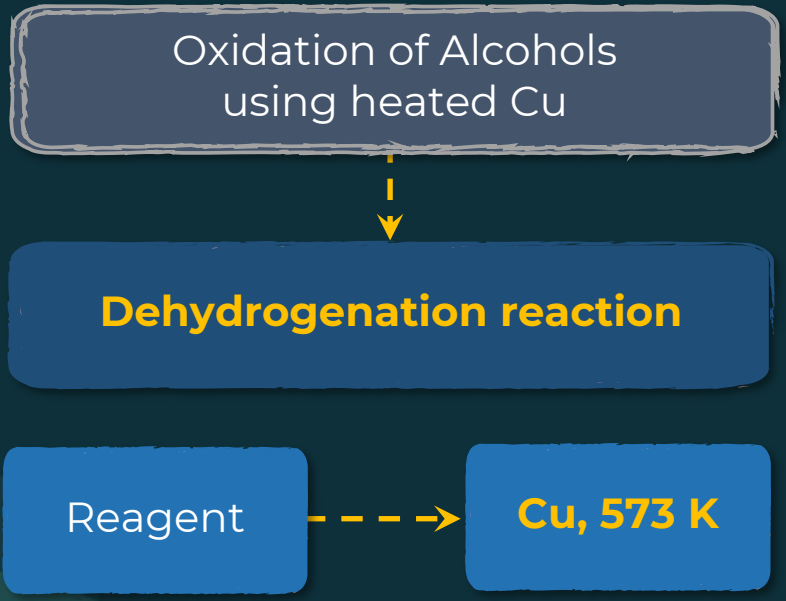


Oxidation of 1° Alcohols to Carboxylic Acids

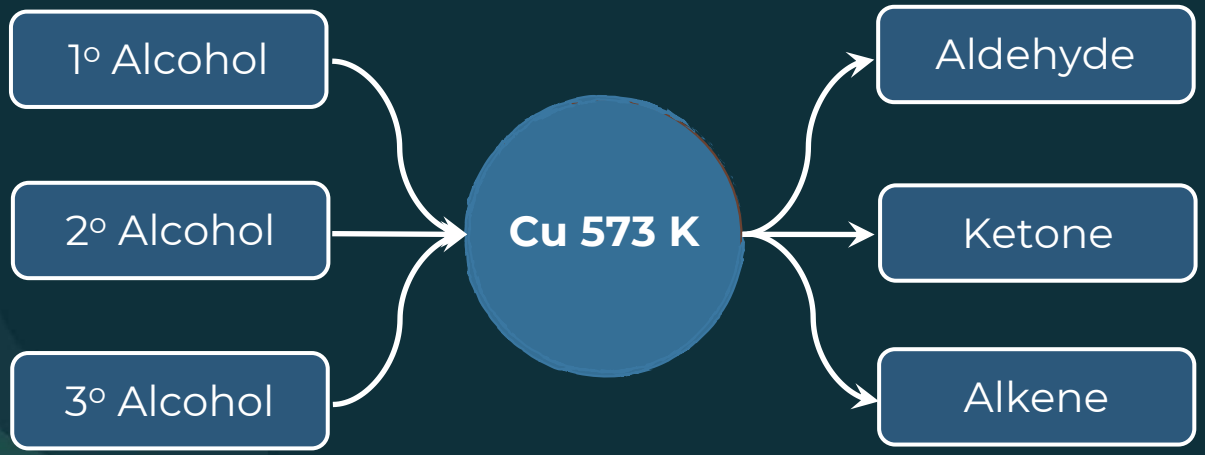


The reaction with **$KMnO_4$** is usually carried out in **basic** aqueous solution, wherein **MnO_2 precipitates** as the oxidation takes place.

Oxidation of Alcohols Using Heated Cu



Oxidation of Alcohols Using Heated Cu

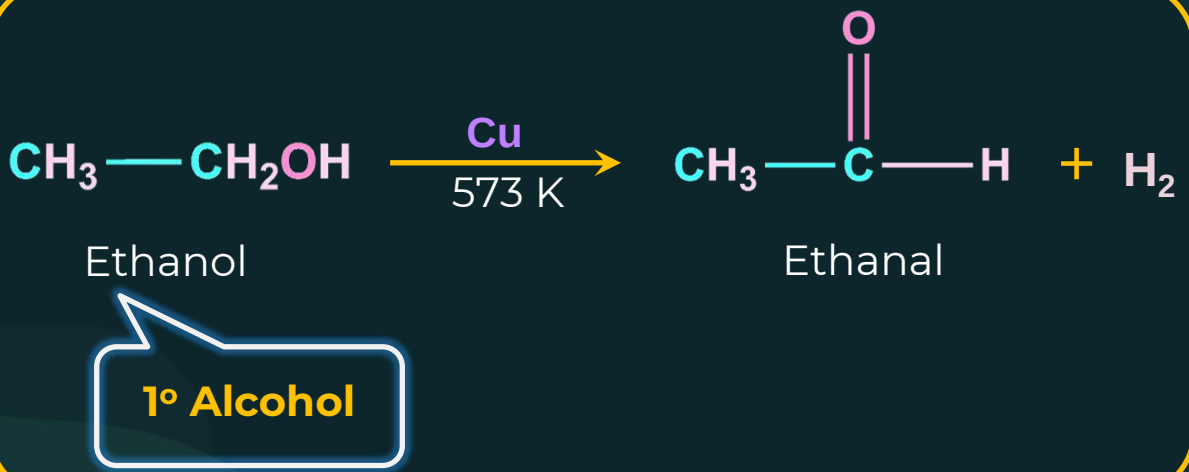


Note

Primary and secondary alcohols undergo **dehydrogenation** in the presence of heated copper, but **tertiary** alcohols undergo **dehydration.**

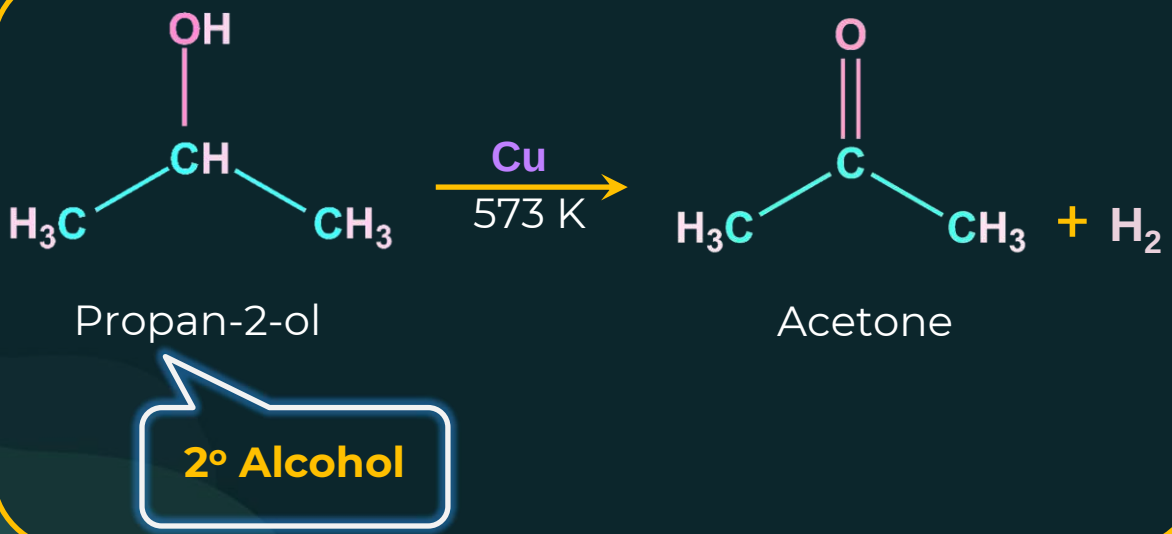
Oxidation of Alcohol Using Heated Cu

Example



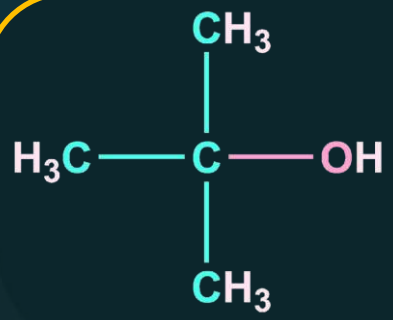
Oxidation of Alcohol Using Heated Cu

Example

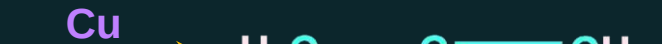


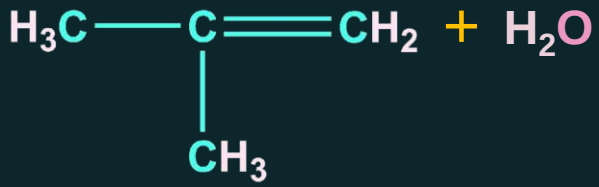
Oxidation of Alcohol Using Heated Cu

Example



2-methylpropan-2-ol





2-methylpropene

3° Alcohol

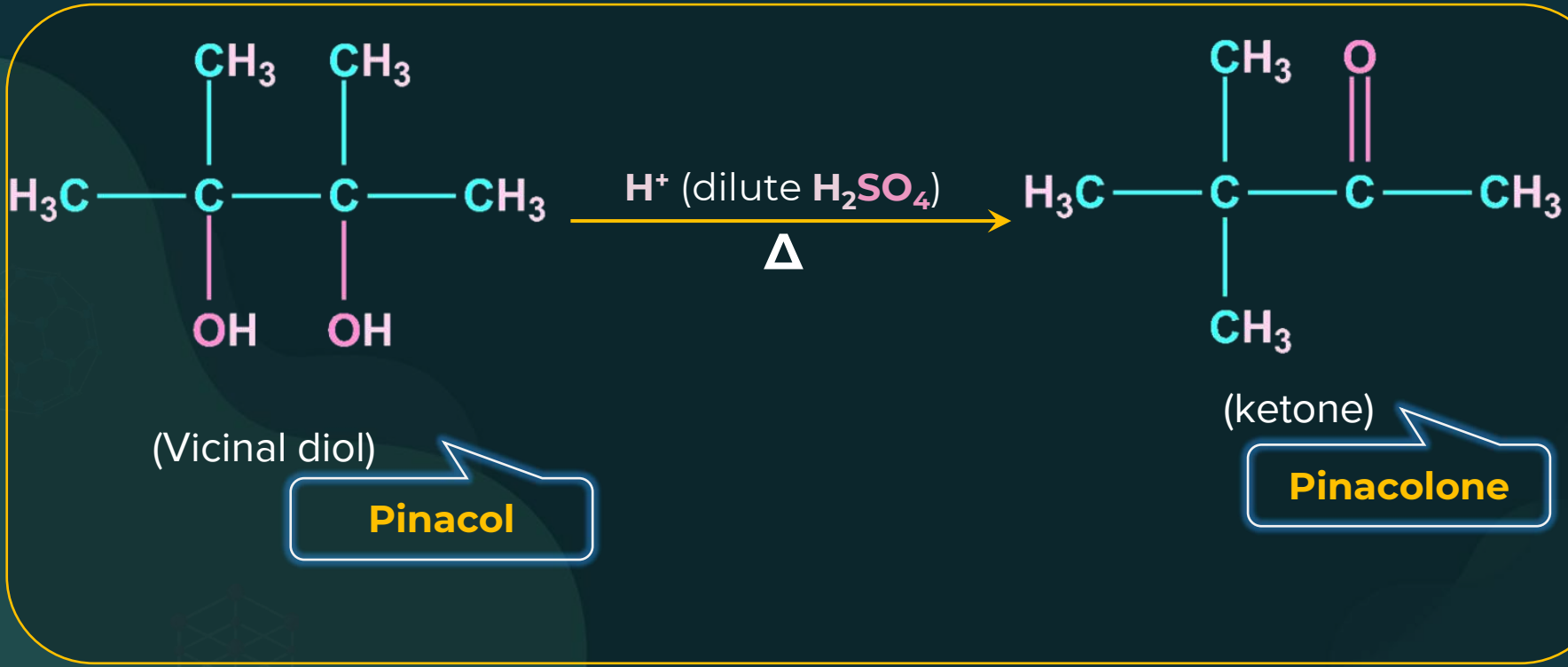
Pinacol-Pinacolone Rearrangement

Vicinal diols → Ketone/Aldehyde

Reagents - - - → H^+ (dilute H_2SO_4), **Δ**

Pinacol-Pinacolone Rearrangement

Example



(Vicinal diol)

Pinacol

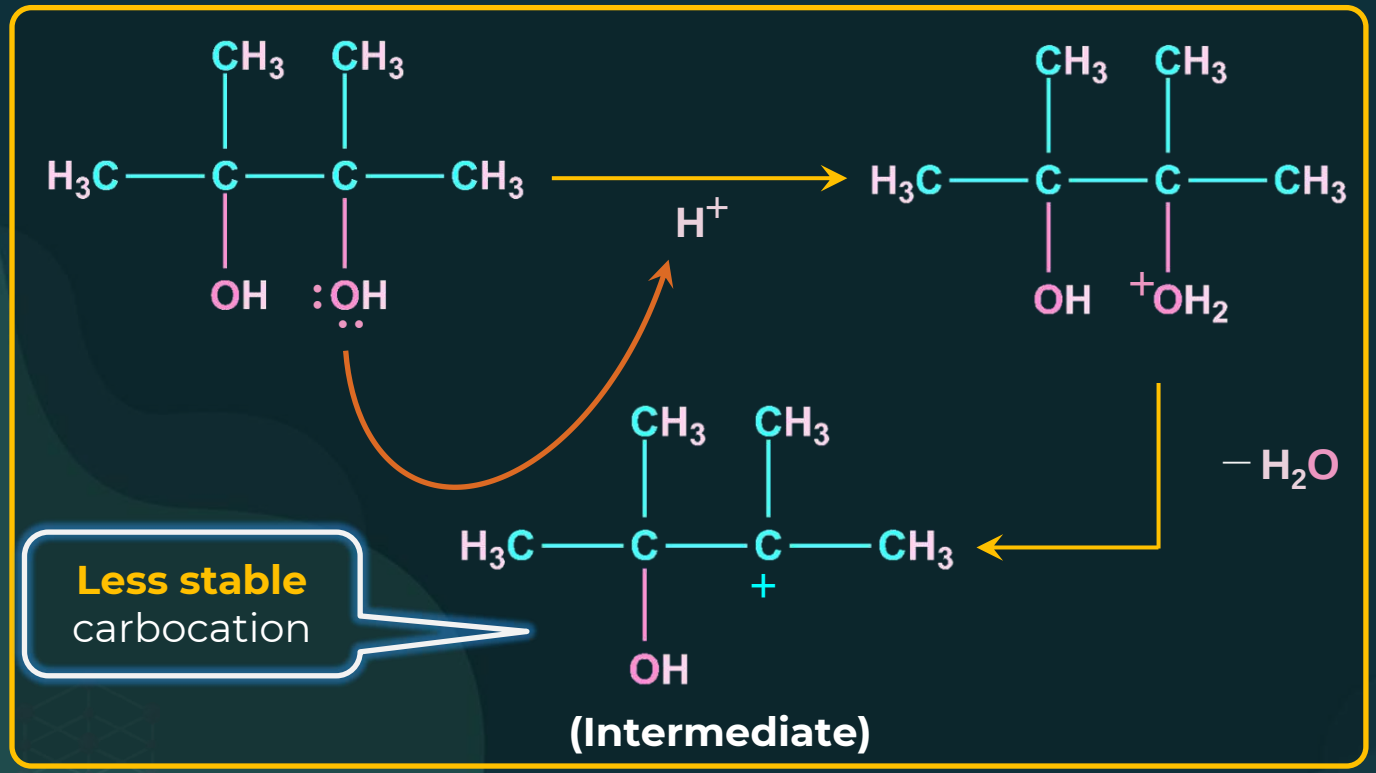
(ketone)

Pinacolone

Steps Involved in Pinacol-Pinacolone Reaction

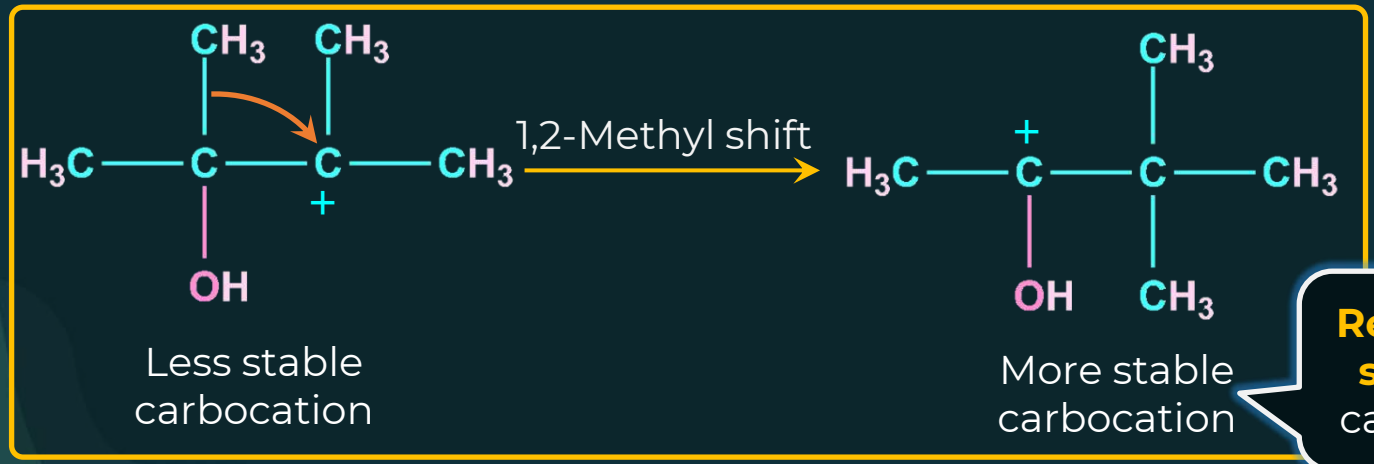
Step 1	Formation of carbocation
Step 2	Rearrangement of carbocation
Step 3	Deprotonation

Formation of Carbocation

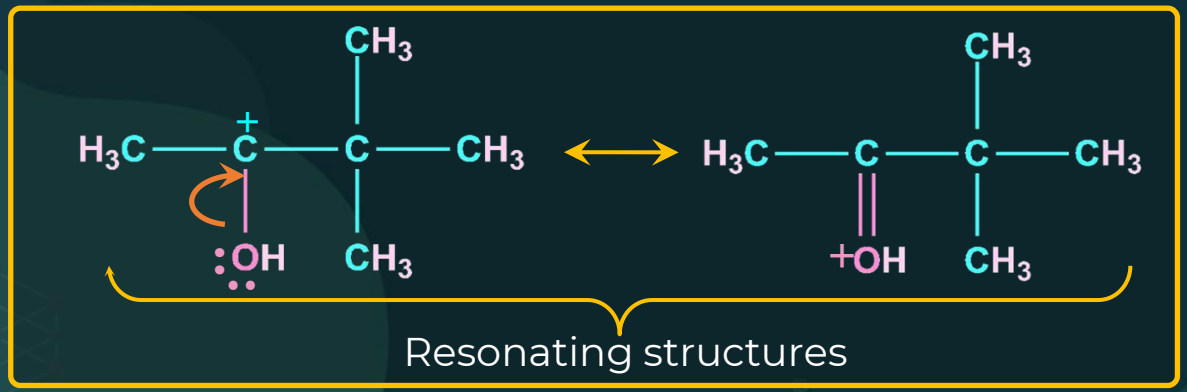


Rearrangement of Carbocation

Step-1

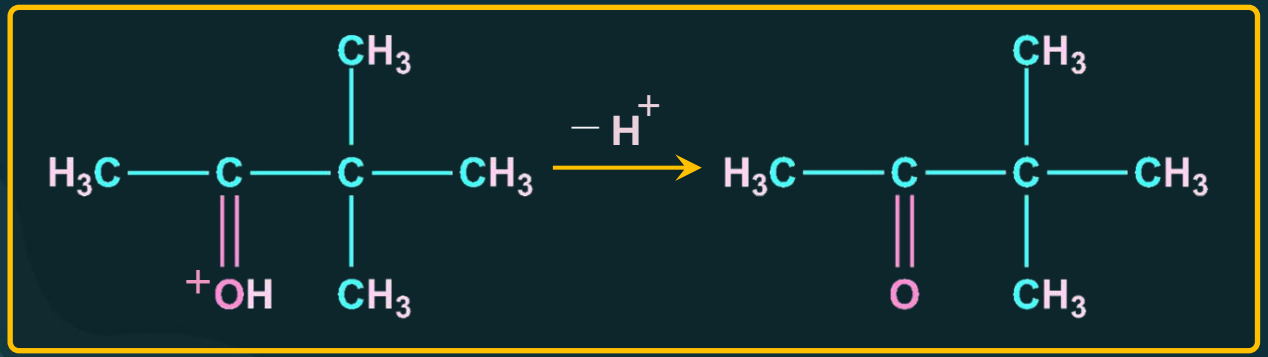


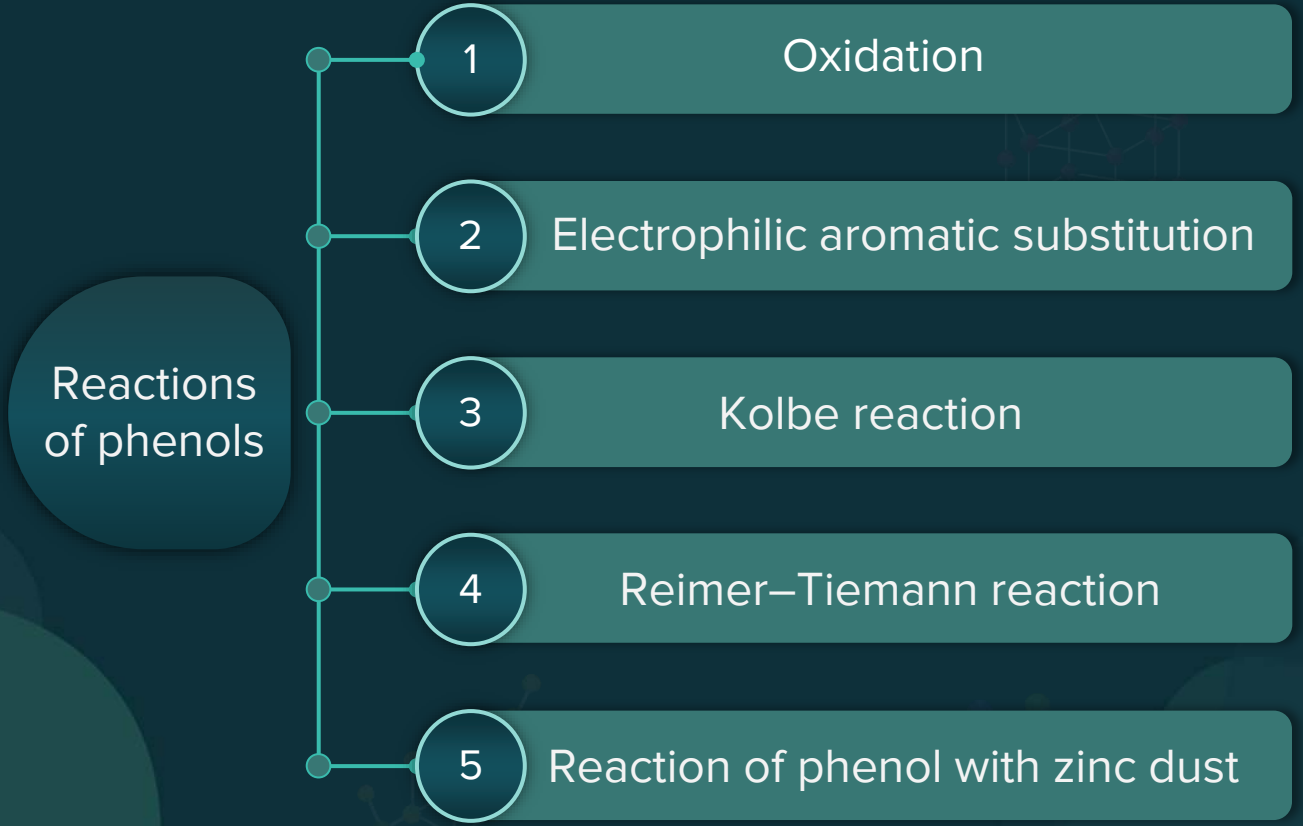
Step-2



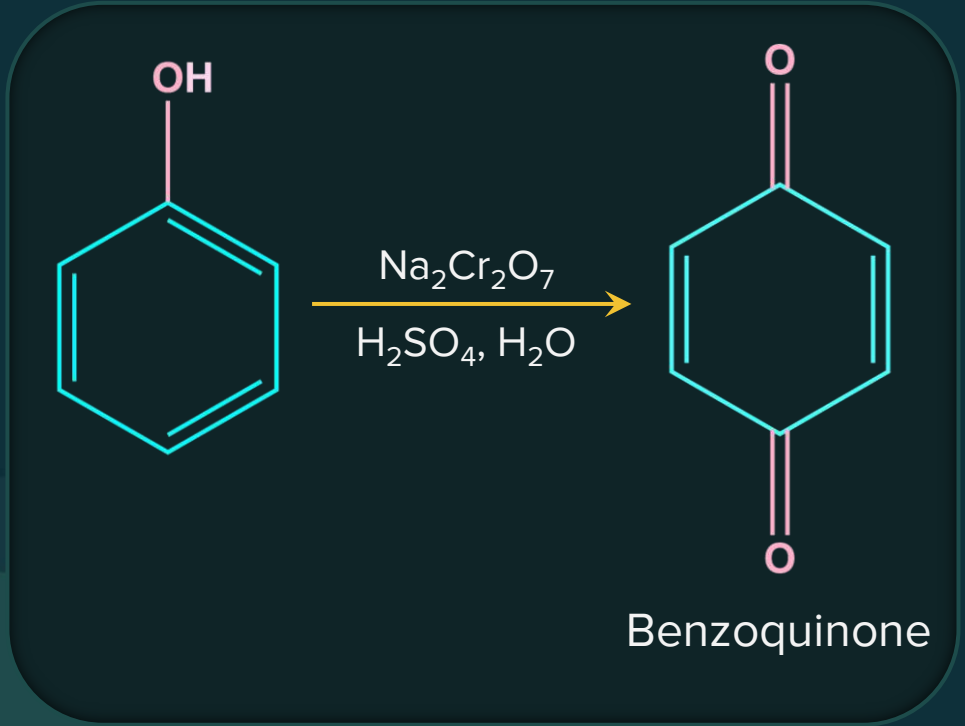
Deprotonation

Step-3



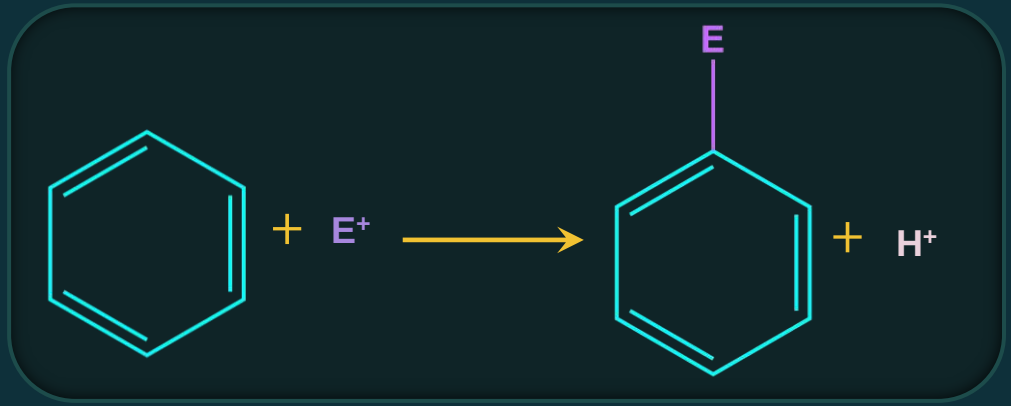

Reactions of phenols
1
Oxidation
2
Electrophilic aromatic substitution
3
Kolbe reaction
4
Reimer–Tiemann reaction
5
Reaction of phenol with zinc dust

Oxidation of Phenol



Electrophilic Aromatic Substitution

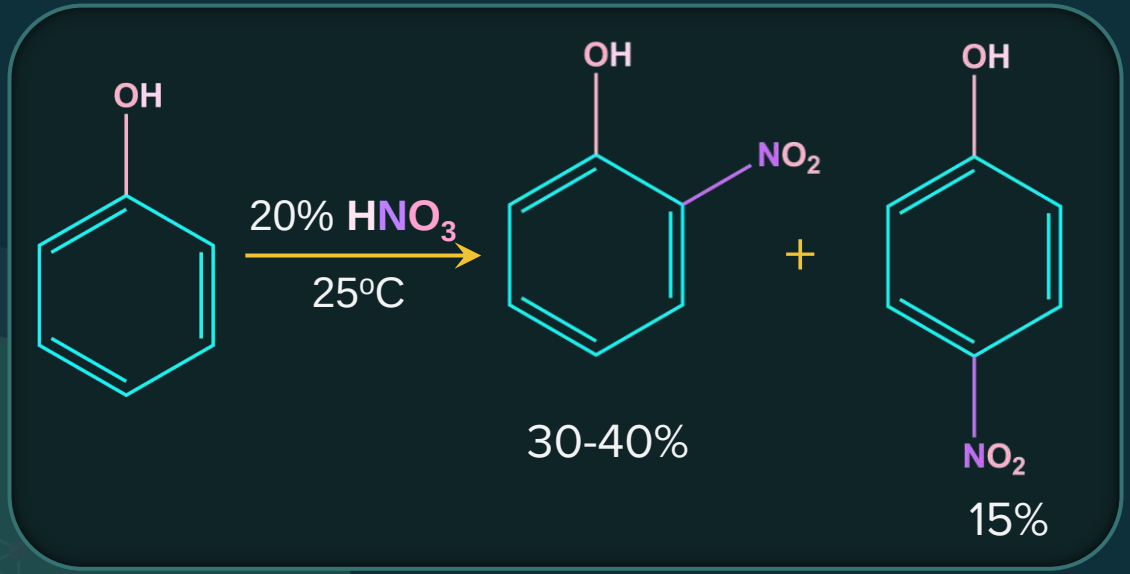
General reaction



-OH group acts as a powerful **activating** group (**+M**) and an **ortho–para** director

Nitration

Phenol reacts with dilute nitric acid to yield a mixture of **o- and p-Nitrophenol**



Nitration

1. Yield is relatively **low** (because of oxidation of the ring)

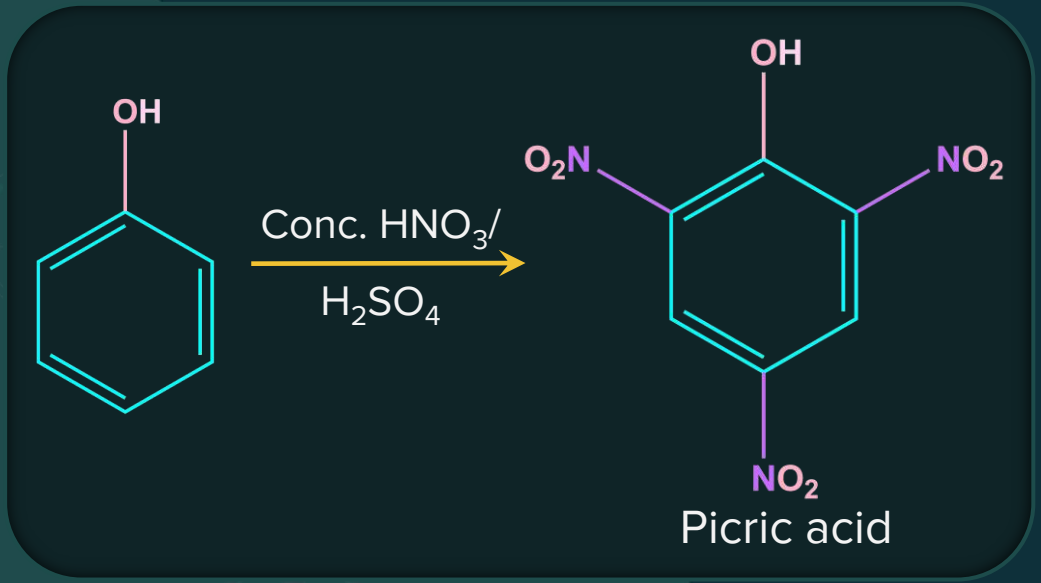
2. Ortho and para isomers can be **separated by steam distillation**

Nitration

o-Nitrophenol	p-Nitrophenol
Intramolecular H-bonding	**Intermolecular** H-bonding
More volatile	**Less** volatile
Passes over with the steam	**Remains** in the distillation flask

Nitration

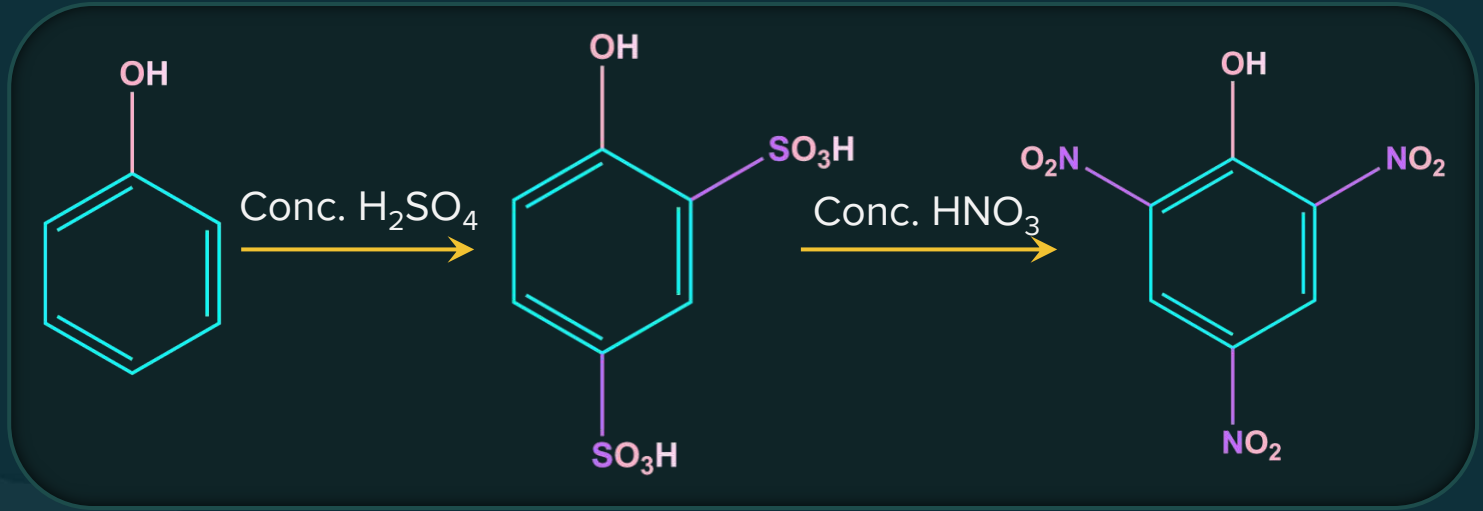
Phenol with conc. nitric acid gives picric acid in **low yield** (because of oxidation of ring).



Picric acid

Nitration of phenols to give picric acid is **highly exothermic.**

Preparation of Picric acid



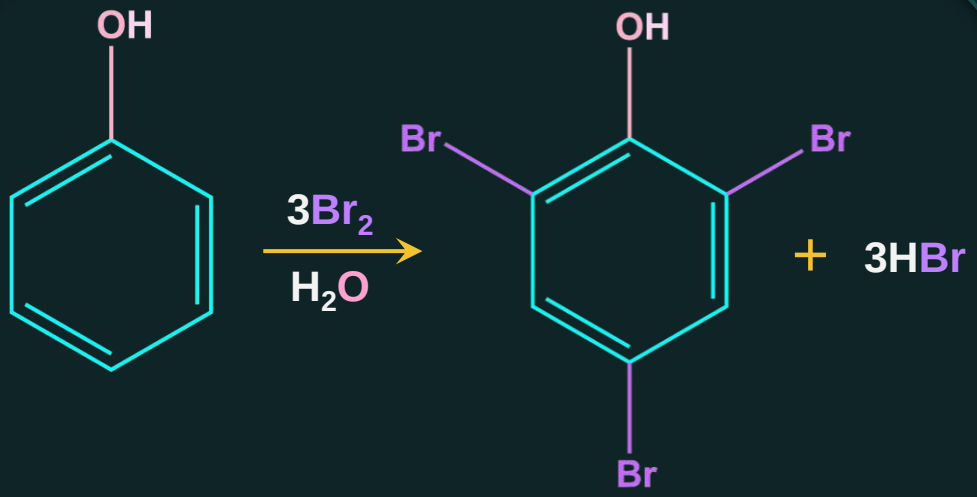
Nowadays picric acid is prepared by treating phenol first with concentrated sulphuric acid, which converts it to phenol-2,4-disulphonic acid, and then with concentrated nitric acid to get 2,4,6-trinitrophenol.

Bromination

Phenol reacts with **bromine** in aqueous solution to yield **2,4,6-Tribromophenol.**

Lewis acid is **not required** for the bromination of this highly activated ring.

Bromination



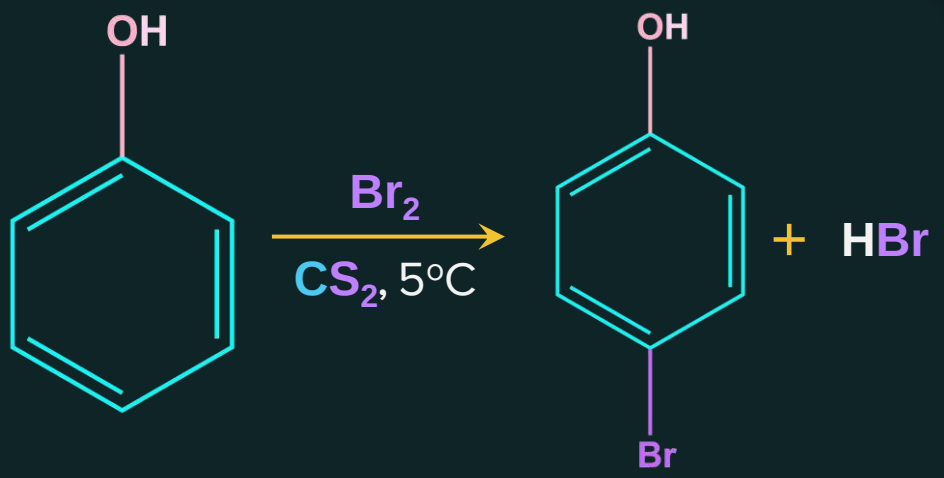
2,4,6-Tribromophenol
(≃ 100%)

Bromination

Monobromination of phenols can be achieved by carrying out the reaction in carbon disulfide at a low temperature, a condition that **reduces** the **electrophilic reactivity** of bromine.

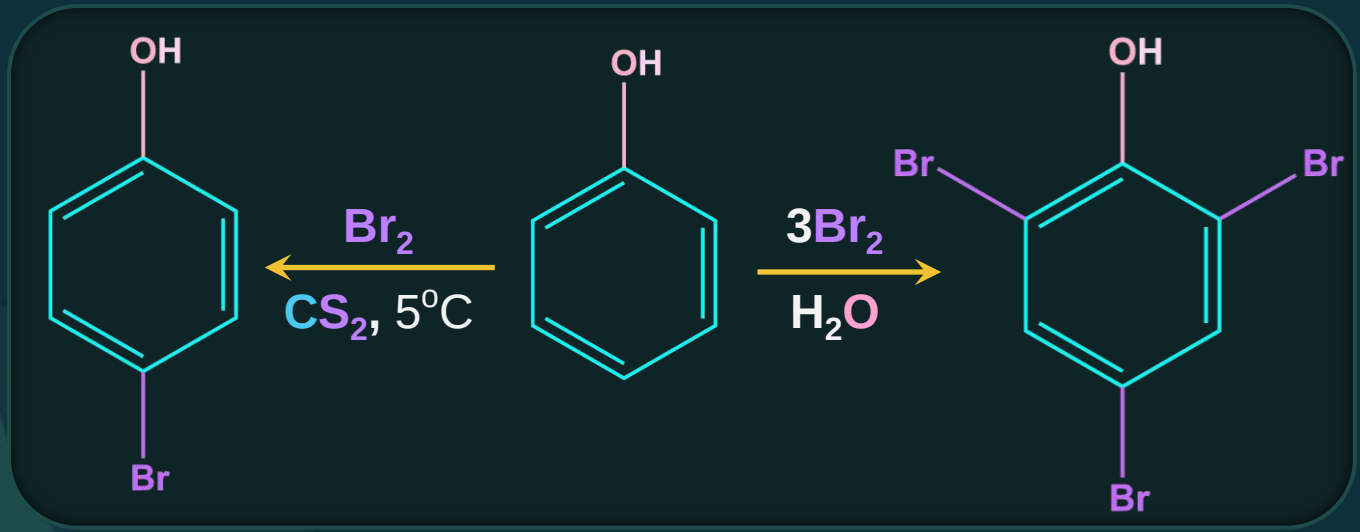
The **major product** is the **para isomer**.

Bromination



p-Bromophenol
(80-84%)

Bromination of Phenol

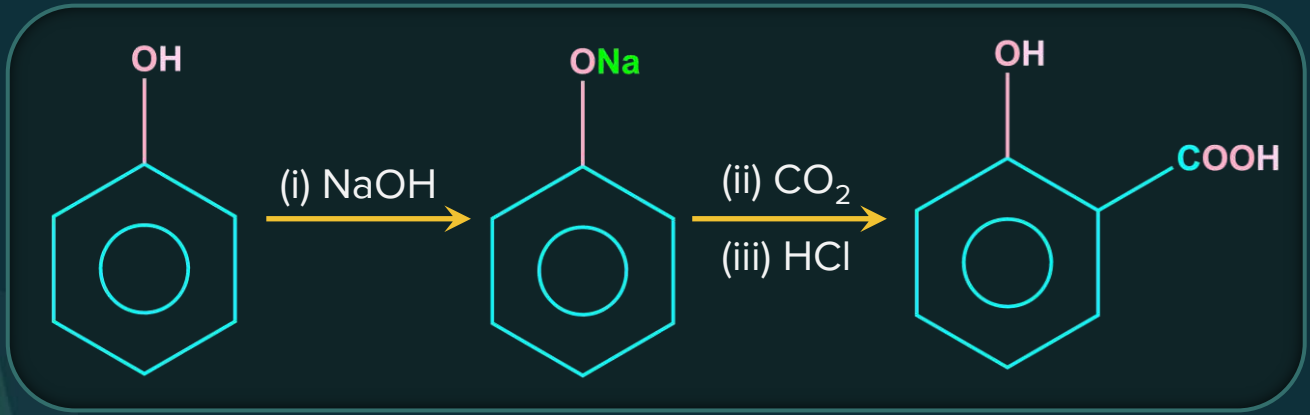


Kolbe Reaction

Kolbe reaction is carried out by allowing **sodium phenoxide** to absorb **carbon dioxide.**

Acidification of the resulting mixture produces **salicylic acid.**

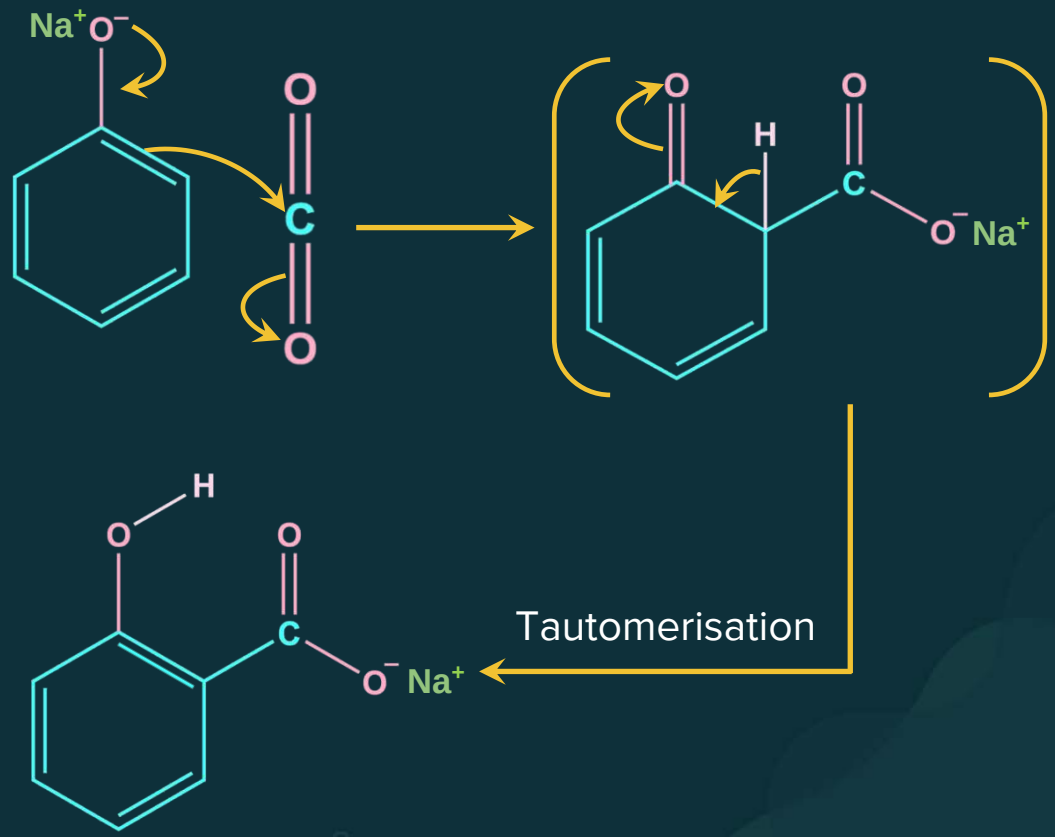
Kolbe Reaction



The phenoxide ion is even **more susceptible** to electrophilic aromatic substitution than the phenol itself.

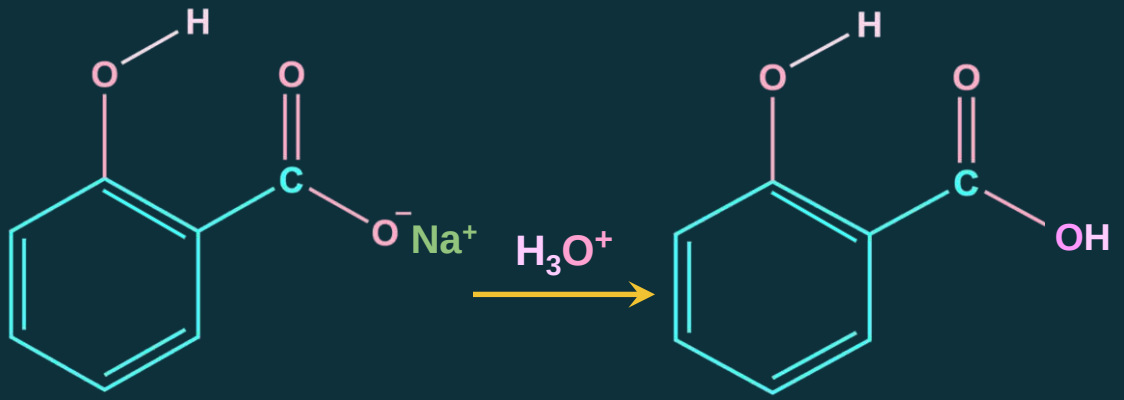
Mechanism

Step 1

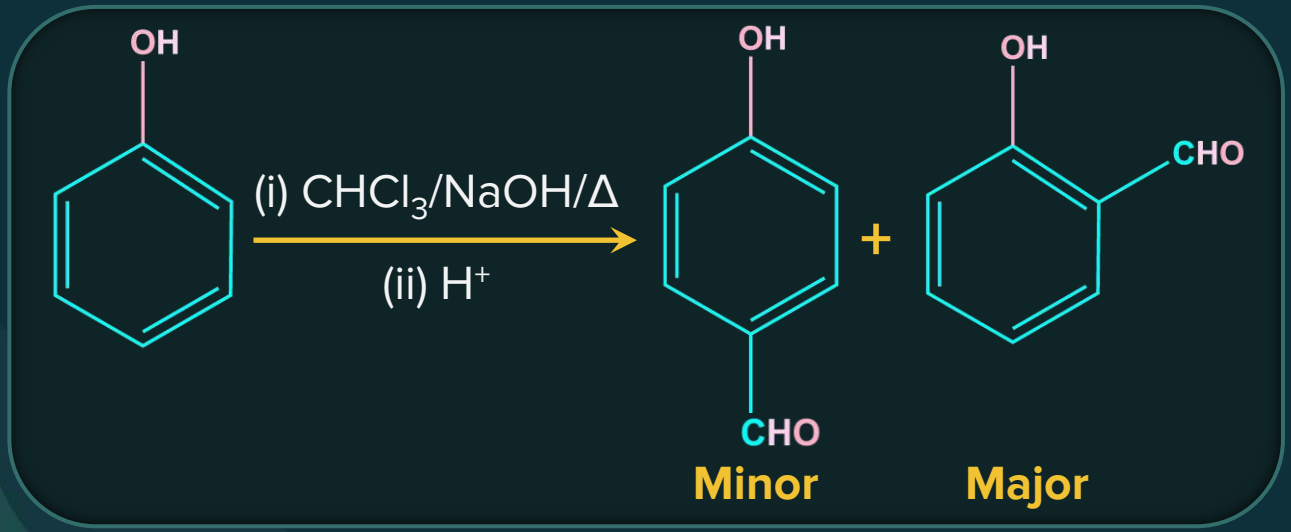


Mechanism

Step 2



Reimer–Tiemann Reaction



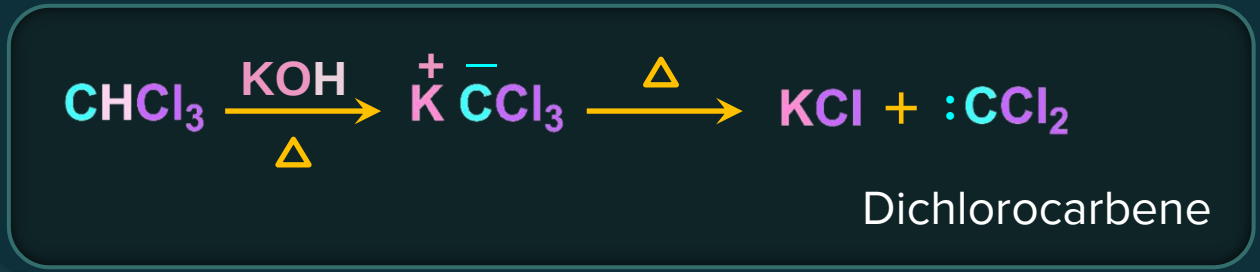
An important way of making **ortho-substituted phenols**

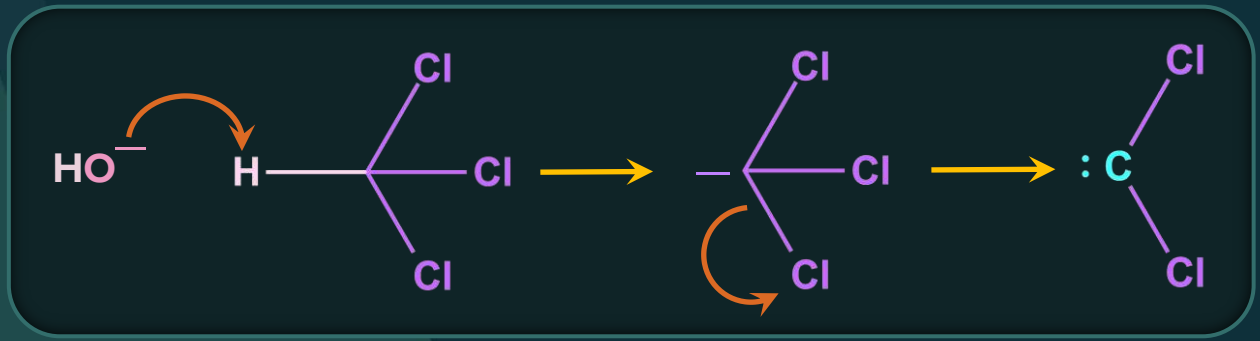
Mechanism

Step 1 Formation of carbene

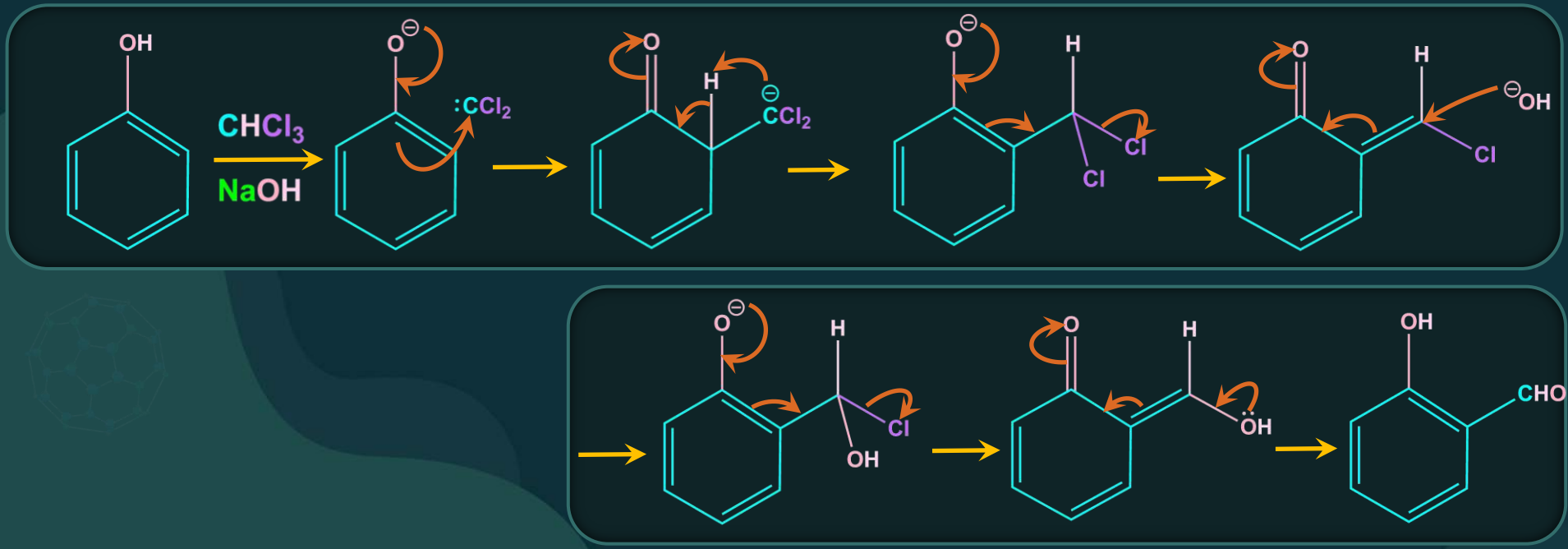
Step 2 Attack of carbene on phenol

α-Elimination

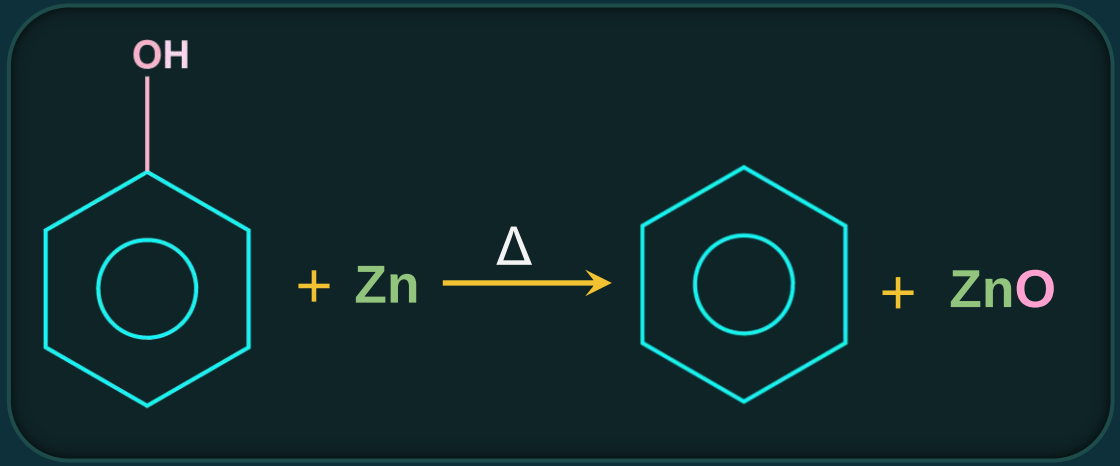




Mechanism



Reaction of Alcohol with Zinc Dust



Commercially Important Alcohols

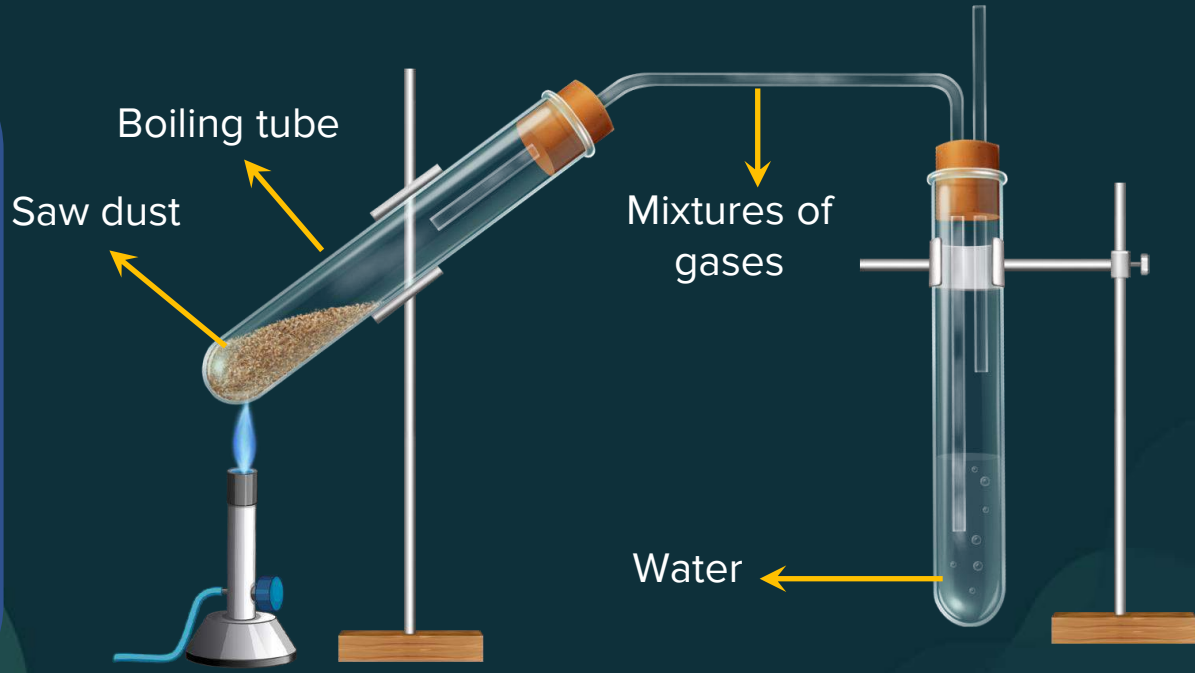
Methanol

Earlier, methanol was produced by the **destructive distillation of wood** (i.e., heating wood to a high temperature in the absence of air).

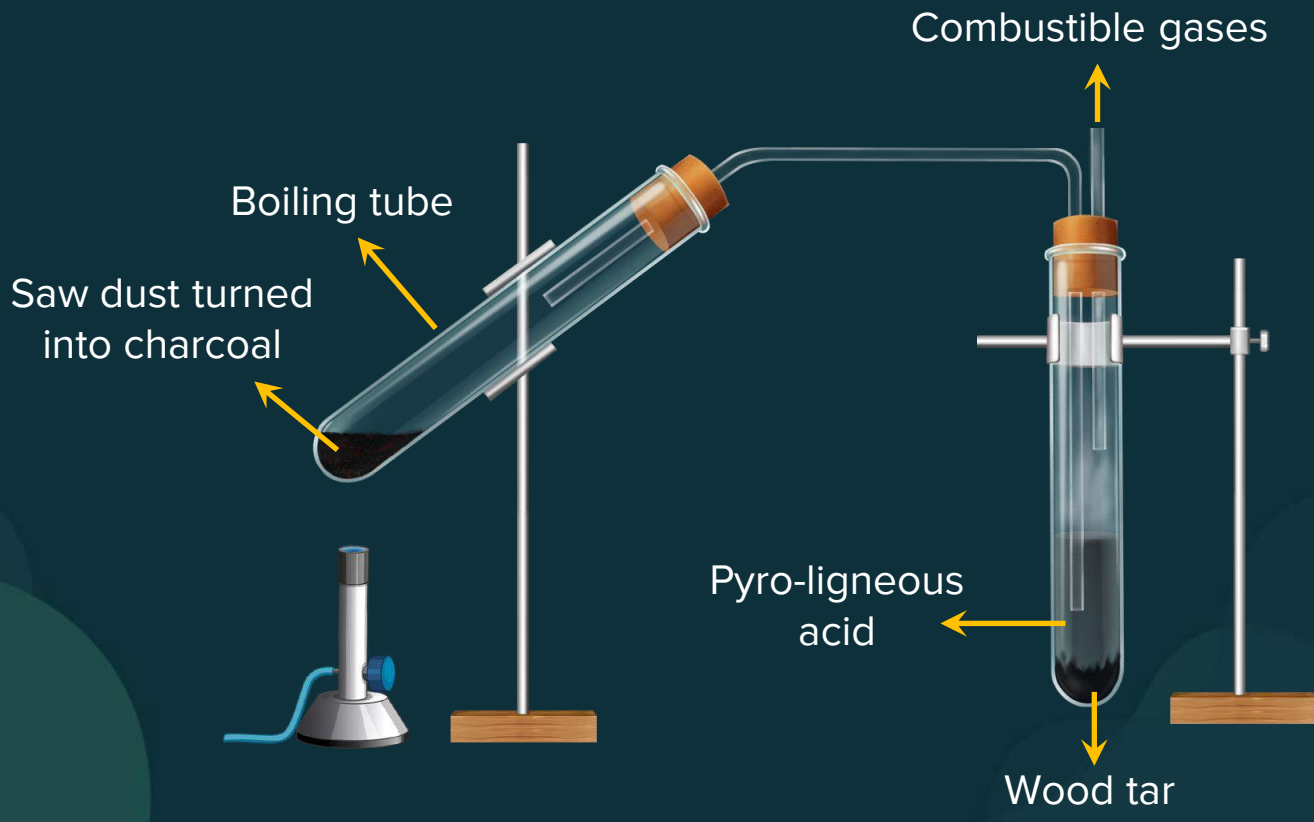
Hence, it was also known as **wood alcohol**.

Preparation of Methanol

Heating wood to 450°–550°C in the absence of oxygen causes it to decompose. Gases (carbon dioxide, carbon monoxide, and methane), liquids, and a solid residue (charcoal) are produced as a result of this process. As a mixture of steam and gases, the gaseous and liquid components separate; and when the mixture is cooled, a distillate is obtained. Consecutively, the distillate splits into pyro-ligneous acid and wood tar.



Preparation of Methanol



Methanol

Now, most methanol is prepared by the **catalytic hydrogenation of CO.**

$$CO + 2H_2 \xrightarrow[300–400^{o}C,\ 200–300\ atm]{ZnO–Cr_2O_3} CH_3OH$$

Uses of Methanol

1. It is used in making **formaldehyde**.

2. It is used as a **solvent** in paints.

Harmful Effects

Methanol is **toxic. Ingestion** of even small quantities of methanol can cause **blindness**; large quantities cause death.

Methanol poisoning can also occur by **inhalation** of the vapours or by prolonged exposure to the skin.

Ethanol

Ethanol can be made by the **fermentation** of sugars.

Synthesis of ethanol in the form of wine by the fermentation of the sugars of fruit juices was probably the **first accomplishment** in the field of organic synthesis.

Preparation

Fermentation is usually carried out by **adding yeast** to a mixture of sugar and water.

Yeast contains **enzymes** that promote a long series of reactions that ultimately **convert a simple sugar** ($C_6H_{12}O_6$) to ethanol and carbon dioxide.

Preparation

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

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

Ethanol

Fermentation **does not** produce beverages with an ethanol content greater than **12–15%**.

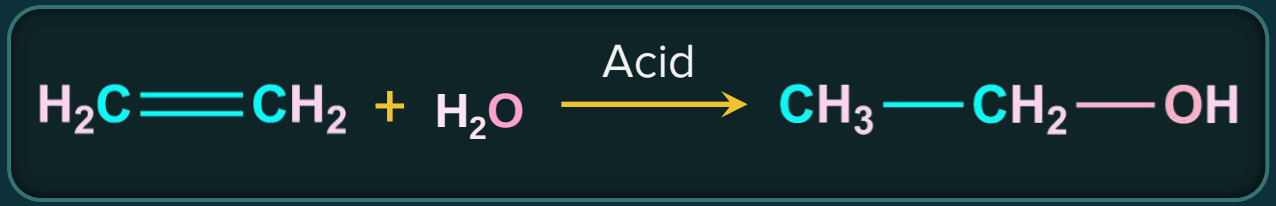
↓

Enzymes of the yeast are **deactivated** at higher concentrations.

↓

To produce beverages of **higher alcohol content**, the aqueous solution must be **distilled**.

Industrial Preparation



About **5%** of the world's ethanol supply is produced this way.

Ethers

Ethers

Ethers are **unreactive towards most bases**, but they can react under acidic conditions.

A protonated ether can undergo **substitution** with the expulsion of an alcohol.

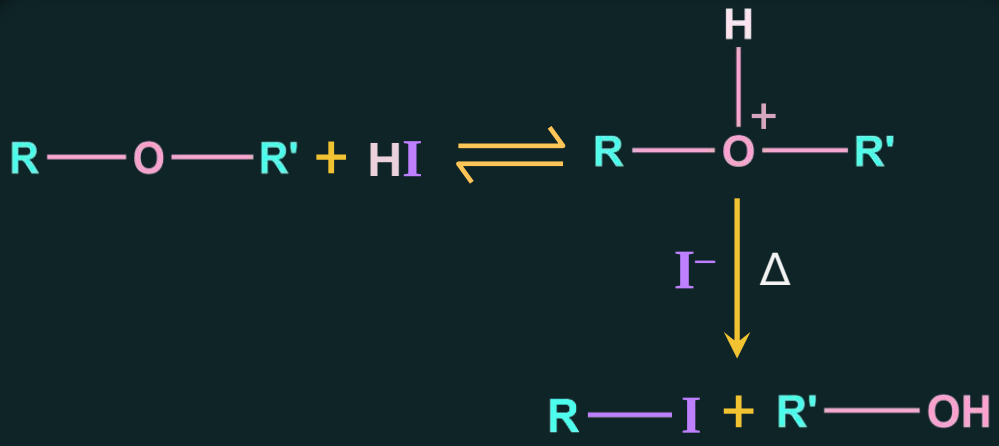
Reaction with HX

Ethers react with **conc. HBr and HI** because these reagents are **sufficiently acidic** to protonate the ethers.

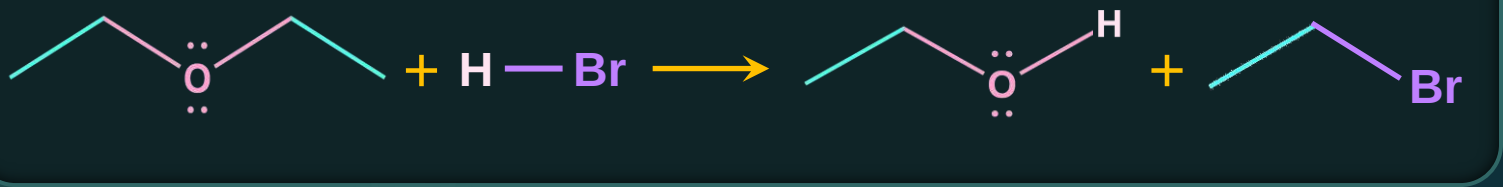
Bromide and **iodide** are good nucleophiles for the **substitution reaction**.

Reaction with HX

General reaction



S_N2 Reaction of Ethers

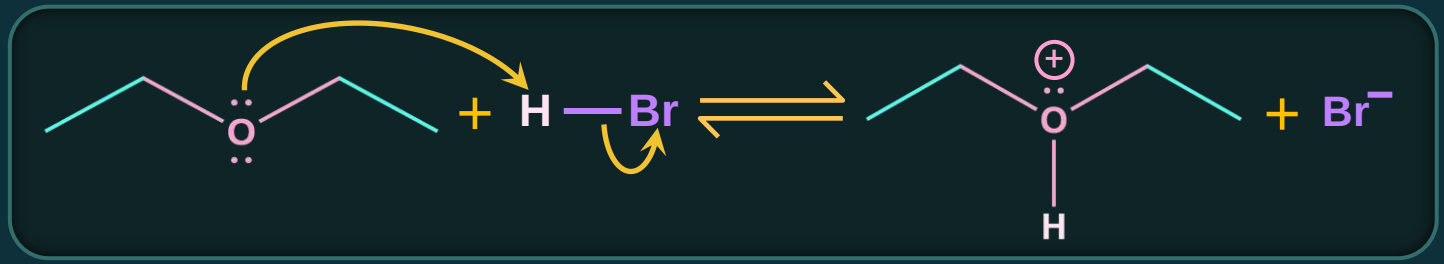


If R or R′ is 3°

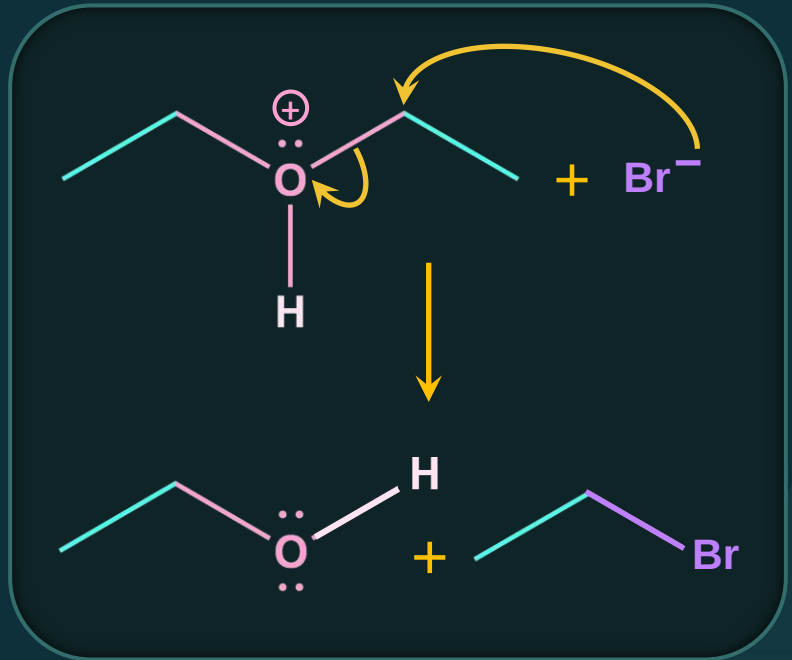
Then the mechanism will be **S_N1;** otherwise, it will be S_N2

Mechanism

Step 1: Protonation

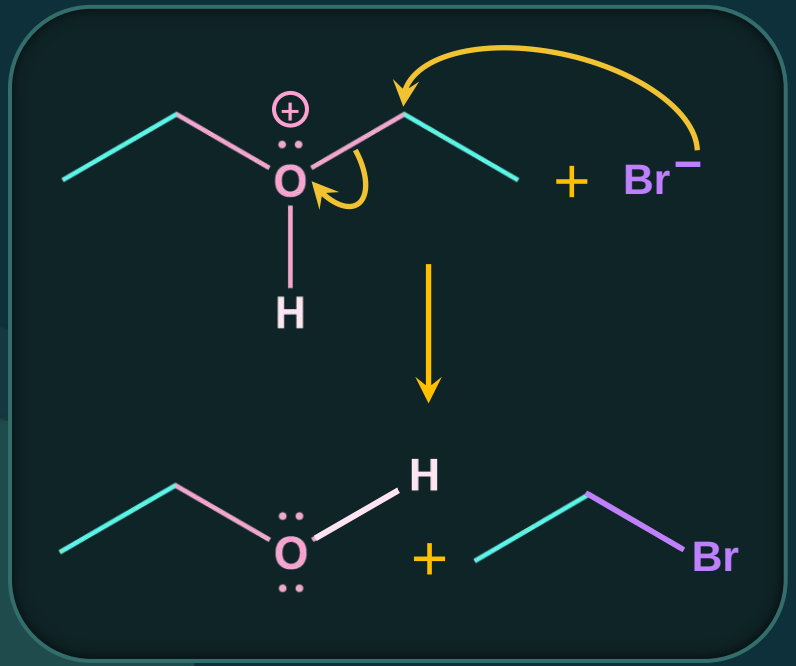


Step 2: Attack of nucleophile



Attack of Nucleophile

Step 2: Attack of nucleophile

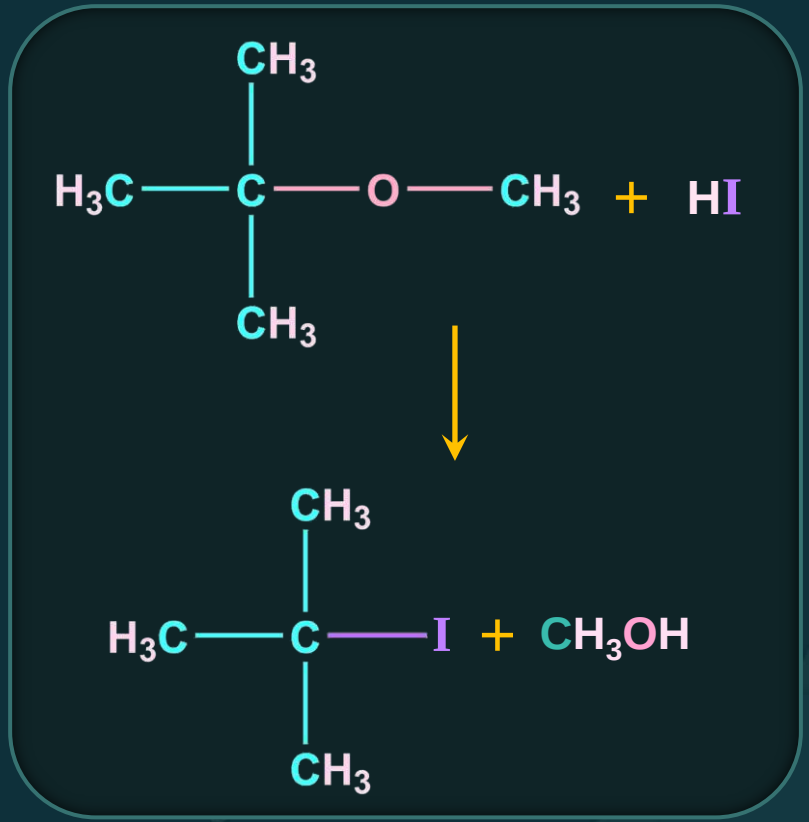


Note

If HBr is present in **excess**, the ethanol (just formed) reacts with the HBr (present in excess) to form a **second molar equivalent** of ethyl bromide.

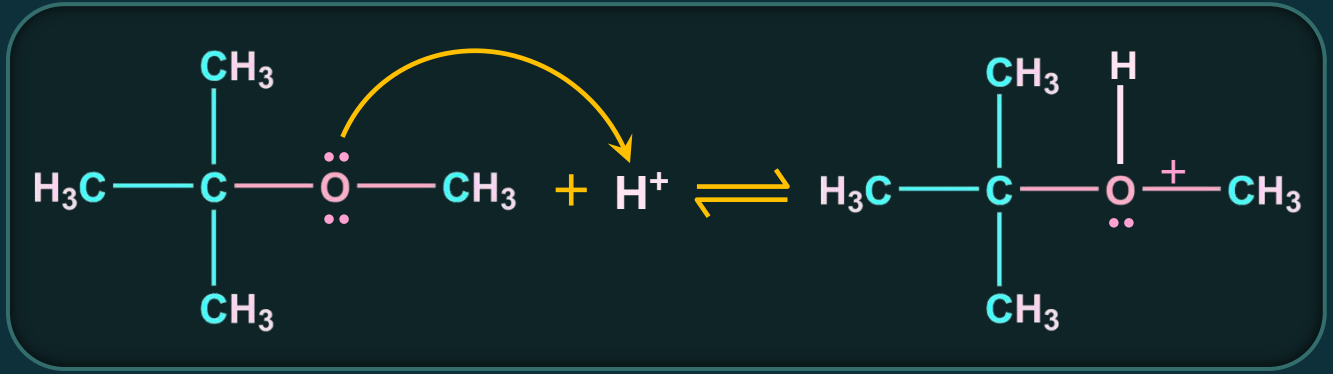
S_N1 Reaction of Ethers

General reaction

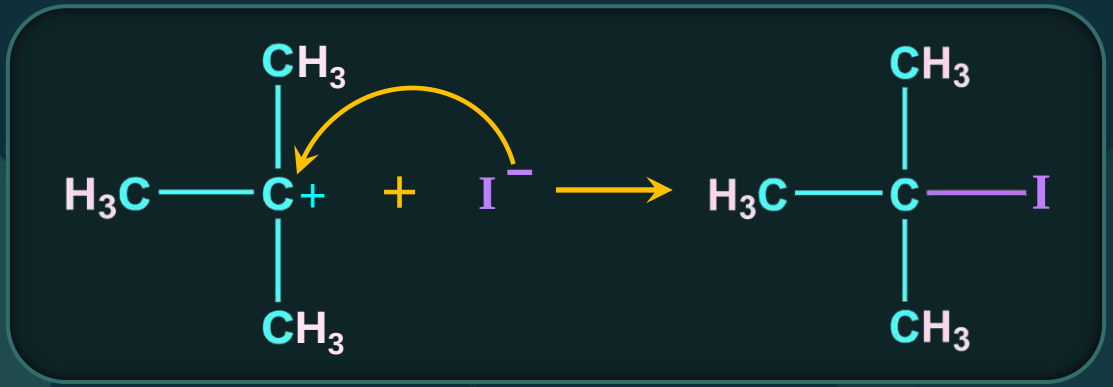


Mechanism

Step 1: Protonation

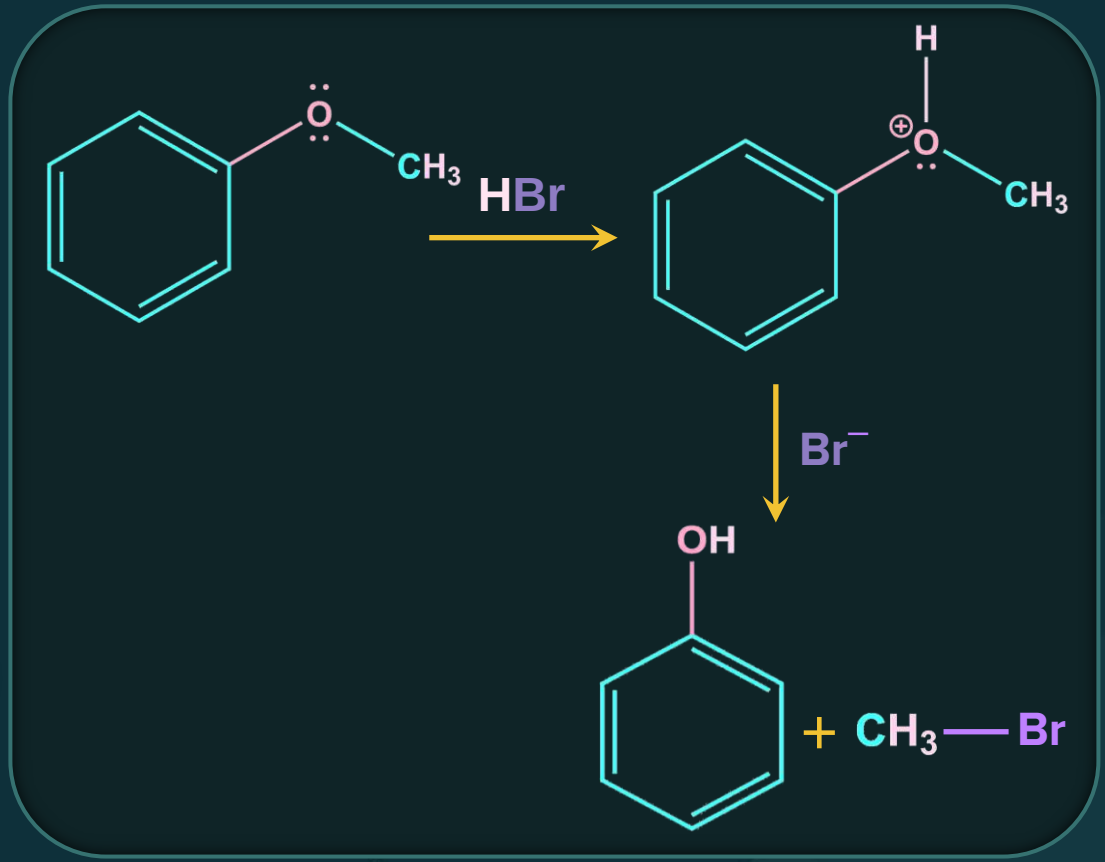


Step 2: Attack of the nucleophile



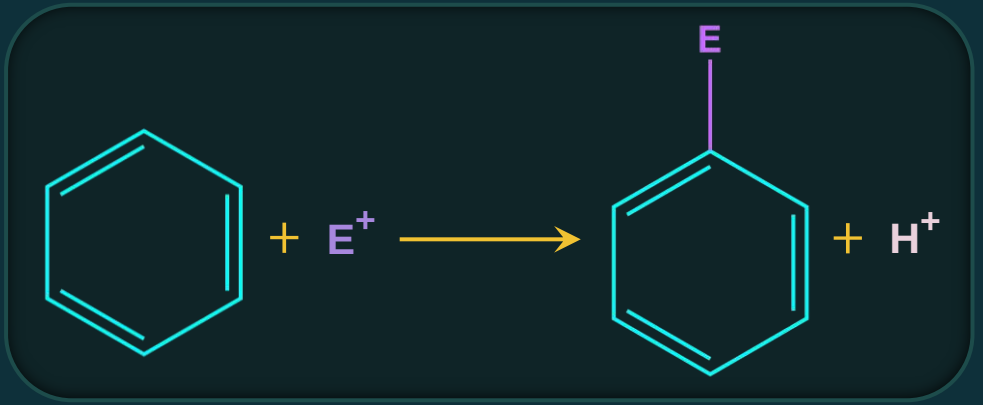
Alkyl Aryl Ether

Alkyl aryl ethers are cleaved at the **alkyl–oxygen bond** due to the more stable aryl–oxygen bond.



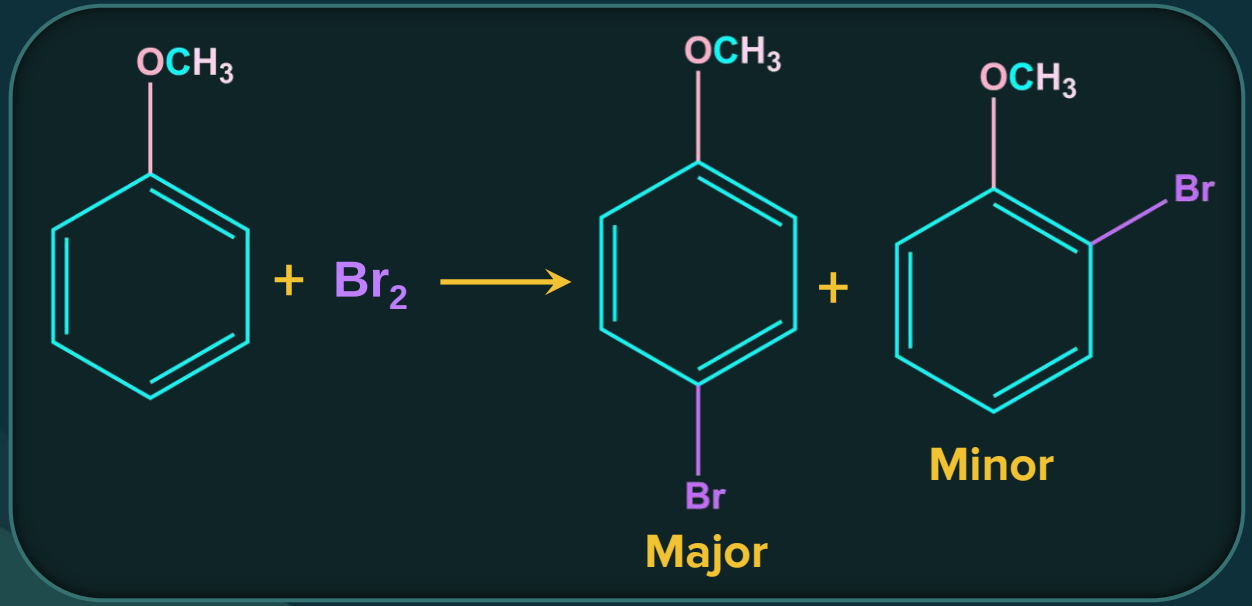
Electrophilic Substitution Reaction

General reaction



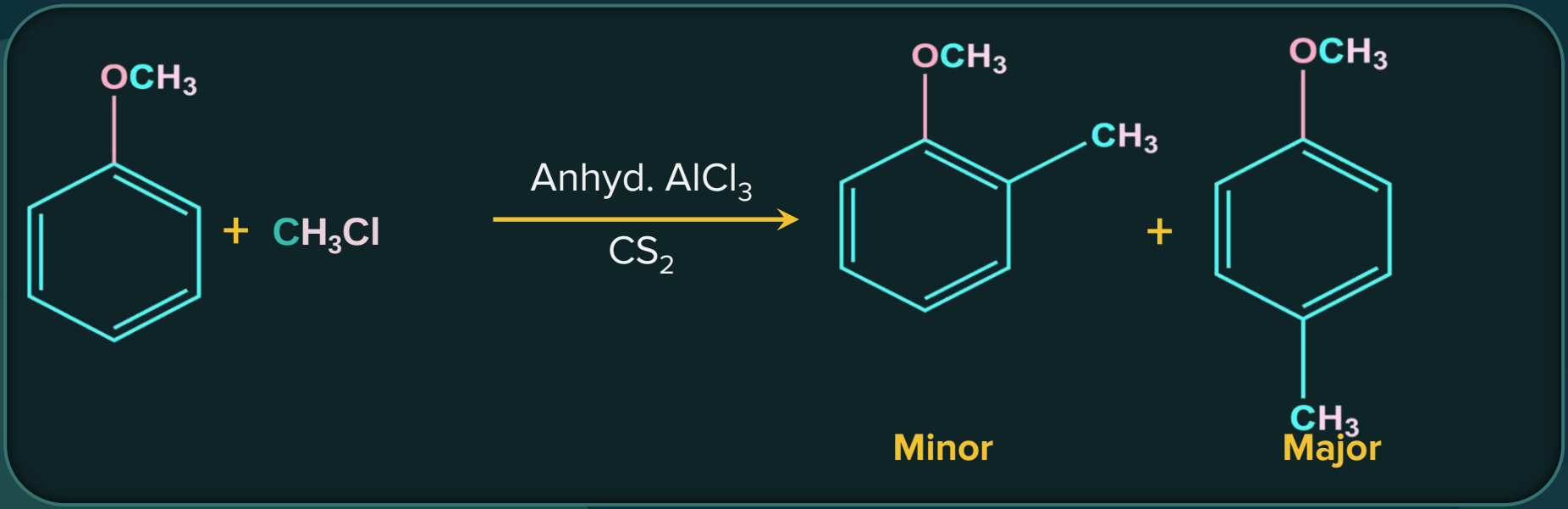
The **alkoxy group (-OR) is ortho–para directing** and activates the aromatic ring towards electrophilic substitution.

Halogenation



Friedel–Crafts Reaction

In Friedel-Crafts reaction, alkyl group is added to the benzene ring.



Friedel–Crafts Reaction

In Friedel-Crafts reaction, acetyl or acyl group is added to the benzene ring.