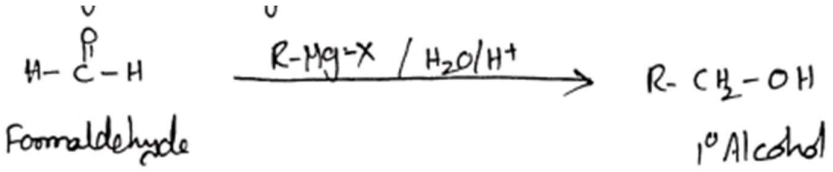
ALCOHOLS

METHODS OF PREPARATION

1. FROM GRIGNARD'S REAGENT

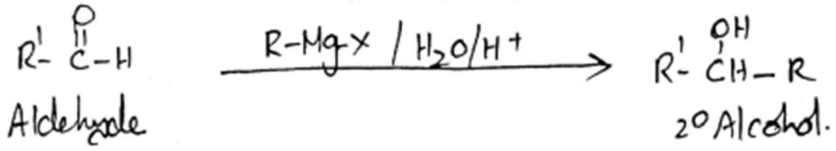
a) Preparation of 1^0 alcohols

Formaldehyde on reaction with Grignard's reagent (RMgX) and on hydrolysis gives 1^0 alcohols.



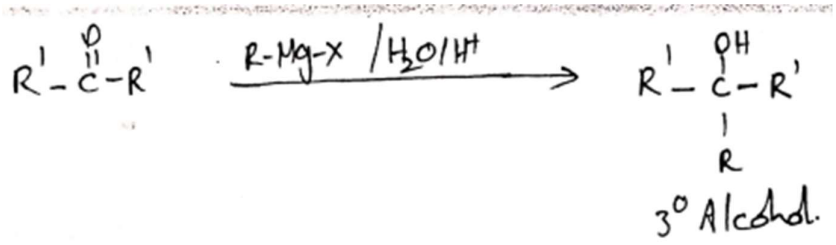
b) Preparation of 2^0 alcohols

Aldehydes except Formaldehyde on reaction with Grignard's reagent (RMgX) and on hydrolysis gives 2^0 alcohols.



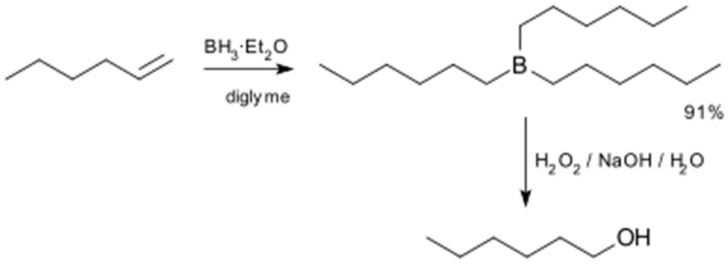
c) Preparation of 3^0 alcohols

Ketones on reaction with Grignard's reagent (RMgX) and on hydrolysis gives 3^0 alcohols



2. HYDROBORATION OF ALKENES

In Hydroboration–oxidation reaction, alkenes are converted into alcohols. In first step, Borane (BH_3) adds to the double bond of alkene. In second step, hydroperoxide attacks the boron atom and forms alcohols



CHEMICAL PROPERTIES

1. OXIDATION OF ALCOHOLS

a) Oxidation with Pyridinium chlorochromate (PCC)

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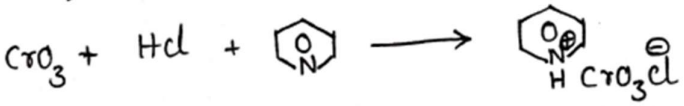
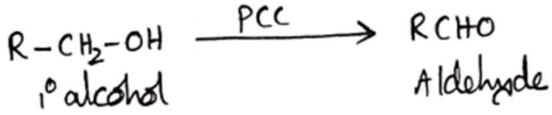
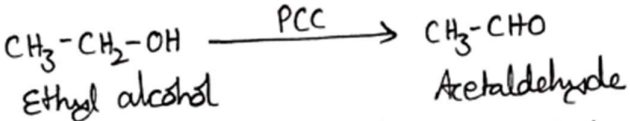
Pyridinium chlorochromate is obtained by adding pyridine to the solution of chromium (VI) oxide (CrO_3) in HCl.

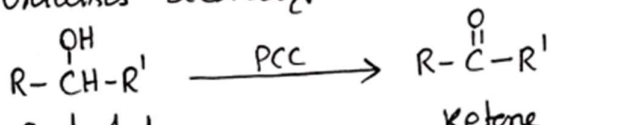


a) PCC oxidises primary alcohol to Aldehyde



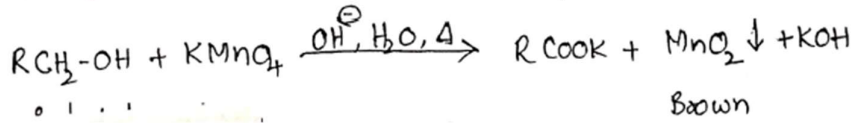


b) PCC oxidises secondary alcohol to Ketone



b) Oxidation with Potassium permanganate ($KMnO_4$)

1° alcohols can be oxidised to carboxylic acids by acidic (or basic) aqueous solution of $KMnO_4$. During the process of oxidation Mn^{+7} is reduced to Mn^{+4} in the form of brown ppt of MnO_4.



c) Oxidation with Ceric ammonium nitrate (CAN)

Alcohol on reaction with ceric ammonium nitrate forms a pink or red colour precipitate due to the formation of a complex compound and ammonium nitrate.

$(NH_4)_2[Ce(NO_3)_6] + 3ROH \rightarrow [Ce(NO_3)_4(ROH)_3] + 2NH_4NO_3$

$(NH_4)_2\ [Ce(NO_3)_6] + 3CH_3OH \rightarrow [Ce(NO_3)_4(CH_3OH)_3] + 2NH_4NO_3$

RELATIVE REACTIVITY OF 1°, 2°, 3° ALCOHOLS

2. Reaction with Lucas Reagent

Lucas test:

This test is used to differentiate 1°, 2° and 3° alcohols

Lucas reagent: HCl and Anhy. $ZnCl_2$

Alcohols on reaction with Lucas reagent forms alkyl halides.

1° alcohols does not gives turbidity

2° alcohols produces turbidity within 5-10 min

3° alcohols gives turbidity immediately.

$$R\text{-}OH \xrightarrow{HCl + ZnCl_2} R\text{-}Cl + H_2O$$

The formation of alkyl halides is indicated by the appearance of turbidity.

3. Dehydration of Alcohols

Dehydration of Alcohols:

Dehydration of alcohols leads to olefins. Dehydration means removal of water molecule.

The process of dehydration can be done by using dehydrating agents like Conc H_2SO_4/Δ, Anhy Al_2O_3/Δ, Anhy $ZnCl_2/\Delta$, P_2O_5/Δ, BF_3/Δ

i) Primary alcohols on dehydration in presence of Conc H_2SO_4/Δ gives alkenes

$CH_3-CH_2-OH \xrightarrow{\text{Conc } H_2SO_4/200^oC} CH_2=CH_2 + H_2O$

Ethyl alcohol — Ethene

$CH_3-CH_2-CH_2-OH \xrightarrow{\text{Conc } H_2SO_4/\Delta} CH_3-CH=CH_2 + H_2O$

Propyl alcohol — Propene

ii) Secondary alcohols on dehydration in presence of dehydrating agents/Δ gives more substituted alkenes

$CH_3-CH_2-\underset{OH}{CH}-CH_3 \xrightarrow{Al_2O_3/\Delta}$

$\rightarrow CH_3-CH=CH-CH_3$ (2-Butene) major product

$\rightarrow CH_3-CH_2-CH=CH_2$ (Butene) minor product.

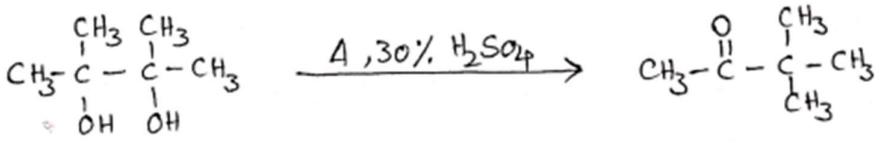
iii) Tertiary alcohols on dehydration in presence of dehydrating agents/Δ gives alkenes

$CH_3-\underset{CH_3}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-CH_3 \xrightarrow{BF_3/\Delta} CH_3-\underset{CH_3}{\underset{|}{C}}=CH_2$

t-butanol — Isobutene

4. PINACOL - PINACOLONE REARRANGEMENT

The conversion of pinacols to ketones (or) aldehydes in presence of acids is known as pinacol - pinacolone rearrangement



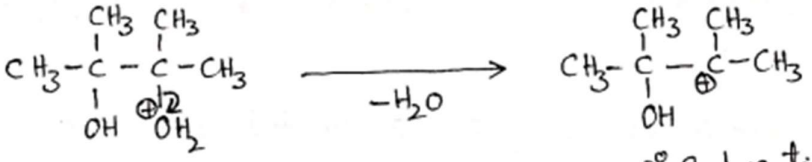
Pinacol — Pinacolone

Mechanism

Step: 1 pinacol on reaction with Proton (H^+) to form oxonium ion

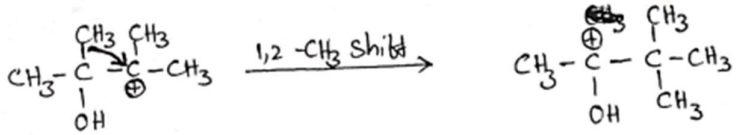
Pinacol — oxonium ion

Step: 2 oxonium ion loss a H_2O molecule to form a Carbocation



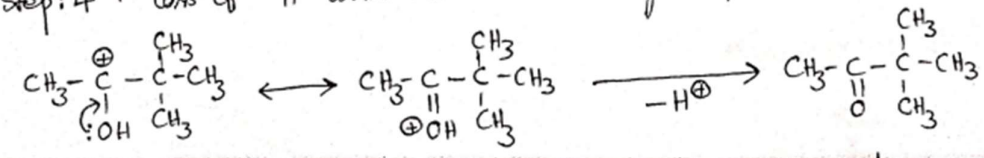
3° Carbocation

Step: 3 3° Carbocation undergoes 1,2 $-CH_3$ (Methyl) shift to form more stable Carbocation.



3° Carbocation — Rearranged Protonated Ketone (more stable Carbocation)

Step: 4 : loss of H^+ from the oxonium ion gives pinacolone



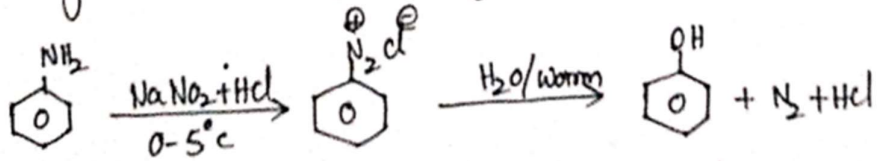
Oxonium ion — Pinacolone

PHENOLS

Methods of preparation

a) Preparation from diazonium salt

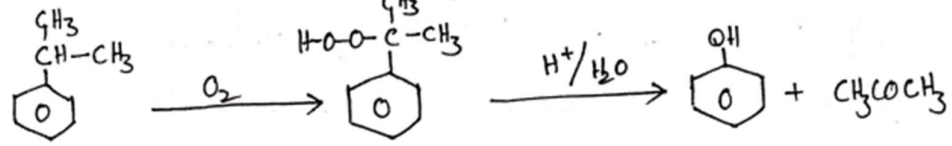
A diazonium salt is formed by heating an aromatic 1° Amine with ($NaNO_2$ + HCl) at 0-5°c. Diazonium salts are hydrolysed to phenols by warming with water or by treating with Dil acids



Aniline — Benzenediazonium salt — phenol.

b) Preparation from Cumene

Cumene is oxidised in the presence of air to cumene hydroperoxide. It is converted to phenol by heating with Dil. acid.

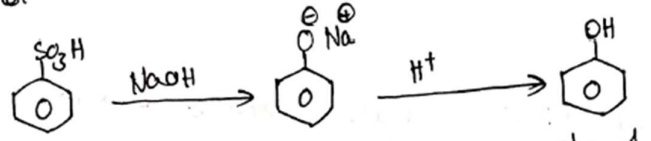


Cumene — Cumene hydroperoxide — phenol.

c) From aryl sulphonates:

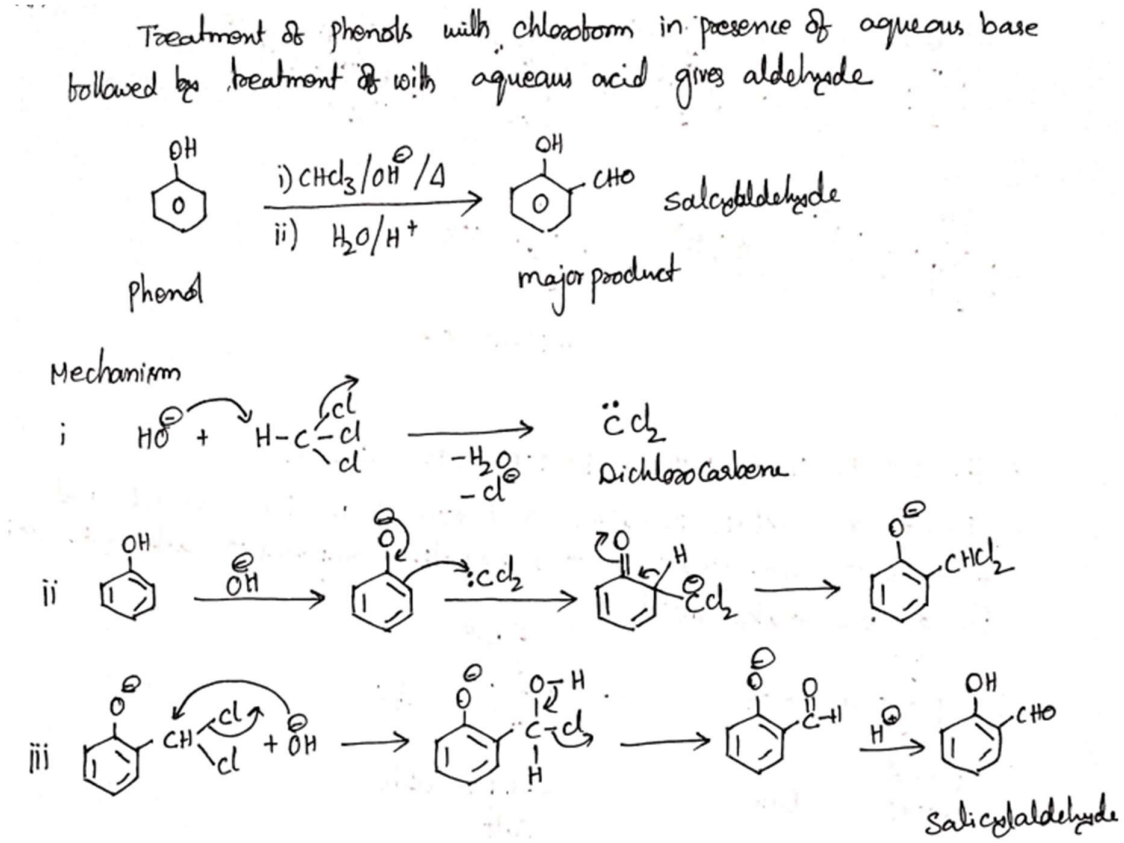
From Benzene sulphonic acid

Benzene sulphonic acid is converted to sodium phenoxide by heating with molten sodium hydroxide, Acidification of sodium phenoxide gives phenol.



Benzene sulphonic acid — Sod. phenoxide — phenol

1. Reimer– Tiemann Reaction



Reaction with Neutral $FeCl_3$:

Phenols reacts with ferric chloride ($FeCl_3$), it forms violet or purple colored complex. This reaction is a common test for identifying the presence of phenolic compounds.

$$3C_6H_5OH + FeCl_3 \rightarrow Fe(OC_6H_5)_3 + 3HCl.$$

Hydrogen bonding in Alcohols and Phenols (intermolecular and intramolecular)

1. The electrostatic forces of attractions between a partially positive charged hydrogen atom of Alcohol/Phenol molecule and a highly electronegative atom is known as a hydrogen bond.
2. This electrostatic bond has the strength of about 10-15 KJ/mol, which indicates the hydrogen bond has low bond energy.
3. Two types of hydrogen bonding were observed in alcohols/phenols. They are

A) Intramolecular hydrogen bonding : Intramolecular hydrogen bonding is defined as the electrostatic forces of attractions between a partially positive charged hydrogen atom of a polar molecule and a highly electronegative atom of the same molecule.

Example: *o* - nitro phenol.

B) Intermolecular hydrogen bonding : Intermolecular hydrogen bonding is defined as the electrostatic forces of attractions between a partially positive charged hydrogen atom of a polar molecule and a highly electronegative atom of the different molecule.

Example: *m* - nitro phenol.

Effect of hydrogen bonding on boiling point:

The boiling point of alcohols are higher due to the association of alcohol molecules. As the number of carbons or the number of alkyl groups increases, decreases the formation of hydrogen bonding.

In isomeric alcohols, 1^o alcohols have higher boiling point while 3^o alcohols have lower boiling point. Examples are tabulated

S.No	Alcohol	Boiling point
1	1-Butanol (1^o alcohol)	118^o C
2	2-Butanol (2^o alcohol)	99^o C
3	2-Methyl-2-Propanol (3^o alcohol)	83^o C

In polyhydric alcohols, As number of -OH group increases, Hydrogen bonding increases and hence boiling point increases.

$HO\text{-}CH_2\text{-}CH_2\text{-}OH$ ------ 197^o C $HO\text{-}CH_2\text{-}CH(OH)\text{-}CH_2\text{-}OH$ ------ 290^o C

Effect of hydrogen bonding on solubility in water

Compounds which can form hydrogen bonding with water are soluble in water. On the other hand which don't form hydrogen bonding with water are less soluble or insoluble in water.

Alcohols can form hydrogen bonding with water and hence readily soluble in water.

As the carbon chain length in alcohols increases the capability of forming hydrogen bonding with water decrease and hence solubility in water decreases.

Methanol, Ethanol and Propanol forms hydrogen bonding with water are soluble in water.

Butanol, Pentanol, Hexanol form hydrogen bonding with water up to some extent and are less soluble in water.

Heptanol and other higher alcohols doesn't form hydrogen bonding with water are insoluble in water.