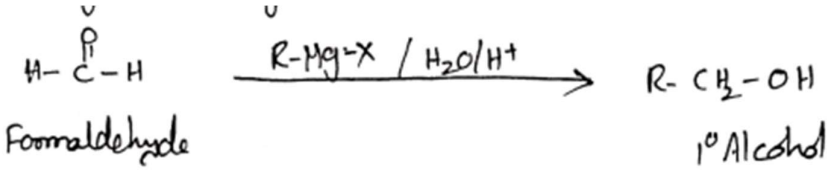
ALCOHOLS

METHODS OF PREPARATION

1. FROM GRIGNARD'S REAGENT

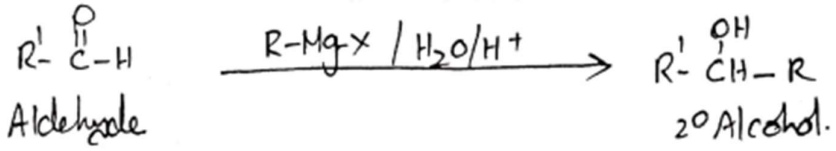
a) Preparation of 1^0 alcohols

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



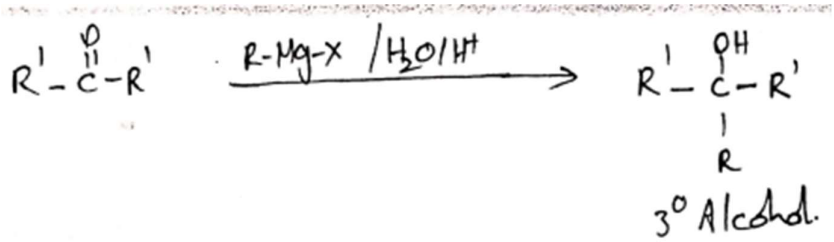
b) Preparation of 2^0 alcohols

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



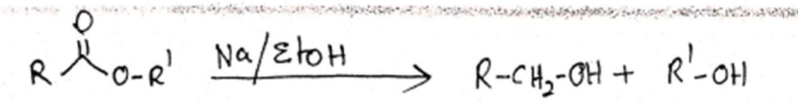
c) Preparation of 3^0 alcohols

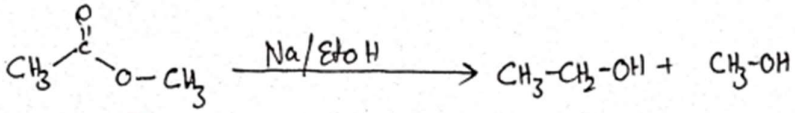
Ketones on reaction with Grignard's reagent (RMgX) and on hydrolysis gives 3^0 alcohols

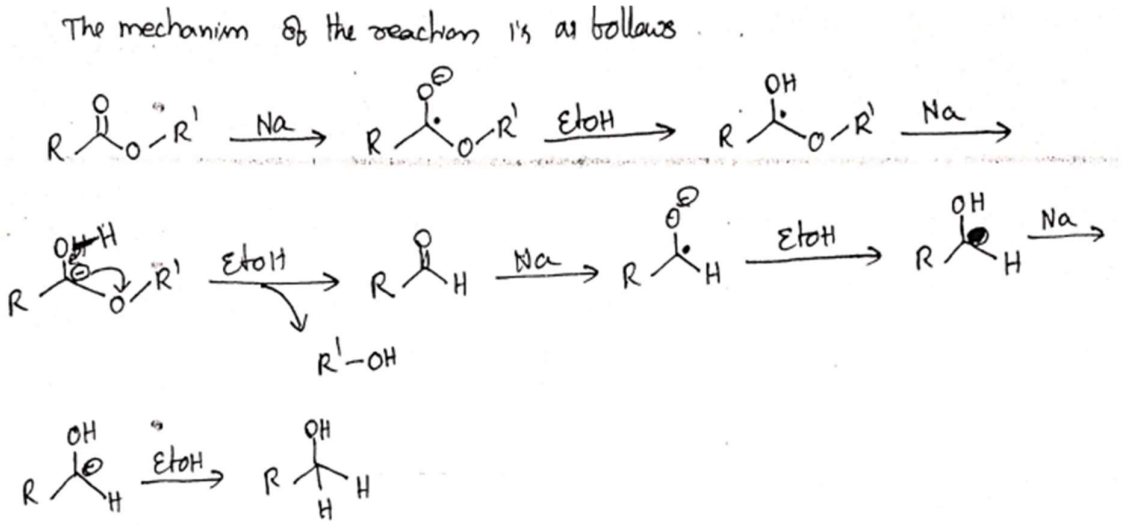


2. BOUVEAULT BLANC REDUCTION

Bouveault - Blanc reduction is a chemical reaction in which an ester is reduced to primary alcohols using Absolute ethanol and sodium metal.







CHEMICAL PROPERTIES

1. Substitution of -OH group by using PCl_3, PCl_5, PBr_3, $SOCl_2$ and HX/Anh $ZnCl_2$

a) Reaction with PCl_3

Alcohols reacts with Phosphorous trichloride (PCl_3) gives alkyl chlorides

$$3\ R\text{-}OH + PCl_3 \xrightarrow{\Delta} 3\ R\text{-}Cl + H_3PO_3$$

Ethyl alcohol reacts with Phosphorous trichloride (PCl_3) gives Ethyl chloride

$$3\ C_2H_5\text{-}OH + PCl_3 \xrightarrow{\Delta} 3\ C_2H_5\text{-}Cl + H_3PO_3$$

b) Reaction with PCl_5

Alcohols reacts with Phosphorous pentachloride (PCl_5) gives alkyl chlorides

$$R\text{-}OH + PCl_5 \xrightarrow{\Delta} R\text{-}Cl + HCl + POCl3$$

Ethyl alcohol reacts with PCl_3 gives Ethyl chloride

$$C_2H_5\text{-}OH + PCl_5 \xrightarrow{\Delta} C_2H_5\text{-}Cl + HCl + POCl3$$

c) Reaction with PBr_3

Alcohols reacts with Phosphorous tribromide (PBr_3) gives alkyl bromides

$$3\ R\text{-}OH + PBr_3 \xrightarrow{\Delta} 3\ R\text{-}Br + H_3PO_3$$

Ethyl alcohol reacts with Phosphorous tribromide (PBr_3) gives Ethyl bromide

$$3\ C_2H_5\text{-}OH + PBr_3 \xrightarrow{\Delta} 3\ C_2H_5\text{-}Br + H_3PO_3$$

d) Reaction with $SOCl_2$

Alcohols reacts with Thionyl chloride ($SOCl_2$) gives alkyl chlorides

$$R\text{-}OH + SOCl_2 \xrightarrow{\Delta} R\text{-}Cl + HCl + SO_2$$

Ethyl alcohol reacts with Thionyl chloride ($SOCl_2$) gives Ethyl chloride

$$C_2H_5\text{-}OH + SOCl_2 \xrightarrow{\Delta} C_2H_5\text{-}Cl + HCl + SO_2$$

e) Reaction with HX/Anh $ZnCl_2$

Alcohols reacts with HX/Anh $ZnCl_2$ gives alkyl halides

$$R\text{-}OH + HX \xrightarrow{\text{Anh } ZnCl_2} R\text{-}X$$

i) Ethyl alcohol reacts HCl/Anh $ZnCl_2$ gives Ethyl chloride

$$C_2H_5\text{-}OH + HCl \xrightarrow{\text{Anh } ZnCl_2} C_2H_5\text{-}Cl$$

ii) Ethyl alcohol reacts HBr/Anh $ZnCl_2$ gives Ethyl bromide

$$C_2H_5\text{-}OH + HBr \xrightarrow{\text{Anh } ZnCl_2} C_2H_5\text{-}Br$$

iii) Ethyl alcohol reacts HI/Anh $ZnCl_2$ gives Ethyl iodide

$$C_2H_5\text{-}OH + HI \xrightarrow{\text{Anh } ZnCl_2} C_2H_5\text{-}I$$

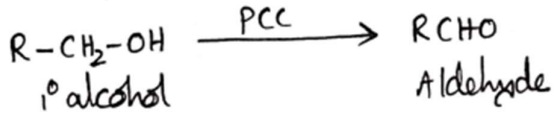
2. OXIDATION OF ALCOHOLS

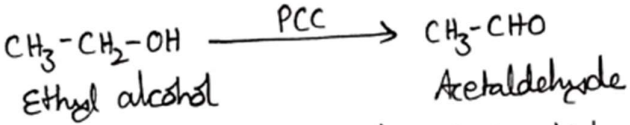
a) Oxidation with Pyridinium chlorochromate (PCC)

Oxidation with Pyridinium chlorochromate (PCC)

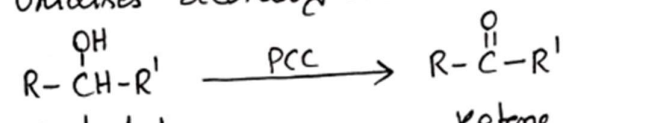
Pyridinium chlorochromate is obtained by adding pyridine to the solution of chromium (VI) oxide (CrO_3) in HCl.

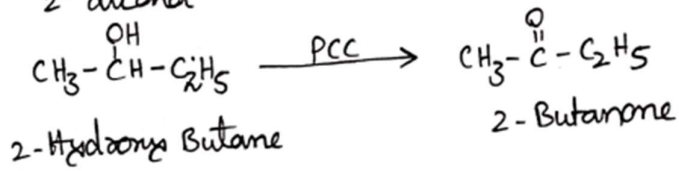
a) PCC oxidises primary alcohol to Aldehyde





b) PCC oxidises secondary alcohol to Ketone



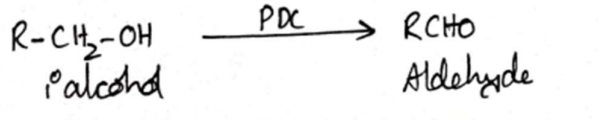


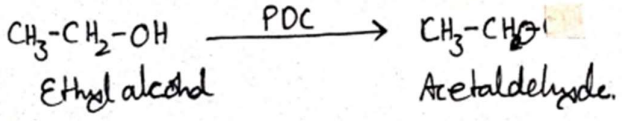
b) Oxidation with Pyridinium dichromate (PDC)

Pyridinium dichromate is obtained by the reaction of chromium trioxide with pyridine in presence of water.

PDC : $(C_5H_5\overset{\oplus}{N}H)_2Cr_2O_7$

PDC oxidises primary alcohol to aldehyde



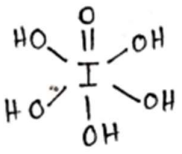


3. OXIDATION OF DIOLS

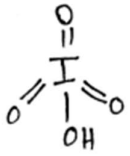
a) Oxidation of Diols using Periodic acid (HIO_4)

Periodic acid is the highest oxoacid of Iodine, in which iodine exists in +7 oxidation state. It exists in two forms.

1. Orthoperiodic acid H_5IO_6
2. Metaperiodic acid HIO_4



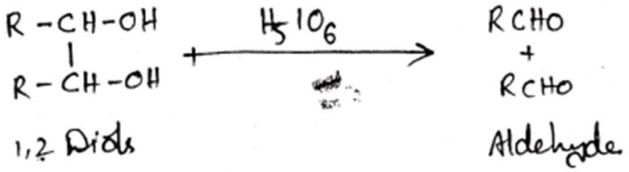
Ortho periodic acid



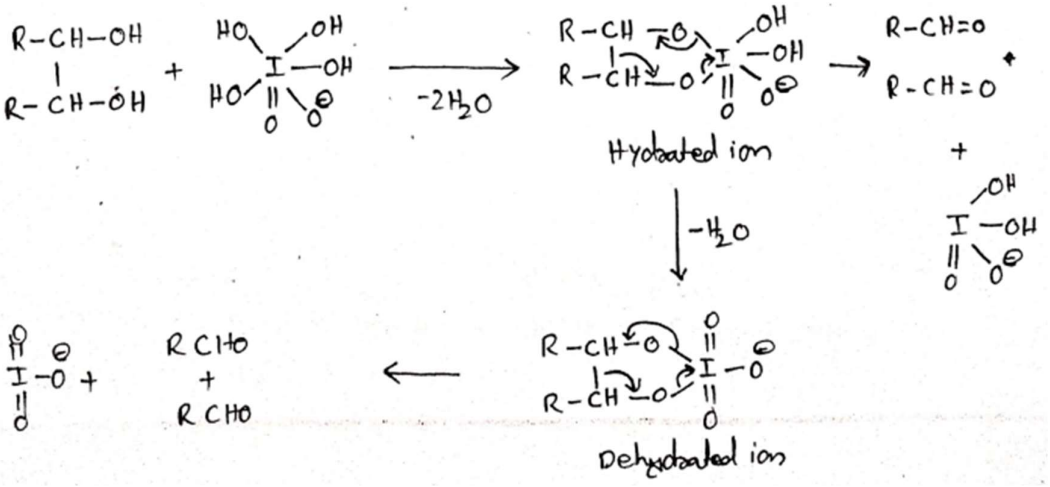
Meta periodic acid

Periodic acid is used as an important oxidising agent. It oxidises 1,2 diols (glycols) α-hydroxy Carbonyl Compounds, dicarbonyl Compounds and α-amino alcohols to aldehydes, Ketones or) acids depending upon the nature of the compound to be oxidised.

Periodic acid oxidises 1,2 diols (glycols) to aldehyde



Mechanism

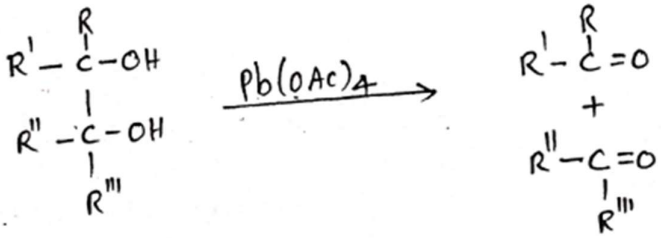


b) Oxidation of Diols using Lead tetraacetate $Pb(OAc)_4$

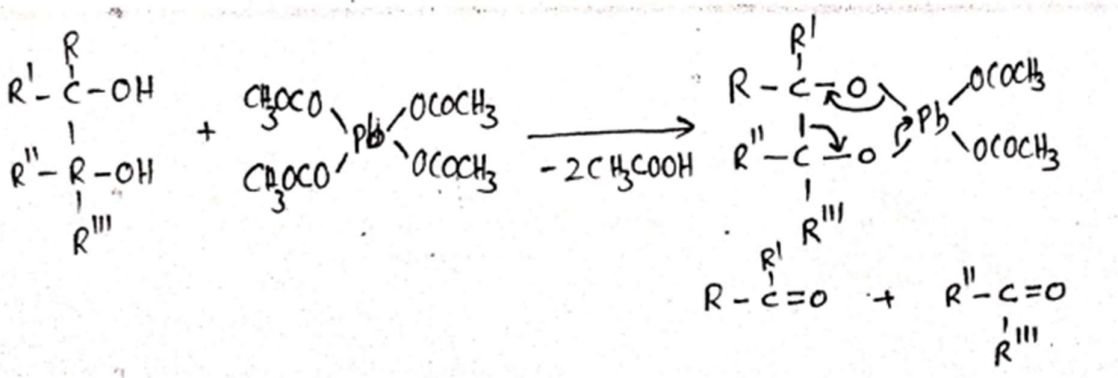
Lead teba acetate is generally employed as an acetoxylating, methoxylating and oxidising agent.

Lead teba acetate oxidises a wide variety of organic compounds such as hydroxyquinone, α-hydroxy acids, 1,2 di ketones, α-hydroxy ketones and 1,2 diols.

1,2 diols are oxidised at room temperature by lead teba acetate to aldehydes, ketones or both according to the structure of the glycol

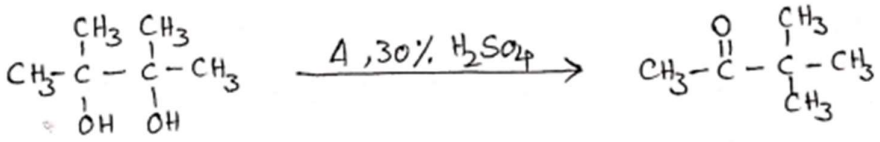


Mechanism



4. PINACOL - PINACOLONE REARRANGEMENT

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



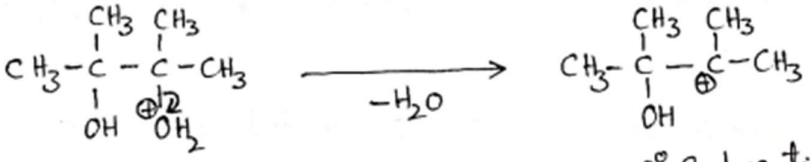
Pinacol — Pinacolone

Mechanism

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

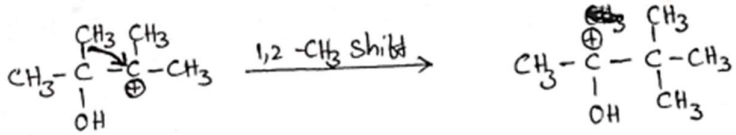
Pinacol — oxonium ion

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



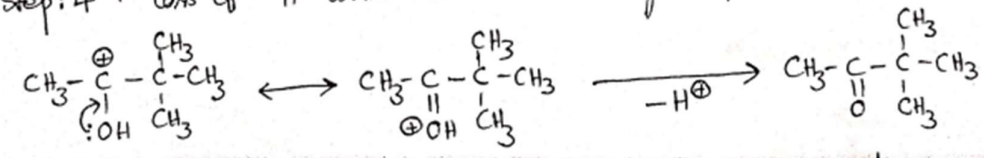
3° Carbocation

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

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

a) 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.

b) Victor – Meyer Test

Victor - Meyer test is used to differentiate 1°, 2° and 3° alcohols.

i) The alcohols were treated with Red Phosphorus and Iodine to convert alcohol in to corresponding iodide.

ii) The obtained iodides are converted in to corresponding nitro alkane using $AgNO_2$.

iii) The resulting nitroalkane is then treated with $NaNO_2$ / Conc H_2SO_4 (HNO_2)

iv) The resulting product in the above step is treated with NaOH (or) KOH which changes the color of the solution.

a) For 1° alcohols:

$$R\text{-}CH_2\text{-}OH \xrightarrow{Red\ P/I/\Delta} R\text{-}CH_2\text{-}I \xrightarrow{AgNO_2} R\text{-}CH_2\text{-}NO_2 \xrightarrow[H_2SO_4]{NaNO_2/Conc} R\text{-}\underset{\underset{N\text{-}OH}{\|}}{C}\text{-}NO_2$$

$$\xrightarrow{KOH} \text{Red color}$$

b) For 2° alcohols

$$R_2\text{-}CH\text{-}OH \xrightarrow{Red\ P/I/\Delta} R_2\text{-}CH\text{-}I \xrightarrow{AgNO_2} R_2\text{-}\underset{\underset{}{}}{C}\text{-}NO_2 \xrightarrow{NaNO_2/H_2SO_4} R_2\text{-}\underset{\underset{N=O}{|}}{C}\text{-}NO_2$$

$$\xrightarrow{KOH} \text{Blue color.}$$

c) For 3° alcohols

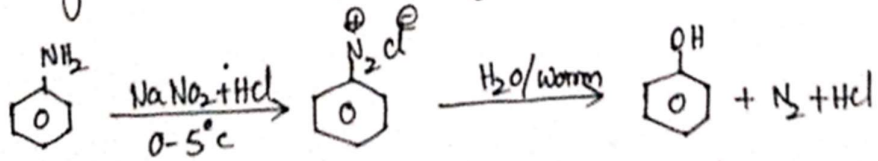
$$R_3\text{-}C\text{-}OH \xrightarrow{Red\ P/I/\Delta} R_3\text{-}C\text{-}I \xrightarrow{AgNO_2} R_3\text{-}C\text{-}NO_2 \xrightarrow{NaNO_2/H_2SO_4} \text{No reaction}$$

PHENOLS

Methods of preparation

a) Preparation from diazonium salt

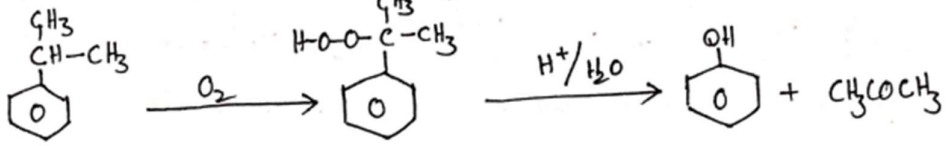
A diazonium salt is formed by heating an aromatic 1° Amine with ($NaNO_2$ + HCl) at 0-5°c. Diazonium salts are hydrolysed to phenols by warming with water or by treating with Dil acids



Aniline — Benzenediazonium salt — phenol.

b) Preparation from Cumene

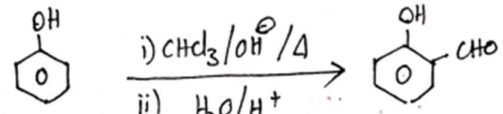
Cumene is oxidised in the presence of air to cumene hydroperoxide. It is converted to phenol by heating with Dil. acid.



Cumene — Cumene hydroperoxide — phenol.

1. Reimer– Tiemann Reaction

Treatment of phenols with chloroform in presence of aqueous base followed by treatment of with aqueous acid gives aldehyde

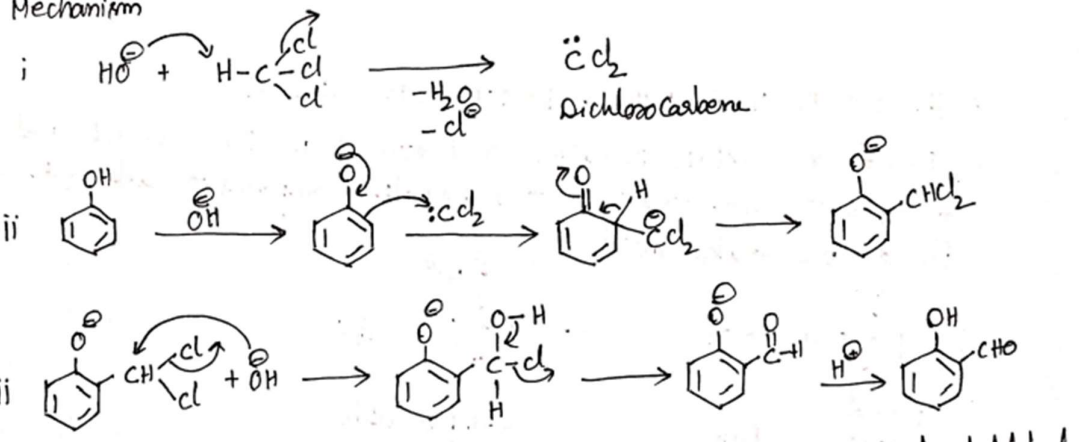


Salicylaldehyde

Phenol

major product

Mechanism

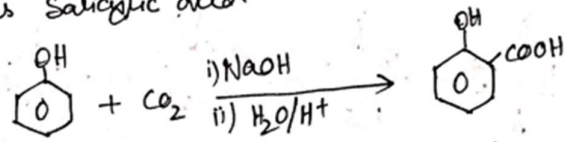


Salicylaldehyde

2. Kolbe – Schmidt Reaction

KOLBE SCHMIDT REACTION

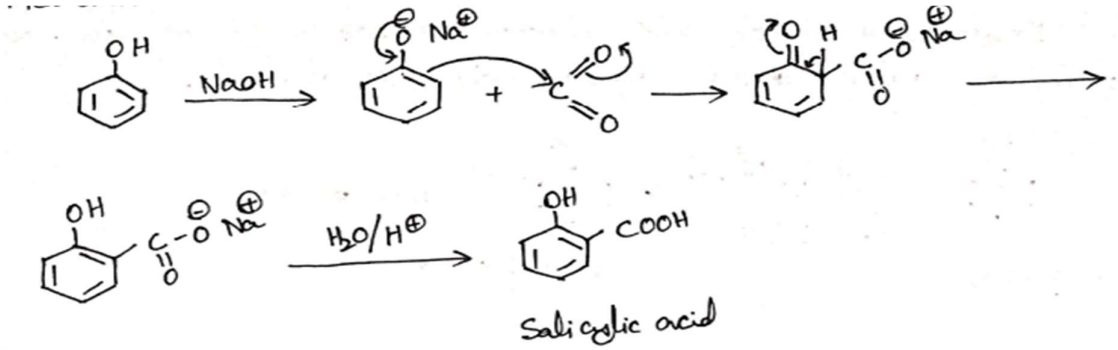
Phenol in presence of Base, (NaOH) reacts with Carbondioxide at high temperature and pressure to yield Sodium Salicylate which on acidification yields Salicylic acid.



phenol

Salicylic acid

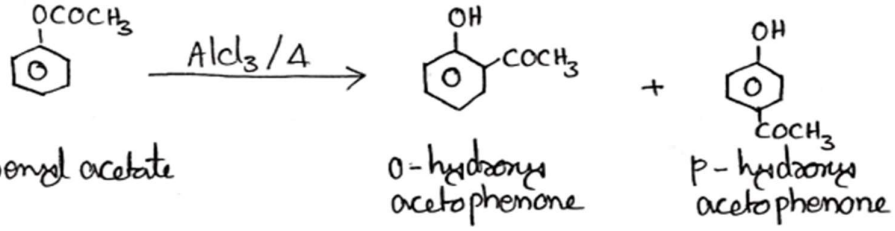
Mechanism



Salicylic acid

Fries rearrangements

Esters of phenols on heating with Lewis acids ($AlCl_3$) undergo rearrangement to give phenolic ketones.
Typical example for Fries rearrangement is rearrangement of phenyl acetate to give mixture of ortho- and para- hydroxy acetophenone.



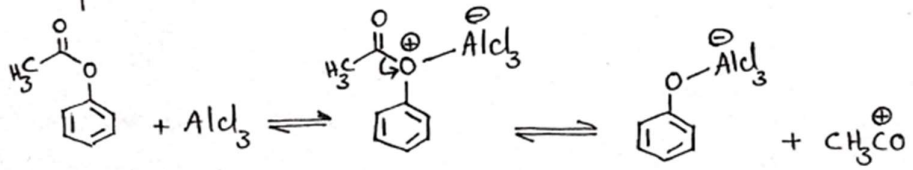
phenyl acetate — o-hydroxy acetophenone — p-hydroxy acetophenone

At low temperature (<60°c) favours the formation of p-isomer
Higher temperature (>160°c) favours the formation of o-isomer.

Mechanism

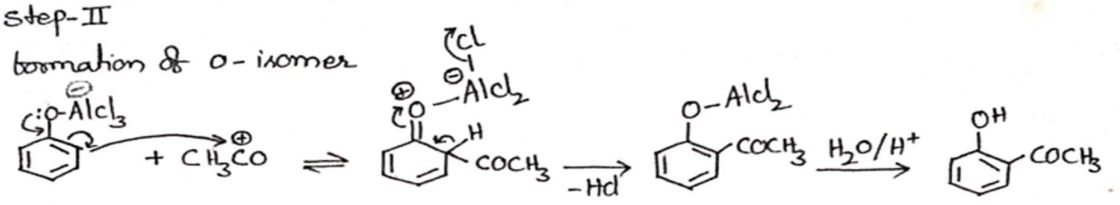
It is a two stepped process in which
a) The first step is the formation of acylium ion
b) The second step is that, the acylium ion substitutes at ortho (or) para positions, as in Friedel Crafts acylation.

Step-I



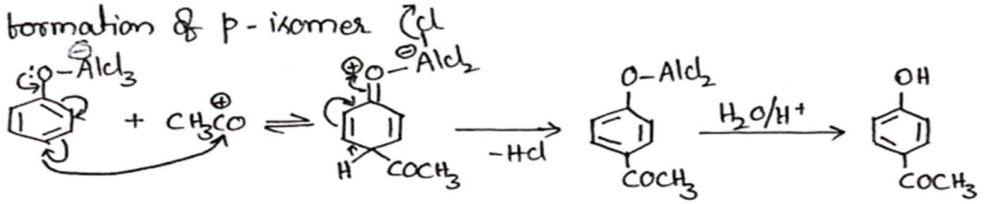
Step-II

formation of o-isomer



Ortho isomer

formation of p-isomer

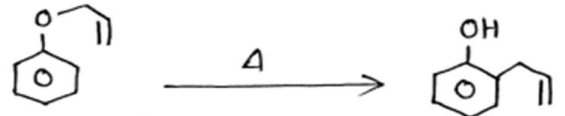


Para isomer.

Claisen Rearrangement

Thermal rearrangement of Allyl phenyl ethers to ortho - (or) - para (if ortho positions are preoccupied) allyl phenols.

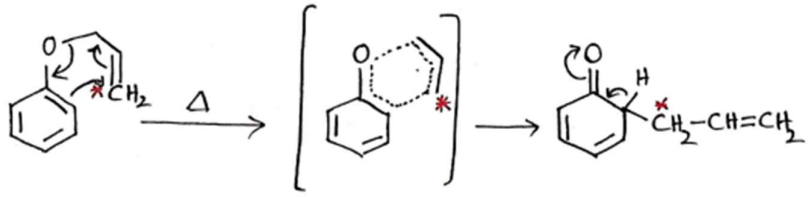
rearrangement of Allyl phenyl ether to o-allyl phenol.



Allyl phenyl ether — o-allyl phenol.

It is concerted intramolecular rearrangement, which proceeds through a cyclic six membered transition state and leads to an intermediate called cyclohexadienone. This intermediate regains the aromatic nucleus via tautomerisation to yield o-allyl phenol.

Experimental evidences revealed that, the ^{14}C labelled atom in the allyl group is inverted during rearrangement to ortho position.



Cyclic transition state

⇌ Tautomerism