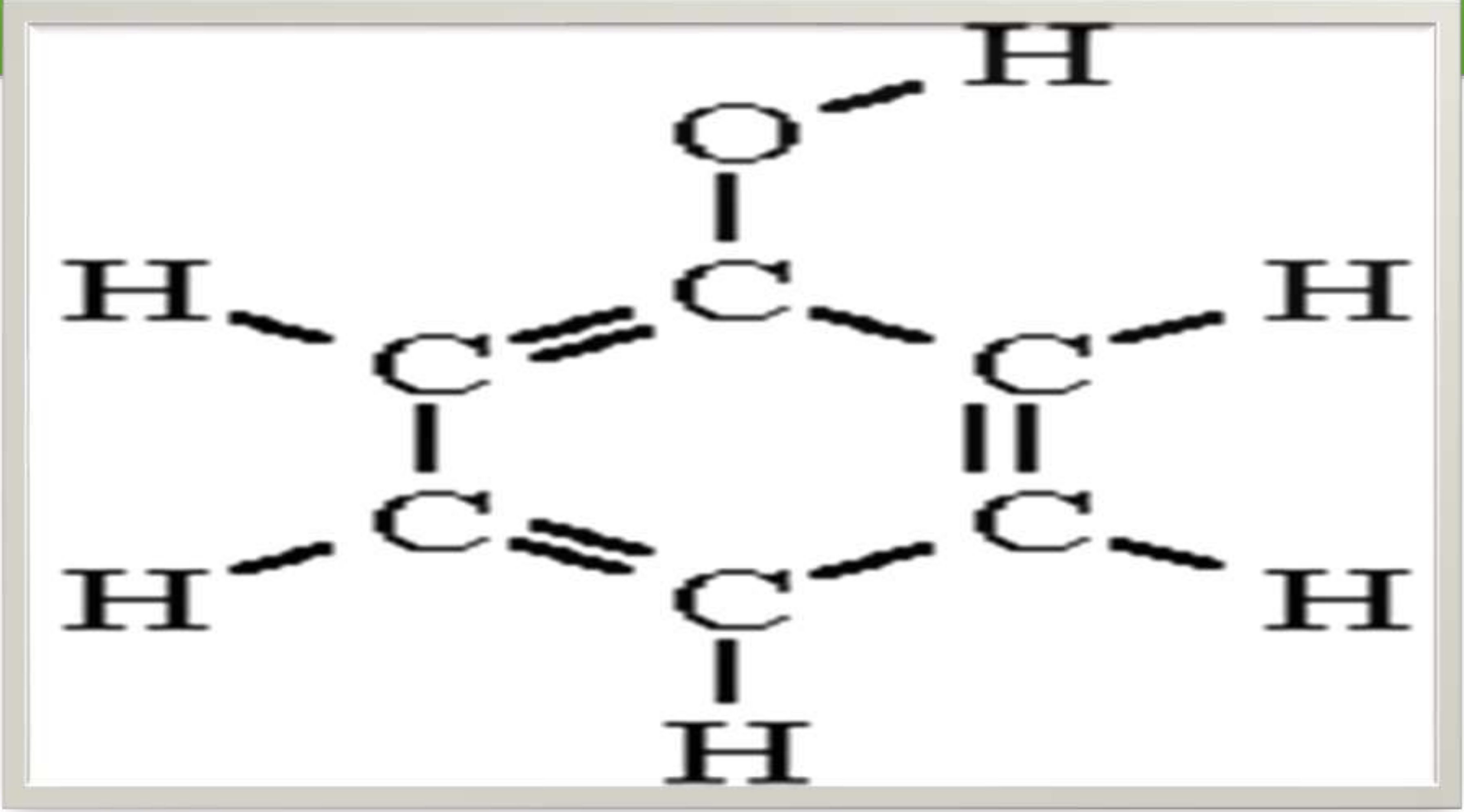
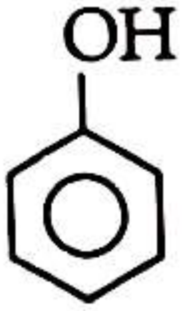
Phenols



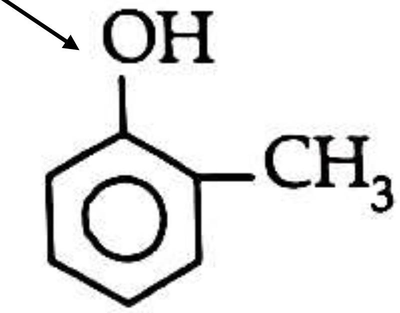
Classification of Phenols

Depending upon the number of OH groups

Monohydric Phenols

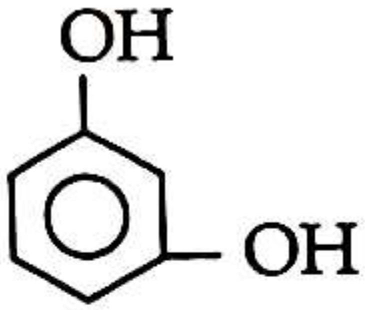


Phenol



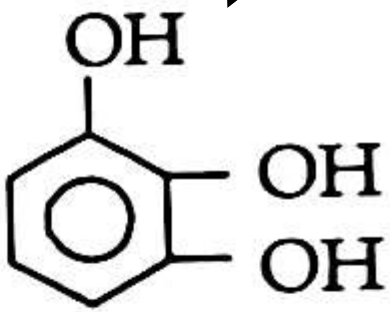
o-Cresol

Dihydric Phenols



Resorcinol

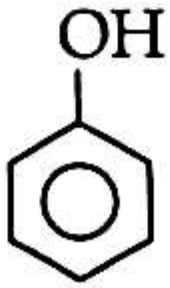
Trihydric Phenols



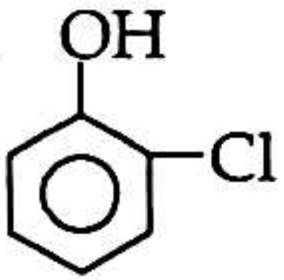
Pyrogallol

Nomenclature of Alcohols

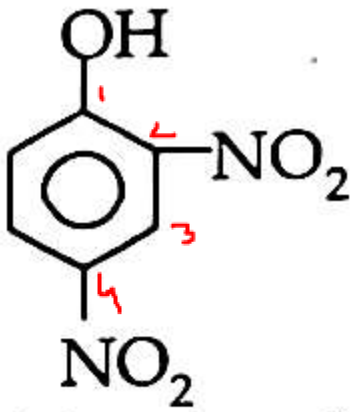
IUPAC name is benzenol
But generally named as phenol



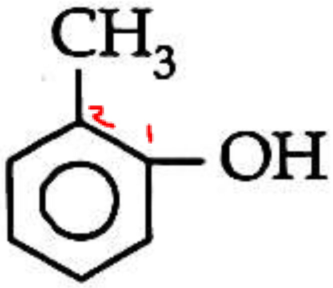
Phenol



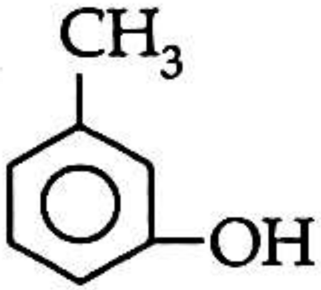
2-Chlorophenol
(*o*-Chlorophenol)



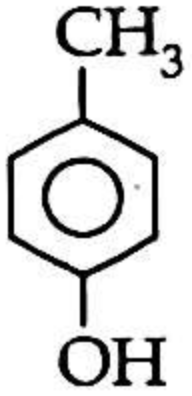
2, 4-Dinitrophenol



2-Methylphenol



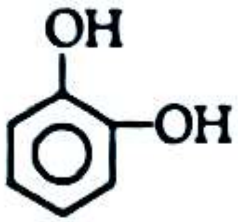
3-Methylphenol



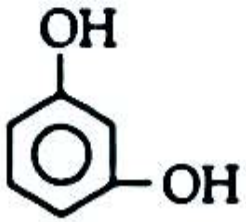
4-Methylphenol

Nomenclature of Alcohols

- Naming Dihydric & trihydric phenols

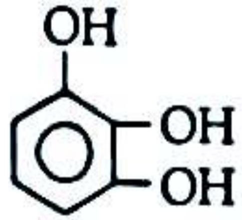


1, 2-Benzenediol
or
1, 2-Dihydroxy-
benzene
(Catechol)

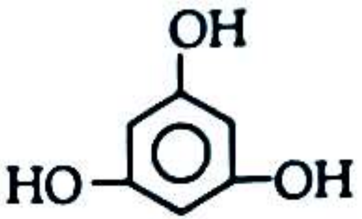


1, 3-Benzenediol
or
1, 3-Dihydroxy-
benzene
(Resorcinol)

1, 4-Benzenediol
or
1, 4-Dihydroxybenzene
(Hydroquinone
or
p-Quinol)

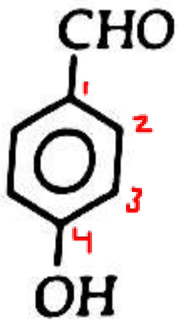


1, 2, 3-Benzenetriol
or
1, 2, 3-Trihydroxy-
benzene
(Pyrogallol)

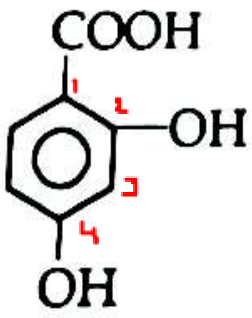


1, 3, 5-Benzenetriol
or
1, 3, 5-Trihydroxy-
benzene
(Phloroglucinol)

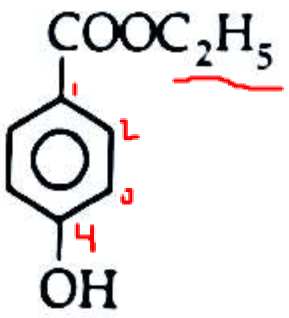
- Naming phenols in the presence of other functional groups



4-Hydroxybenzaldehyde



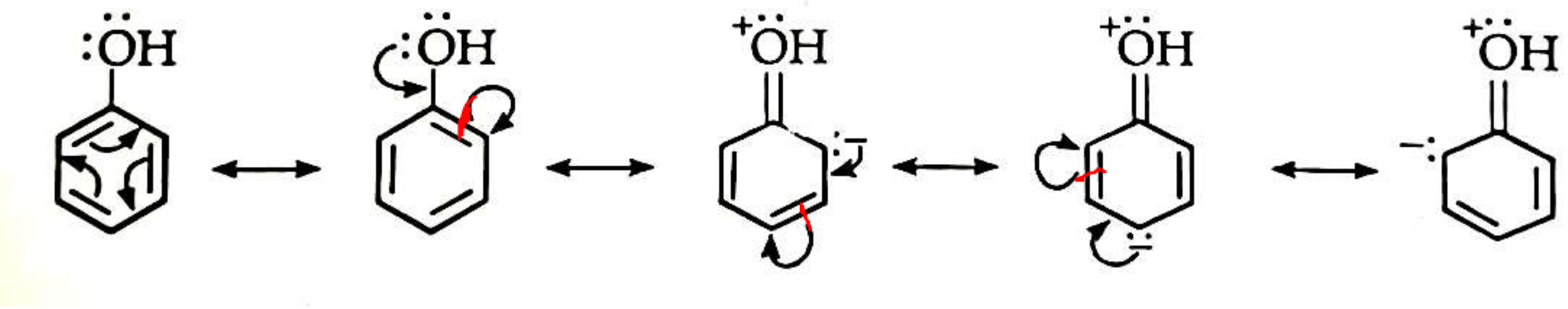
2, 4-Dihydroxybenzoic
acid



✓ Ethyl-4-hydroxy-
benzoate

Resonance structure of Phenols

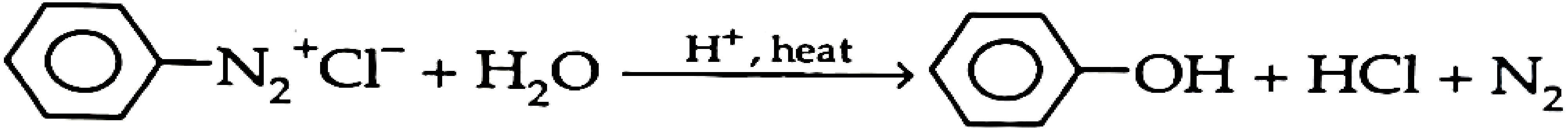
- Phenol has following resonating structures



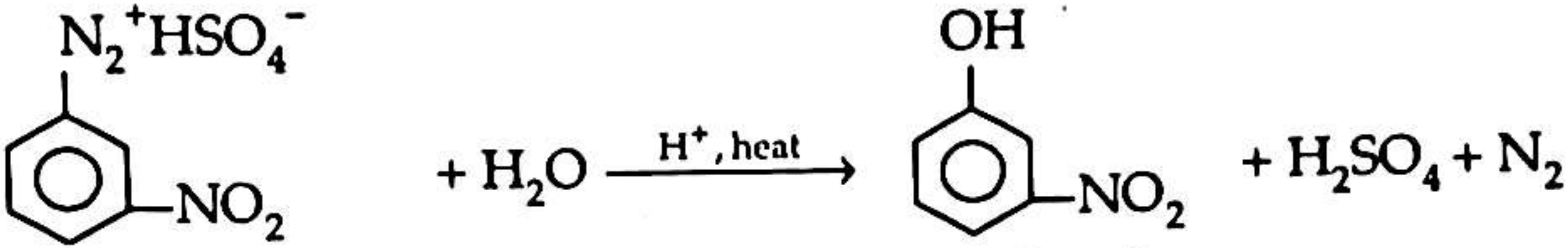
- Due to resonance, the oxygen atom acquires a positive charge. So O-H bond breaks onto oxygen atom easily to lose the H^+ ion
- So phenols are acidic in character

Methods of preparation of Phenols

- **By hydrolysis of diazonium salts**



Benzene diazonium chloride



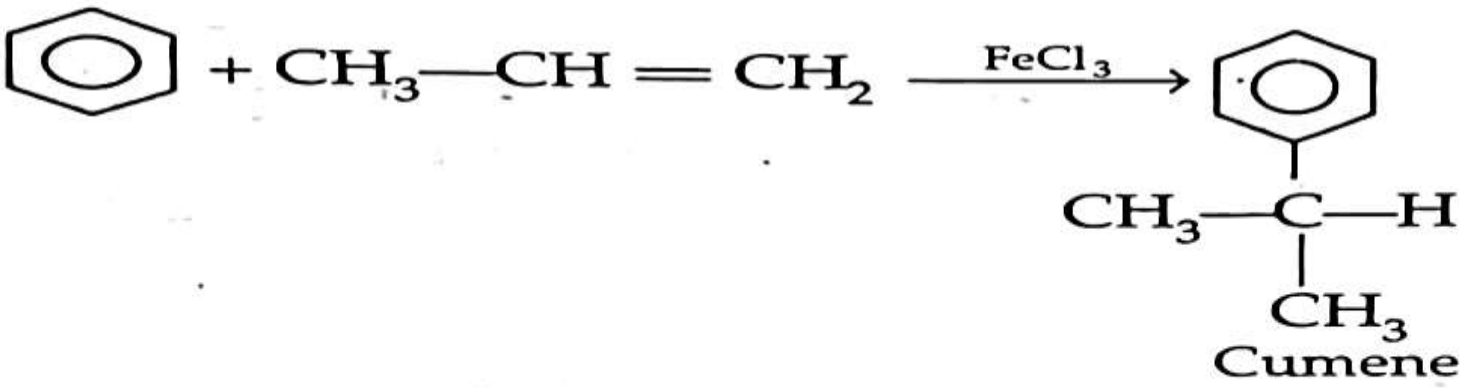
m-Nitrobenzene diazonium hydrogen sulphate

m-Nitrophenol

Methods of preparation of Phenols

❑ From isopropyl benzene(Cumene)

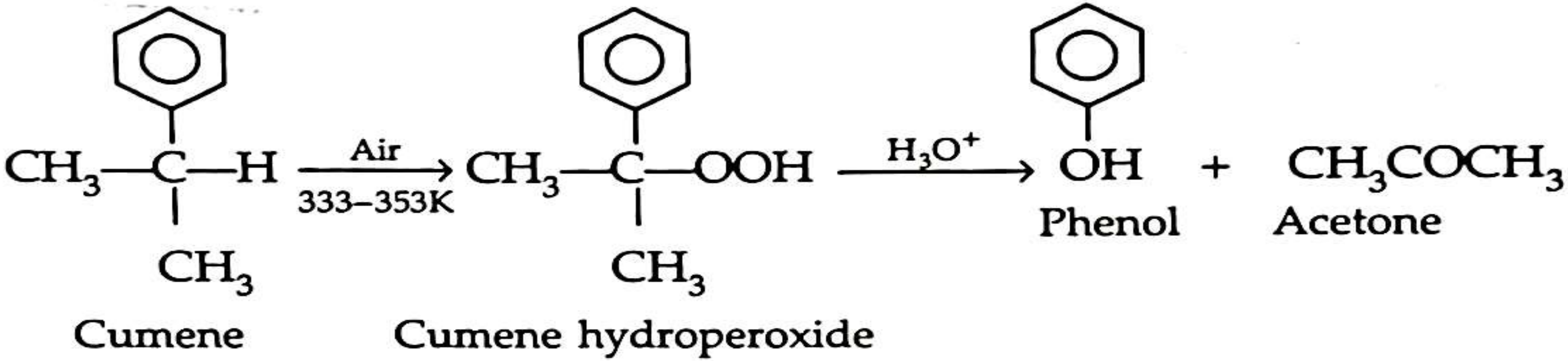
- Cumene is prepared from benzene as follows



$C_6H_6 + CH_3-CH=CH_2 \xrightarrow{FeCl_3} C_6H_5-CH(CH_3)-CH_3$

Cumene

- Cumene on oxidation with air gives cumene hydroperoxide which upon acidic hydrolysis gives phenol



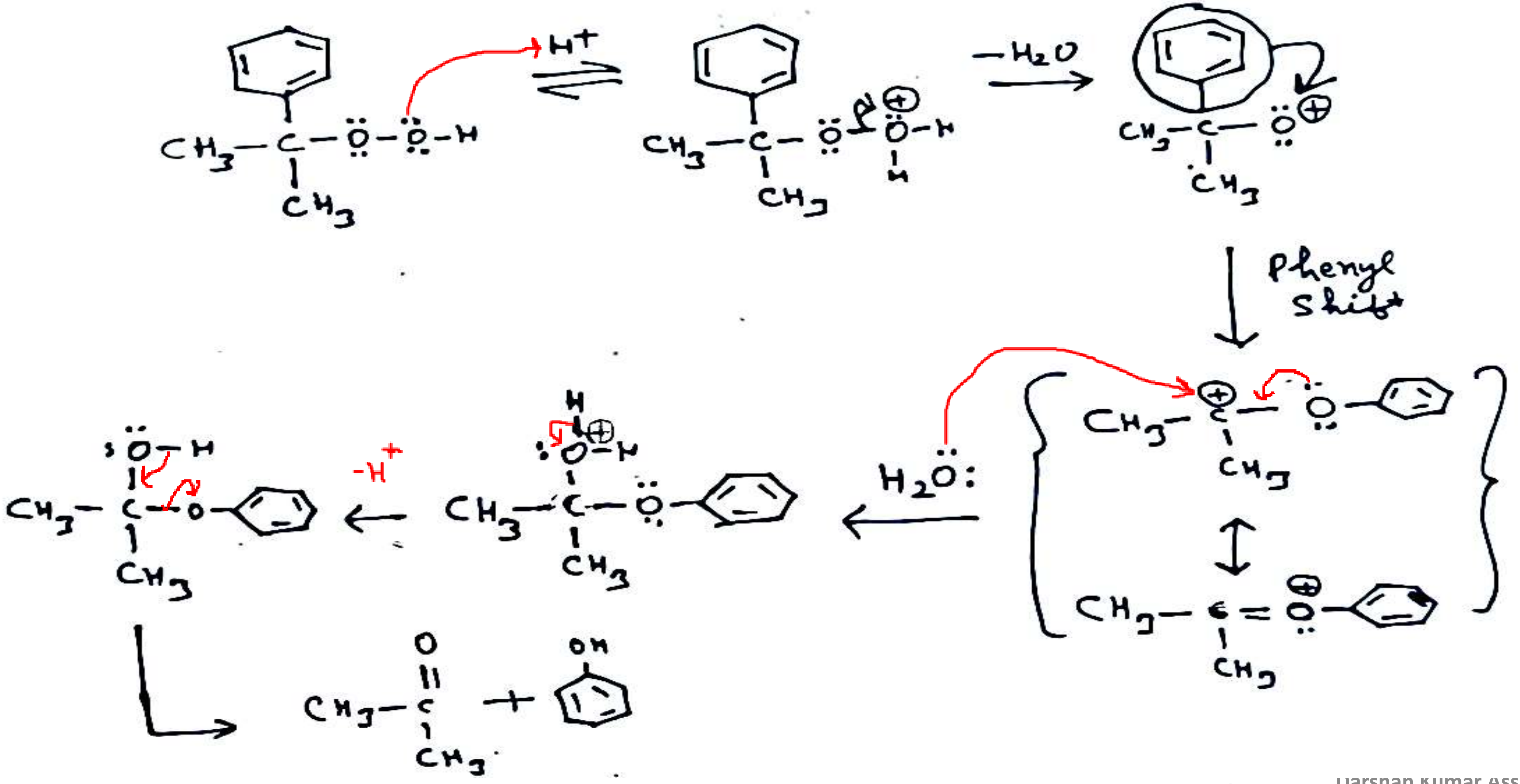
$C_6H_5C(CH_3)_2H \xrightarrow[333-353K]{Air} C_6H_5C(CH_3)_2OOH \xrightarrow{H_3O^+} C_6H_5OH + CH_3COCH_3$

Cumene   Cumene hydroperoxide   Phenol   Acetone

Methods of preparation of Phenols

❑ From isopropyl benzene(Cumene)

➢ **Mechanism of the reaction**



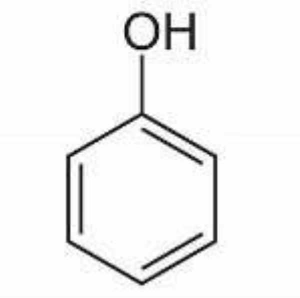
Physical properties of Phenols

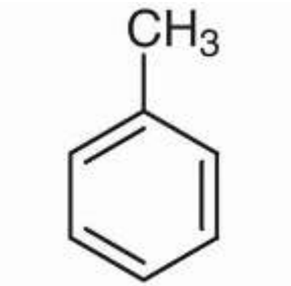
❑ Phenols have higher boiling point than corresponding hydrocarbons

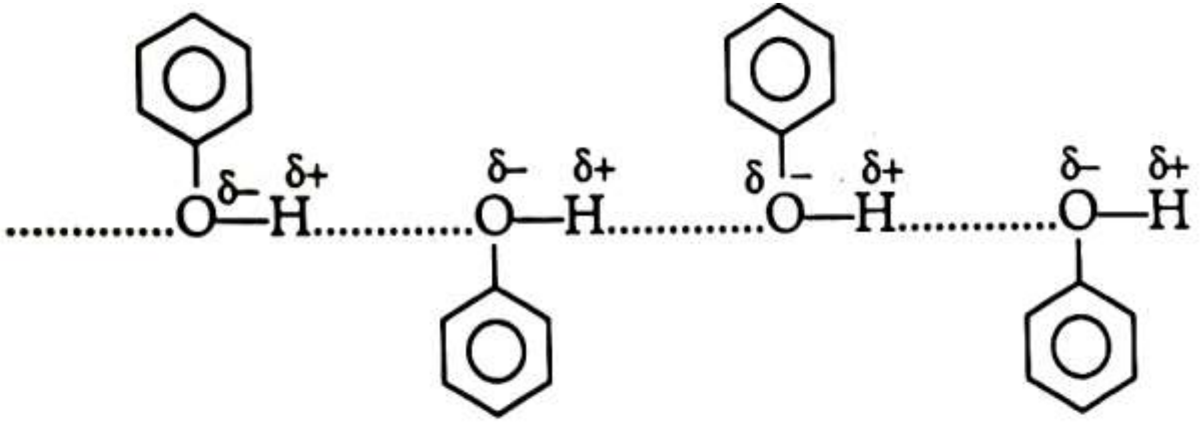
- It is due to intermolecular hydrogen bonding

For example

Phenol	Toluene
Molecular mass = 94	Mol. Mass = 92
B. Pt. 455 K	B. Pt. 384 K





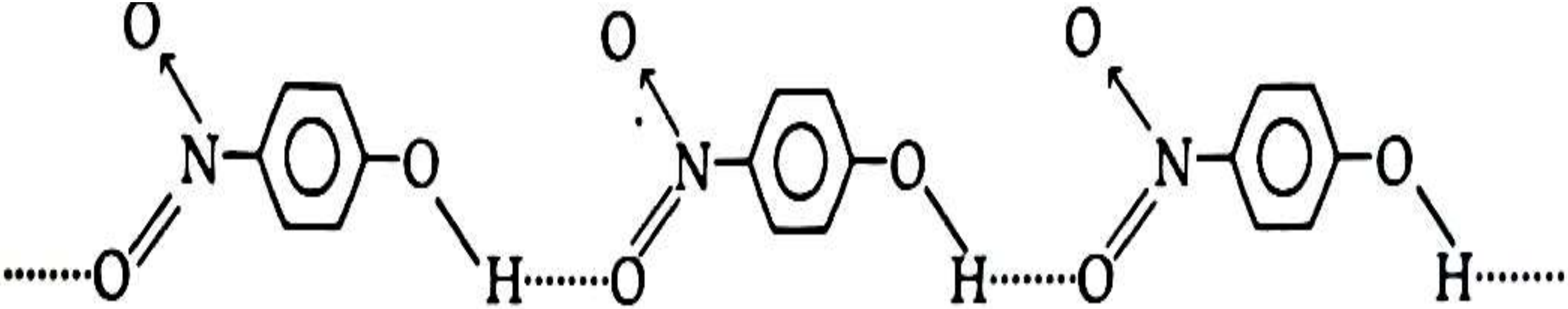


- O-Nitrophenol has lower boiling point than m- & p-Nitrophenols .Why?

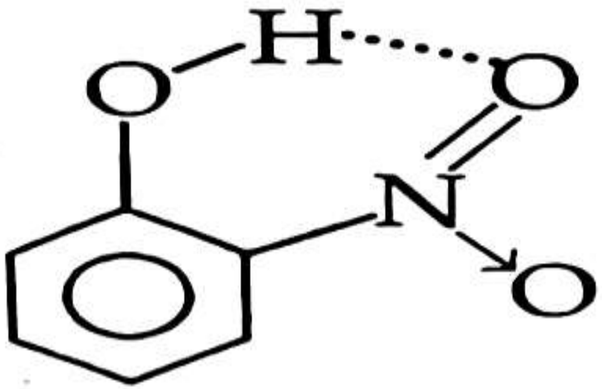
❑ Solubility

- Phenol is soluble in water due to formation of hydrogen bonding with it but solubility is low because polar character of OH group is masked by large sized phenyl group.
- O-Nitrophenol has less solubility in water as compared to m- & p- isomers. Why?

Physical properties of Phenols



Intermolecular Hydrogen Bonding



Intramolecular hydrogen bonding

Chemical properties of Phenols

❑ Reactions due to phenolic group

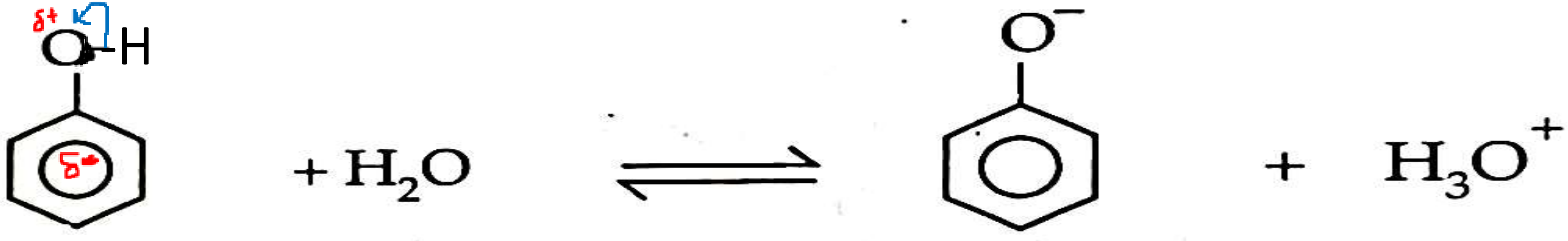
❖ **Acidic character (However acidic character is very weak)**

- ➢ **Reacts with alkali metal hydroxides to form phenoxide salts**

  $ArOH + NaOH \rightarrow ArO^- Na^+ + H_2O$

❖ **Why Phenols are acidic in character?**

- ➢ **It is due to greater resonance stabilisation of phenoxide ion than phenol. So less resonance stabilised phenol changes into more resonance stabilised phenoxide ion by loss of proton in an aqueous medium.**

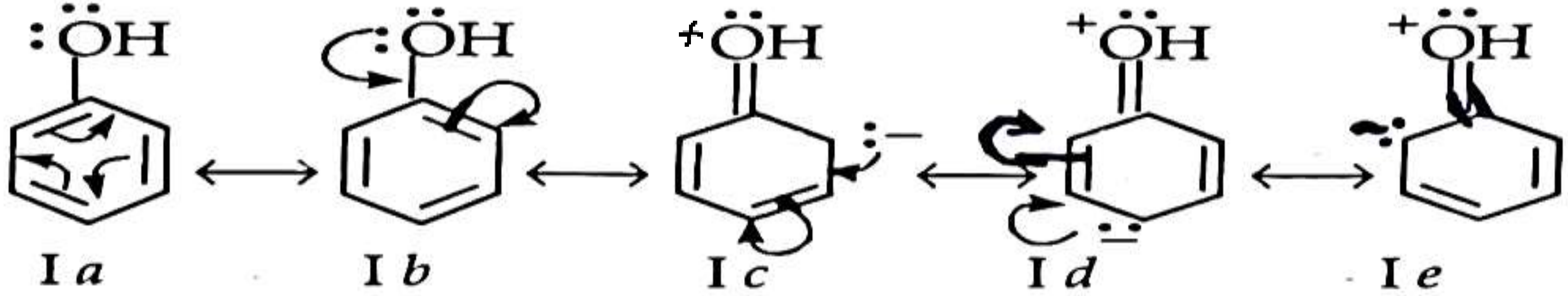


Phenol
Less resonance stabilised

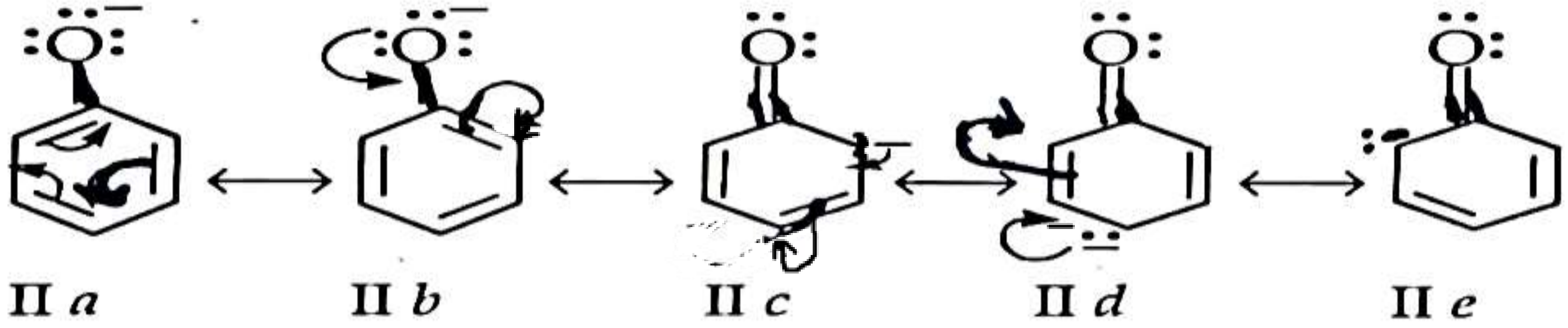
Phenoxide ion
More resonance stabilised

Chemical properties of Phenols

❑ How phenoxide ion is more resonance stabilized?



Phenol



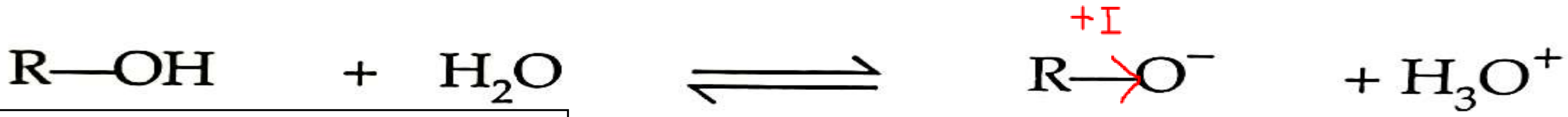
Phenoxide ion

- There are equal number of resonating structures
- In phenol, structures Ic to Ie involve charge separation & there is a positive charge on the electronegative oxygen atom so their contribution is very less.
- However in phenoxide ion there is a negative charge on the oxygen atom so all structures are equally important so it is more stable

Chemical properties of Phenols

❑ Phenols are more acidic than alcohols. Why?

- Alcohols on reaction with base form alkoxide ion which is not resonance stabilised



$$R{-}OH + H_2O \rightleftharpoons \overset{+I}{R \rightarrow O^-} + H_3O^+$$

Alcohol

No resonance stabilization

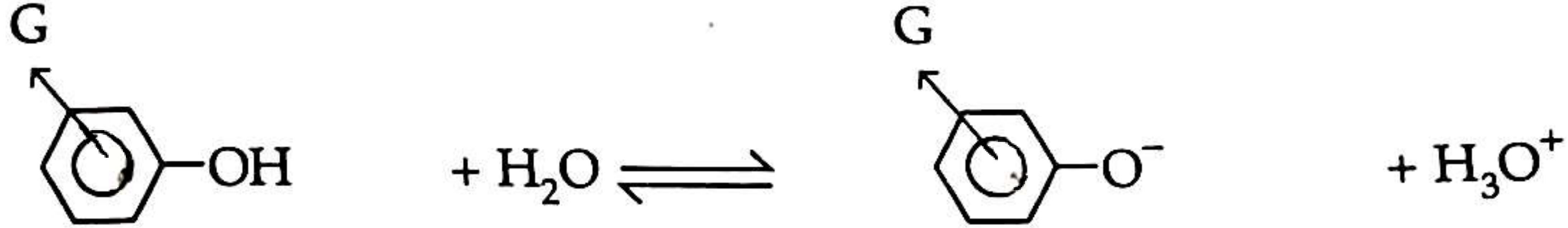
Alkoxide ion

No resonance stabilization, On the other hand, there is destabilization due to +I effect of the alkyl group

❑ Effect of substituents on acidity of phenols

❖ Nature of substituents on the benzene ring

- **Electron withdrawing groups increase the acidic strength of phenols**

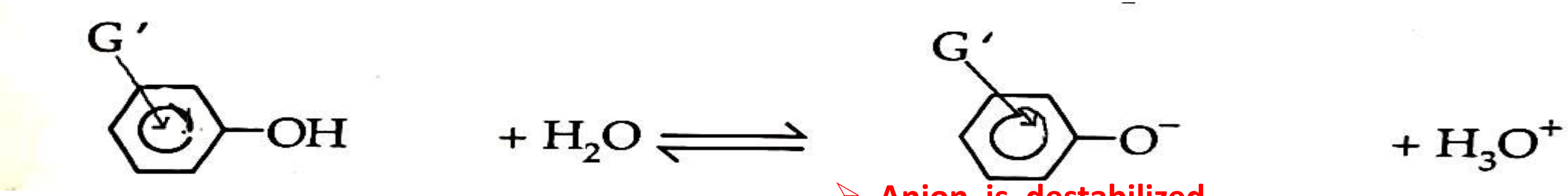


Anion is stabilized due to the dispersal of negative charge

Chemical properties of Phenols

❑ Nature of substituents on the benzene ring

- ➢ Electron releasing groups decrease the acidic strength of phenols



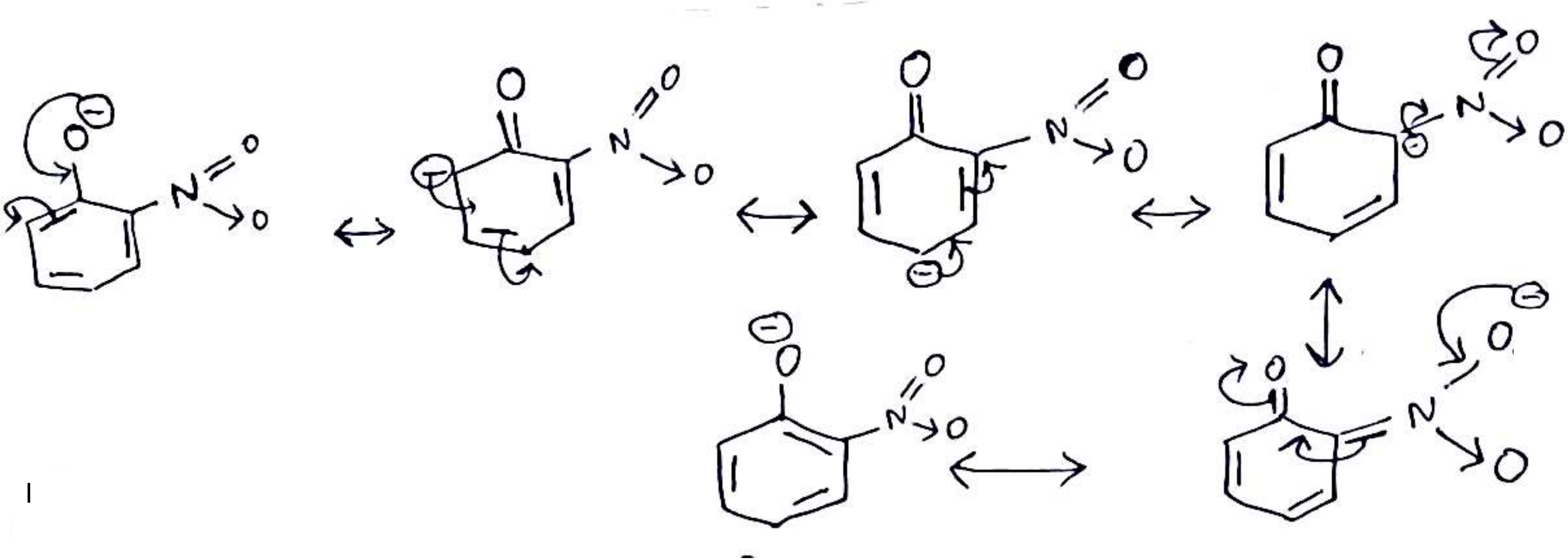
- ➢ Anion is destabilized due to intensification of negative charge

❑ Position of hydroxyl group relative to substituents

- ➢ Electron release or withdrawal may be due to both inductive effect and resonance effect
- ➢ Resonance effect is more at O- & p- positions than at m- position
- ✓ More resonating structures when gp is present at o- or p- position. So due to greater resonance stabilization of o- & p- phenate ion, the acid strengthening effect is more when the electron-withdrawing group is present at o- & p- positions rather than at m- position.

Chemical properties of Phenols

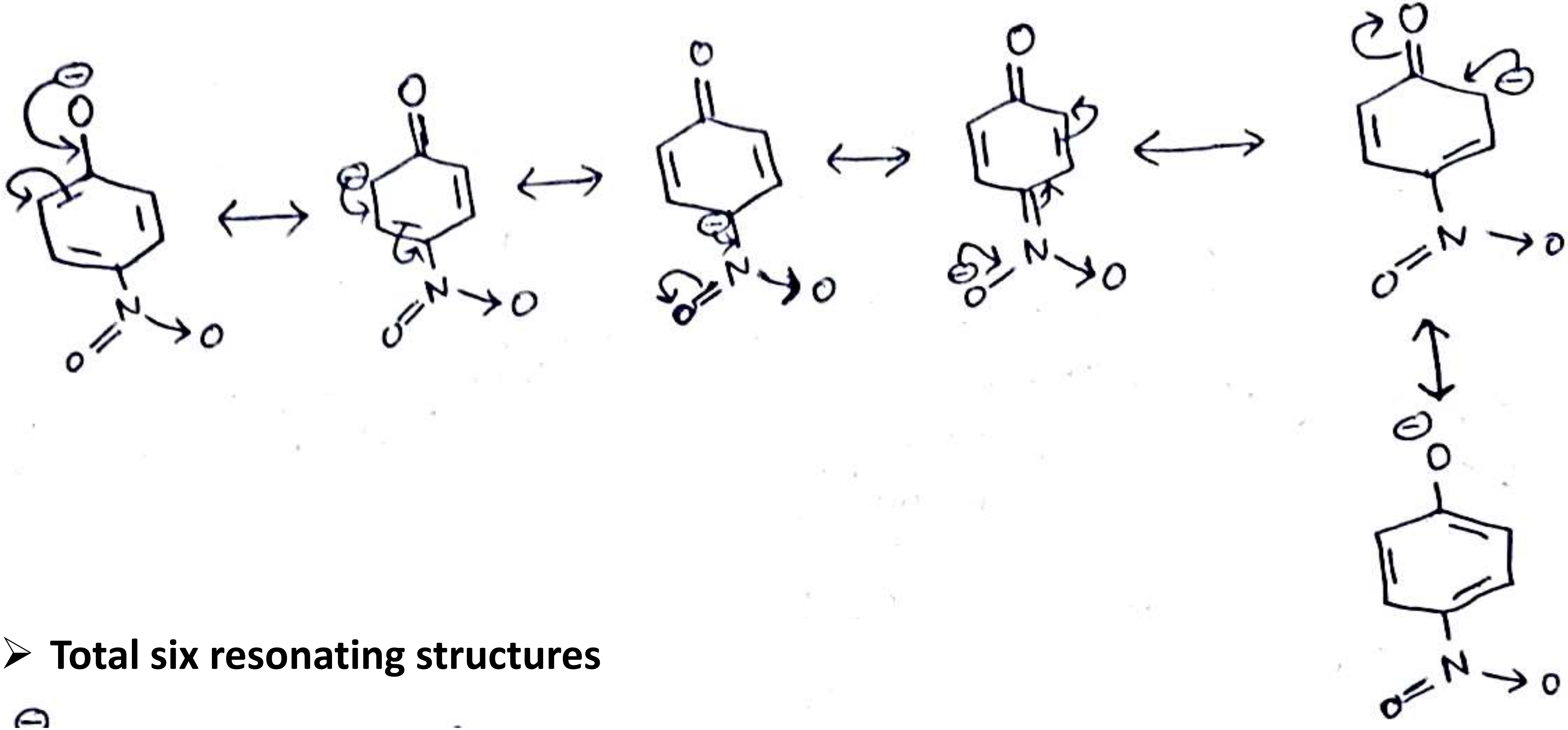
- ❑ **When the group is at the ortho position**



➢ **Total six resonating structures**

Chemical properties of Phenols

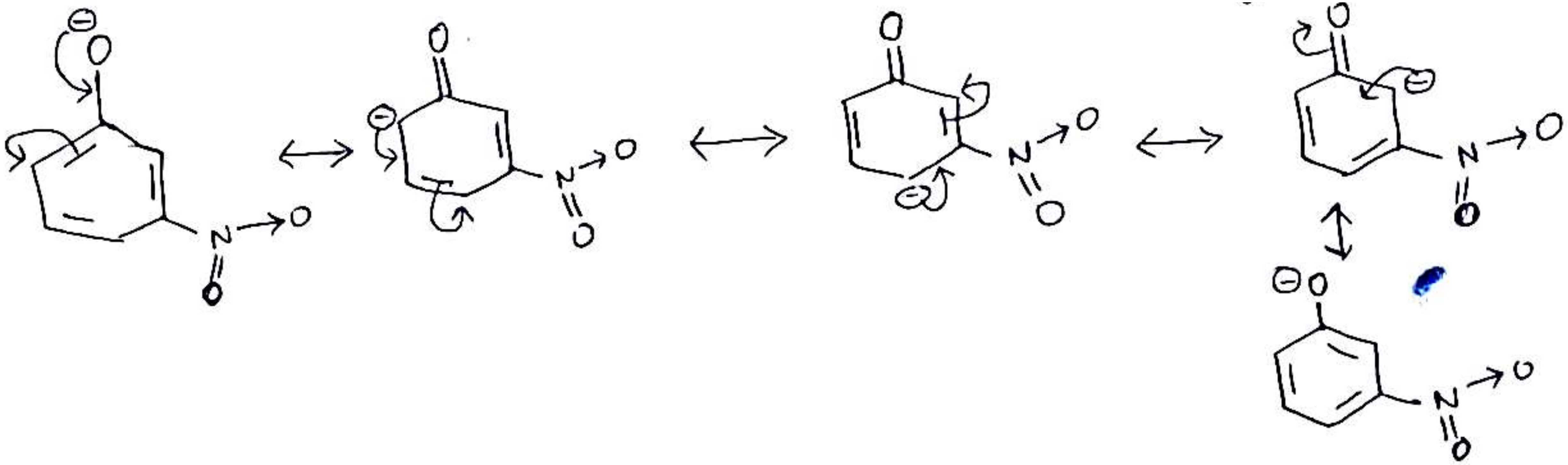
❑ When the group is at the para position



- ➢ **Total six resonating structures**

Chemical properties of Phenols

❑ When the group is at the meta position



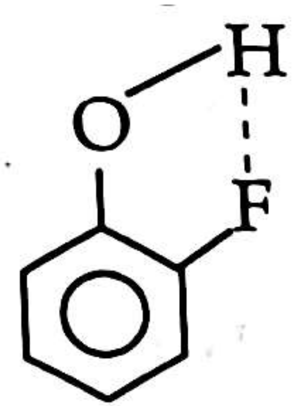
➢ **Total five resonating structures**

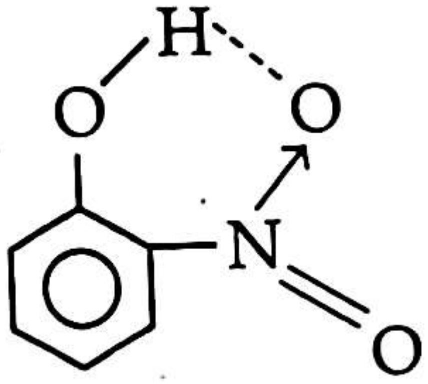
Chemical properties of Phenols

❑ Position of hydroxyl group relative to substituents

- **Inductive effect decreases with distance from the hydroxyl group**

- **O- Fluorophenol is a weaker acid than p-Fluorophenol. Why?**
- **O- Nitrophenol is a weaker acid than p-Nitrophenol. Why?**





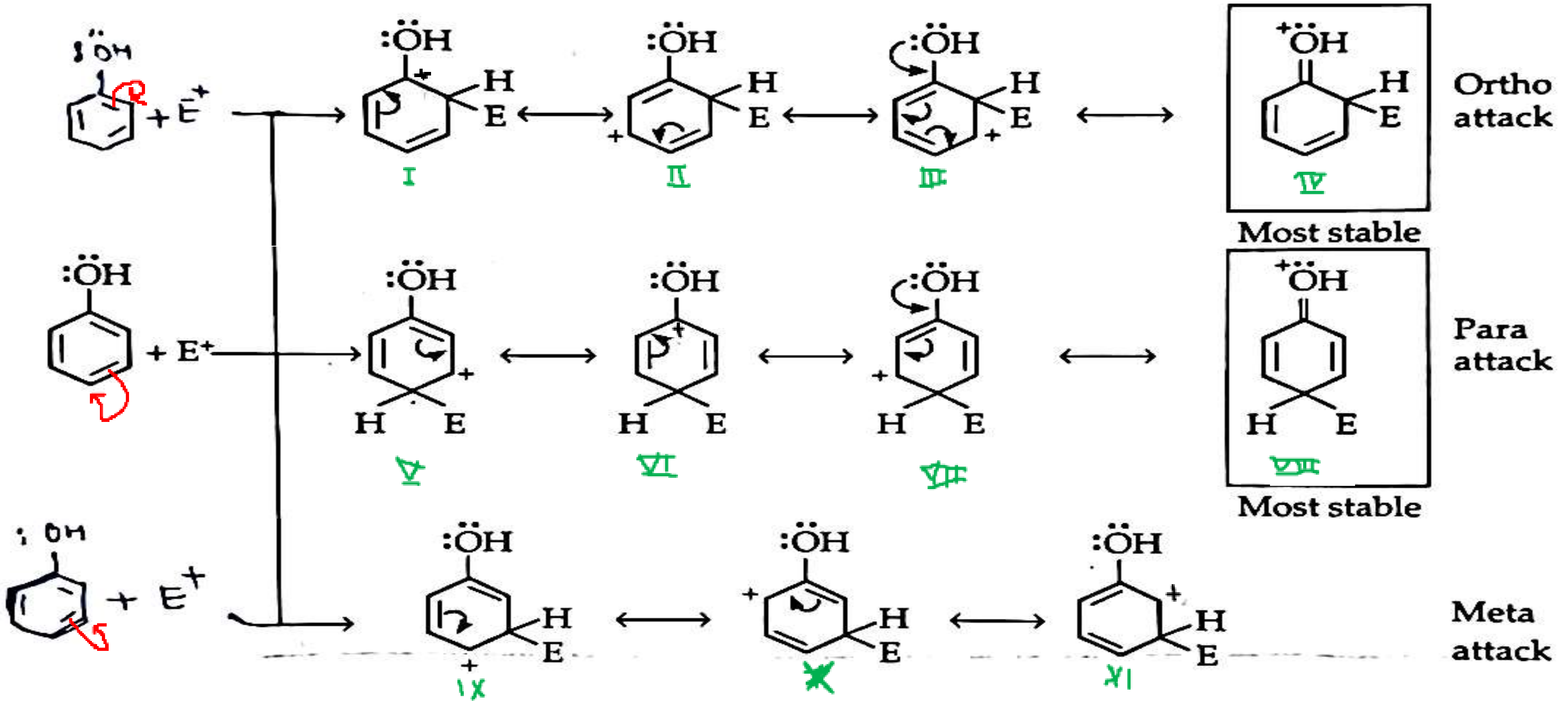
In both cases, there is intramolecular Hydrogen bonding in the ortho isomer. As H atom of the OH group is taking part in H-bond formation so its tendency to ionize decreases.

Chemical properties of Phenols

❑ Reactions of aromatic ring: Electrophilic substitution reactions

❖ OH group is activating and o- & p- directing in nature. Why?

➢ Consider attack of electrophile on o- , m- , & p- positions one by one

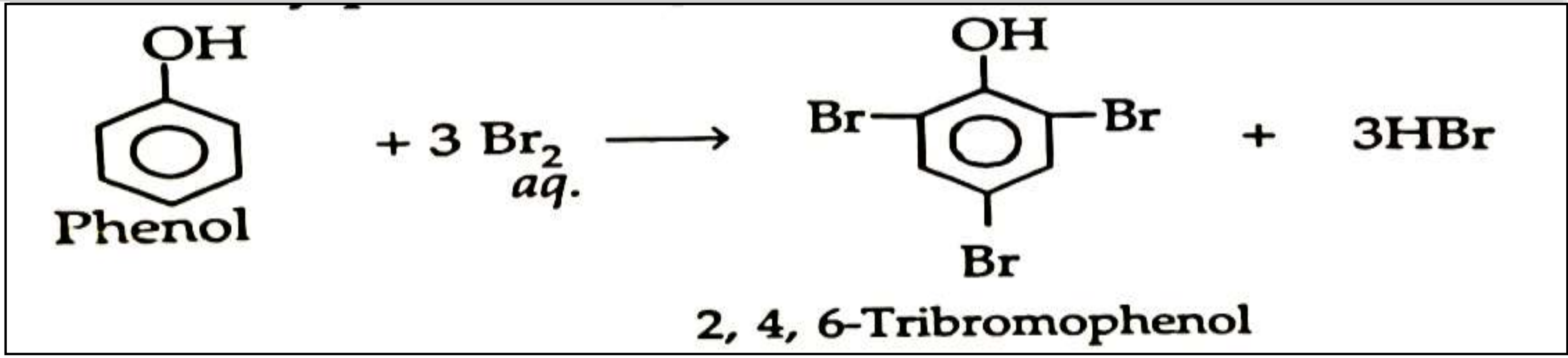


➢ During attack at o- & p- positions, there are four resonating structures of intermediate carbocation where as during attack at m-position there are only three resonating structures. So intermediate carbocation is more stabilised during o- & p- attack.

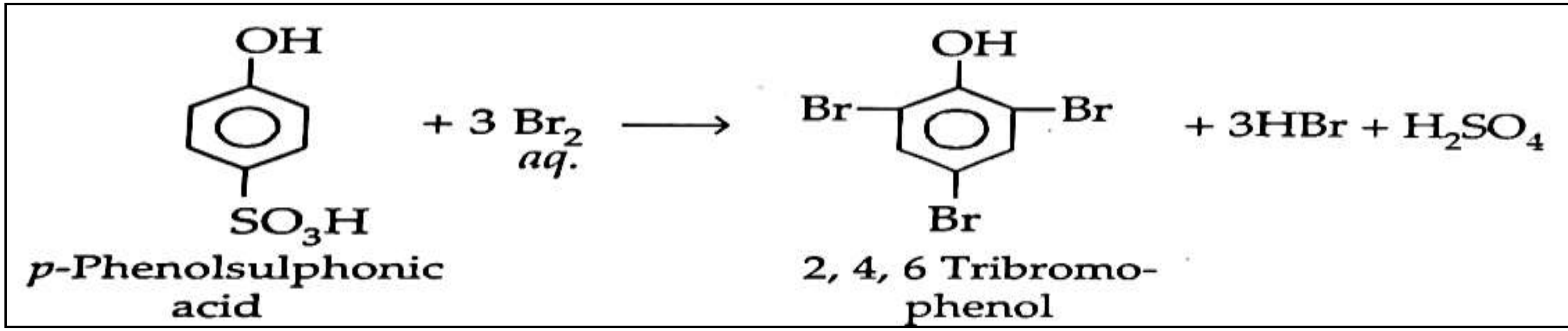
Chemical properties of Phenols

❑ Halogenation

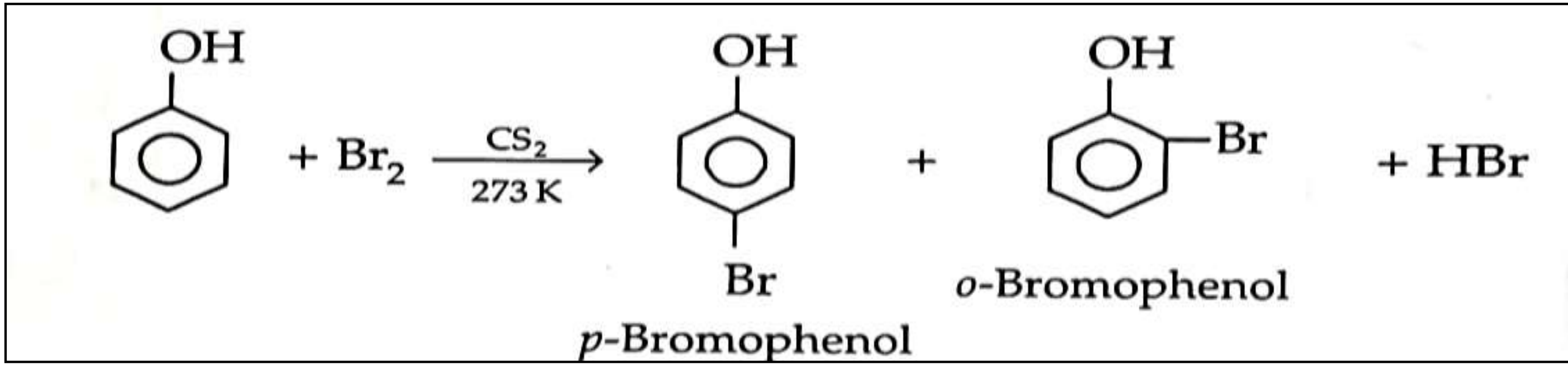
- ➢ **Bromination in an aqueous medium**
- ✓ **(OH group is ionised to form phenoxide ion. Negatively charged oxygen activates the benzene ring)**



- ➢ **Reactivity towards halogenation is very high (Even other groups are replaced by halogen atom)**



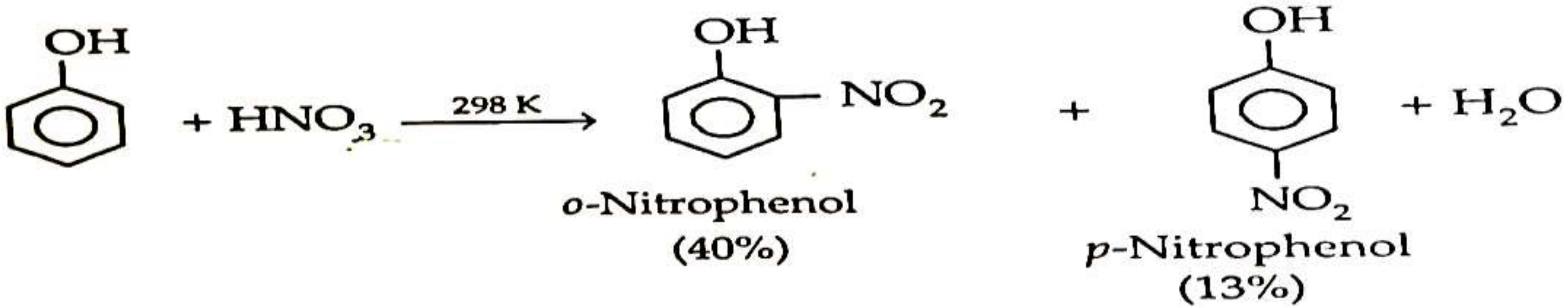
- ➢ **Reaction stops at mono halogen stage at low temperature and in nonpolar solvents**
- ✓ **(OH group is not ionised to form phenoxide ion so activation of ring is less)**



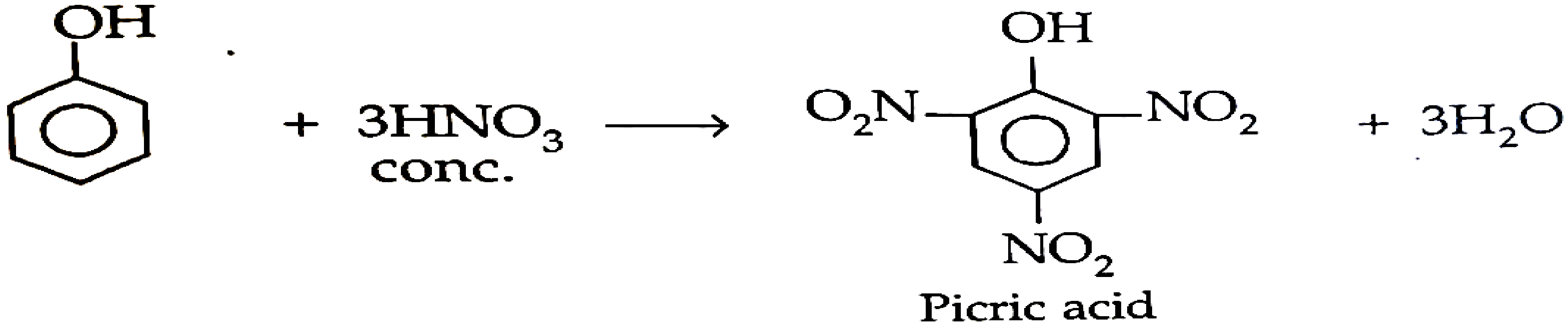
Chemical properties of Phenols

☐ Nitration

- ➢ **With dilute nitric acid**



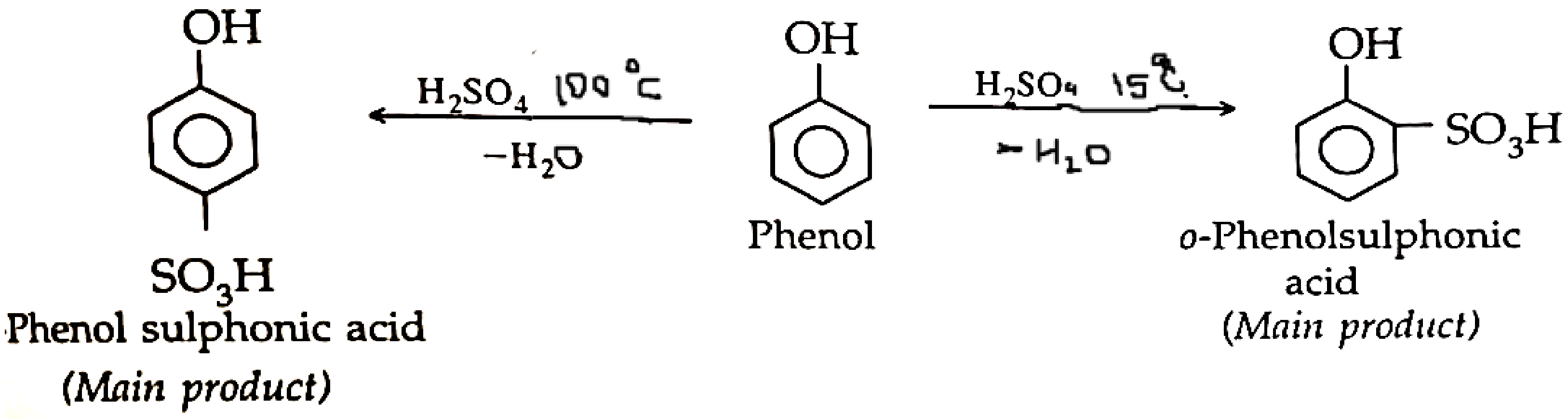
- ➢ **With concentrated nitric acid**



Chemical properties of Phenols

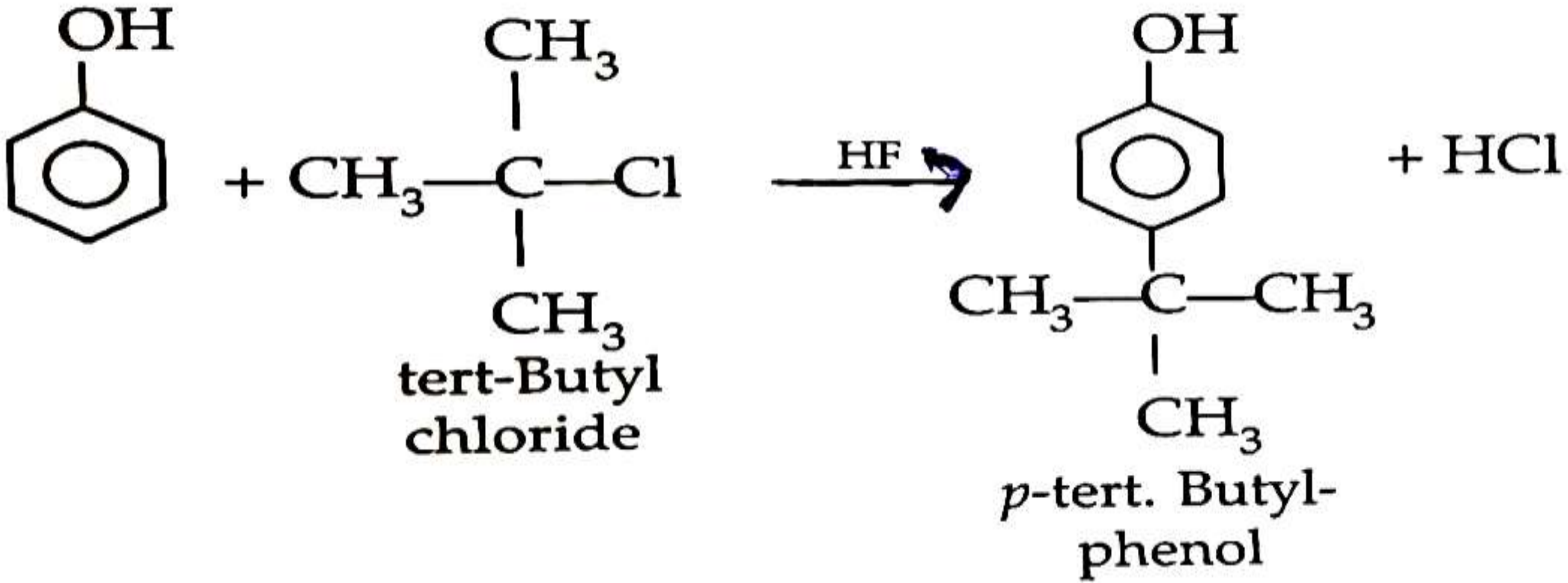
❑ Sulphonation

- ➢ At low temperatures o- isomer is formed and at high temperatures p- isomer is the main product
- ➢ (p-Isomer is thermally more stable)



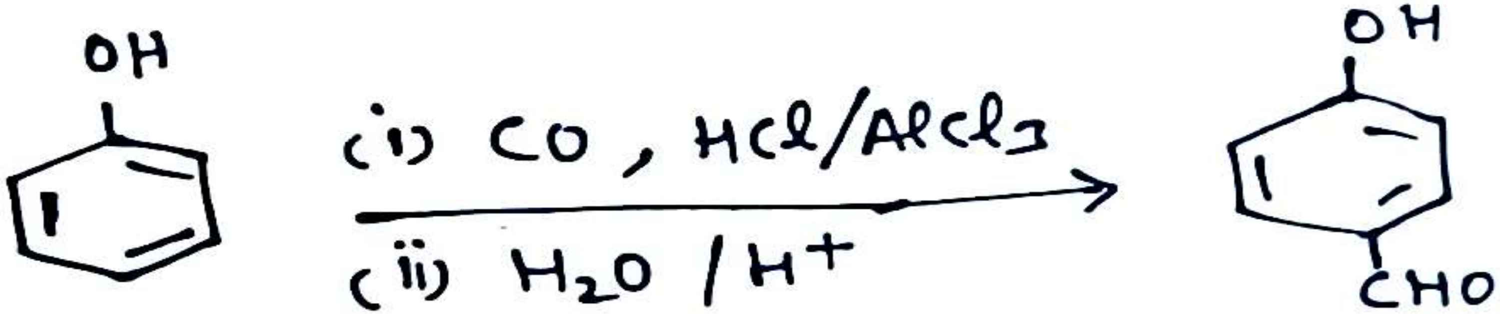
❑ Friedel Craft’s alkylation

- ➢ Carried out in the presence of HF not $AlCl_3$. Why?



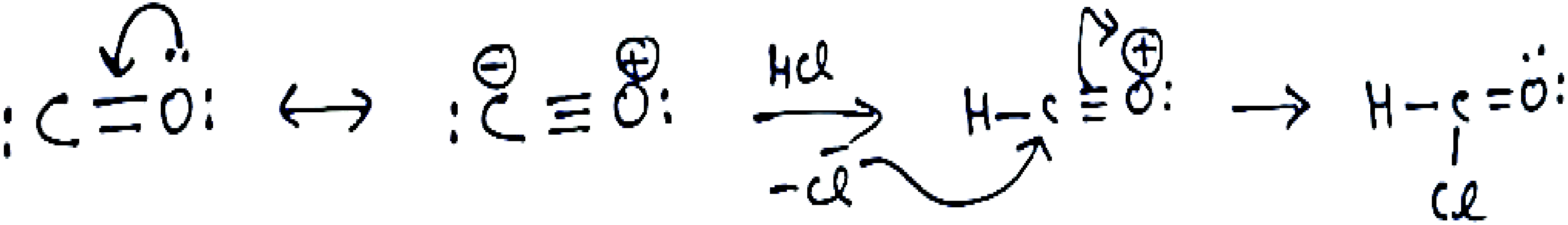
Chemical properties of Phenols

❑ Gattermann Koch Synthesis



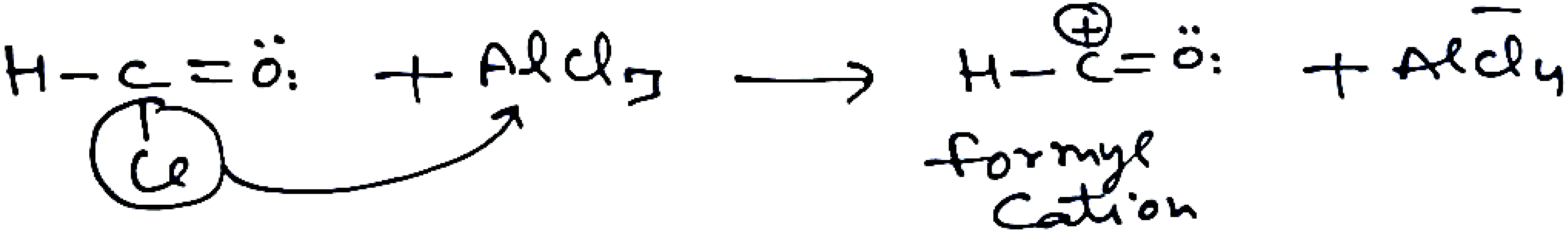
❖ Mechanism

➢ **Step 1** **Formation of Electrophile(Formyl cation)**



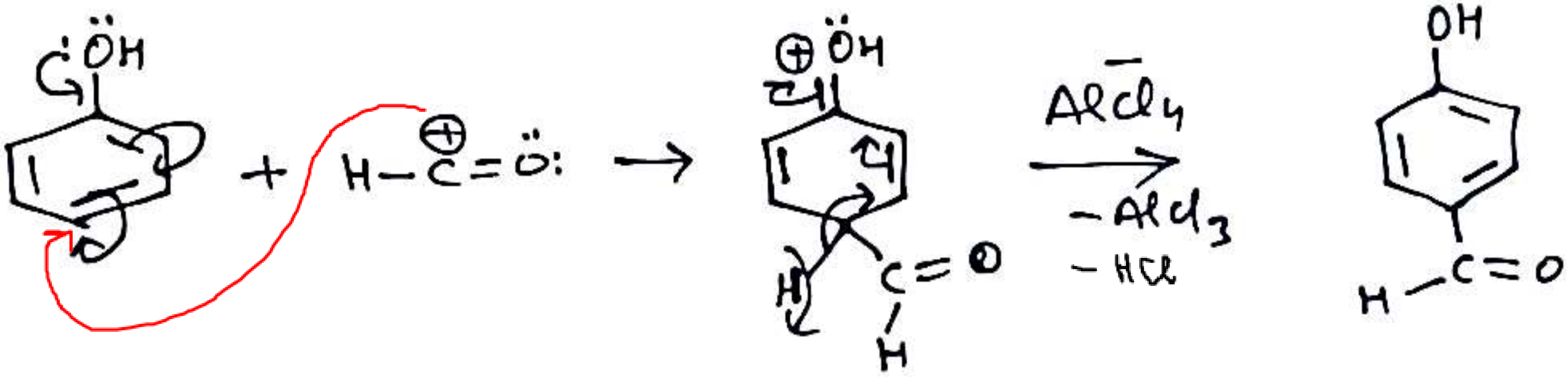
Chemical properties of Phenols

❖ Mechanism



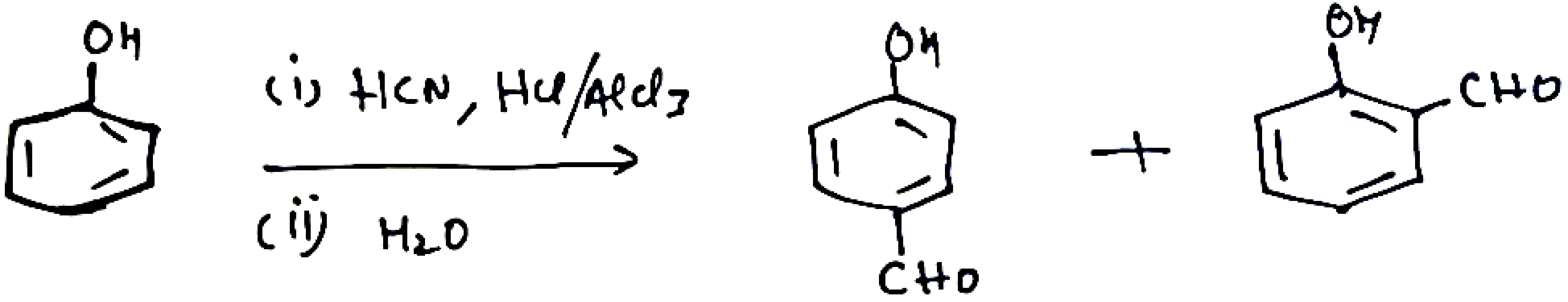
❖ Step 2

➢ **Attack of formyl cation on the para position of phenol and subsequent loss of proton**



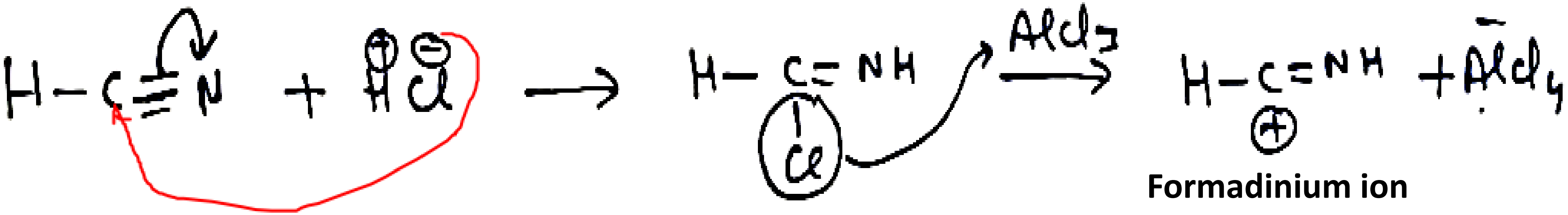
Chemical properties of Phenols

❑ Gattermann Aldehyde Synthesis



❖ Mechanism

➢ **Step 1** **Formation of Electrophile(Formaldinium ion)**



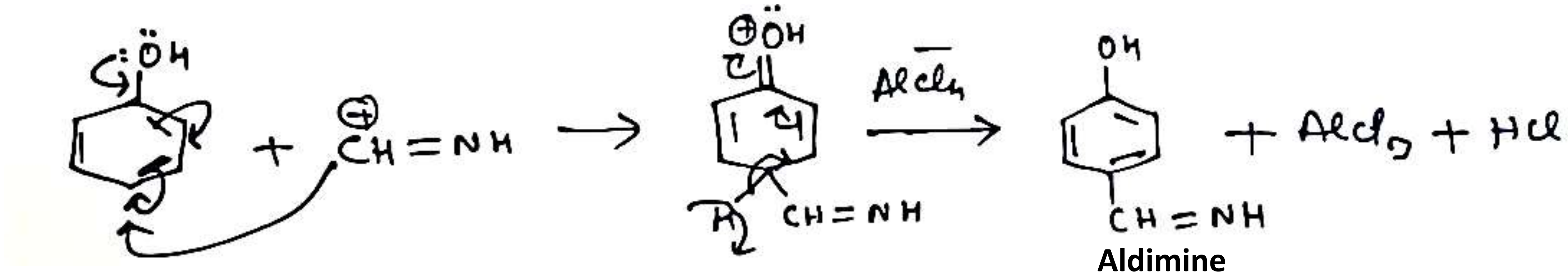
Formadinium ion

Chemical properties of Phenols

❑ Gattermann Aldehyde Synthesis

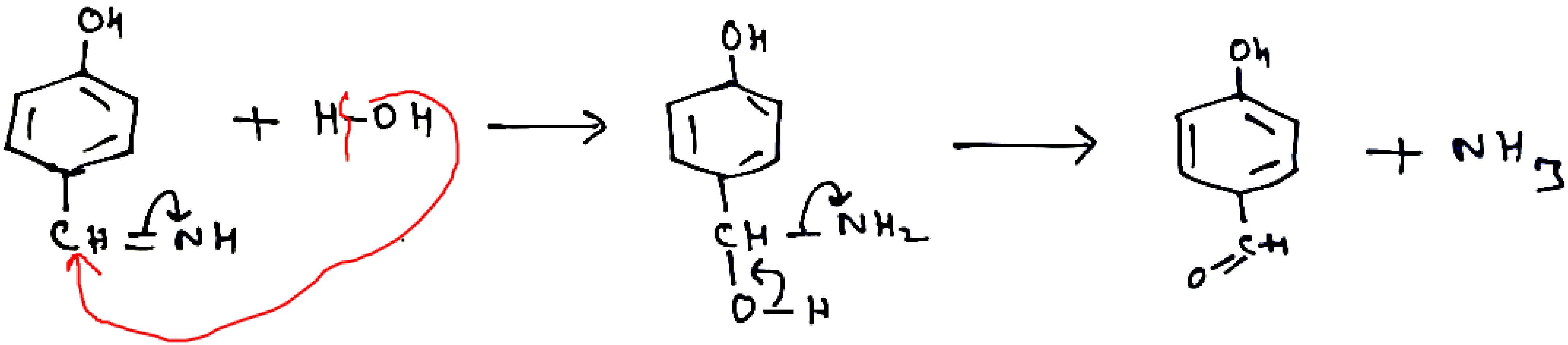
❖ Mechanism

➢ **Step 2 Attack of Formaldinium ion on para position of phenol**



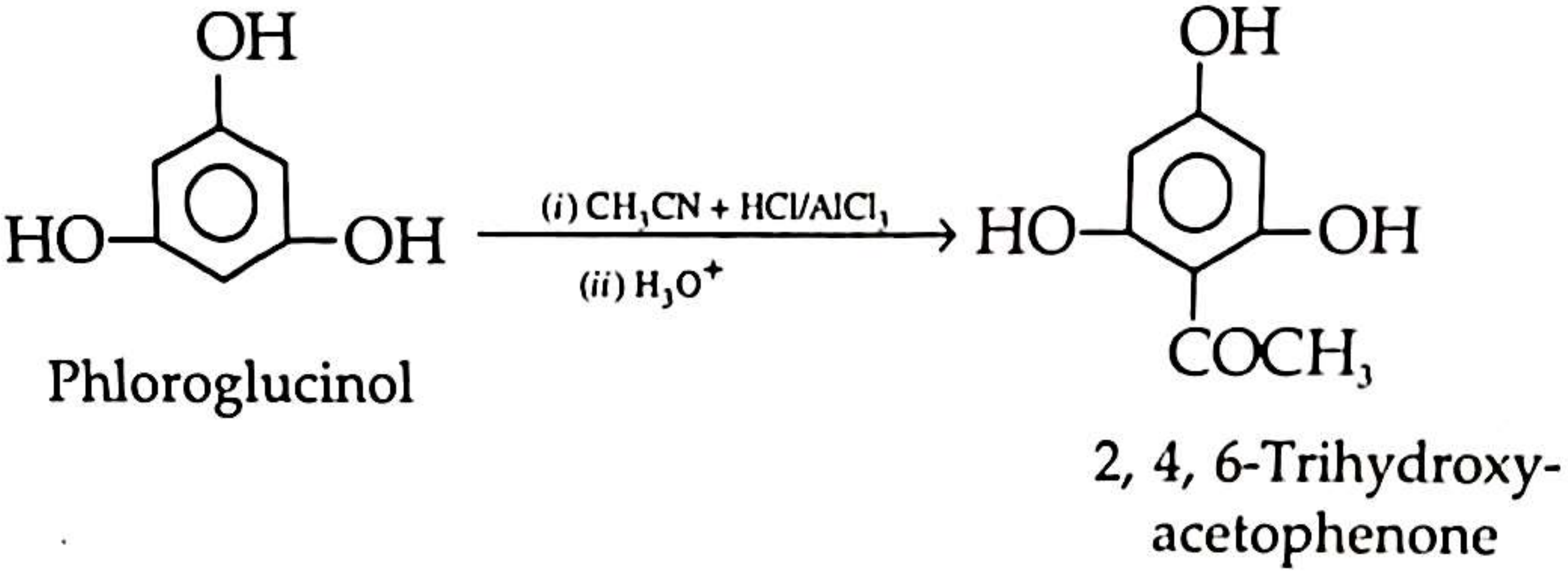
Aldimine

➢ **Step 3 Hydrolysis of imine to give phenolic aldehyde**



Chemical properties of Phenols

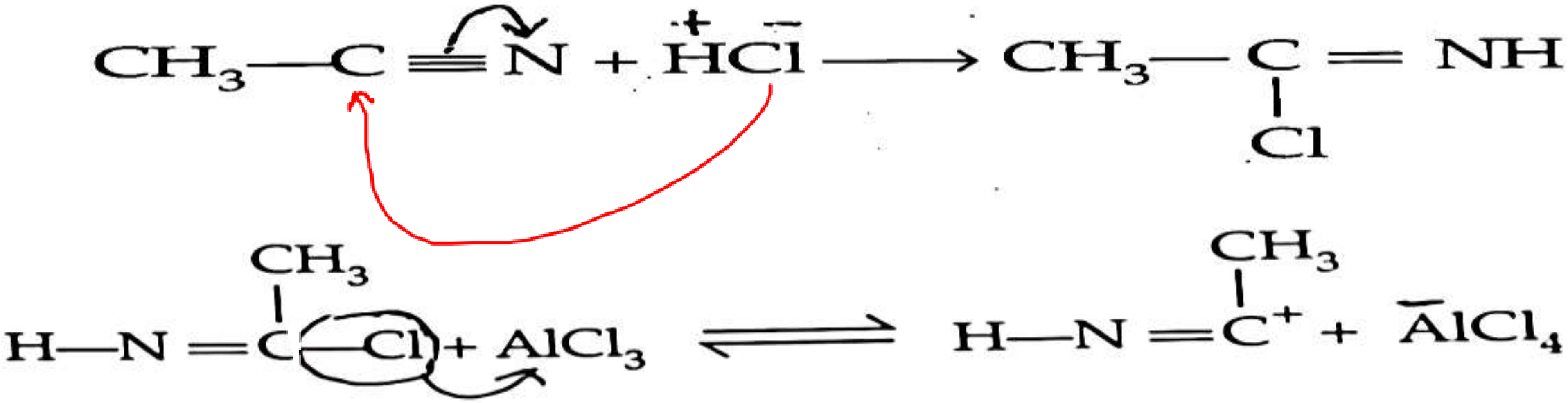
❑ Hauben Hoesch Reaction



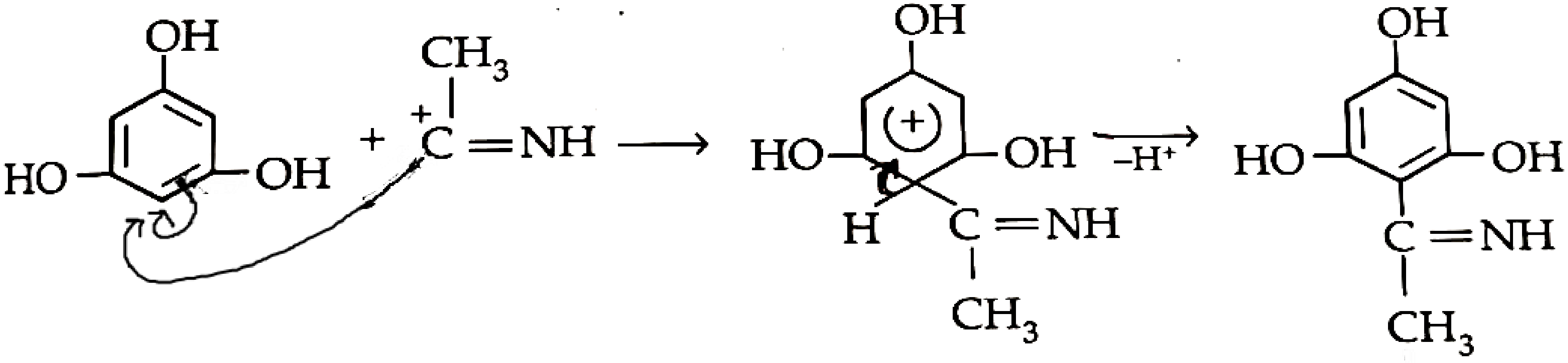
Chemical properties of Phenols

❑ Mechanism

- ❖ **Step 1**
- ➢ **Generation of electrophile**



- ❖ **Step 2**
- ❑ **Attack of electrophile to form ketimine**

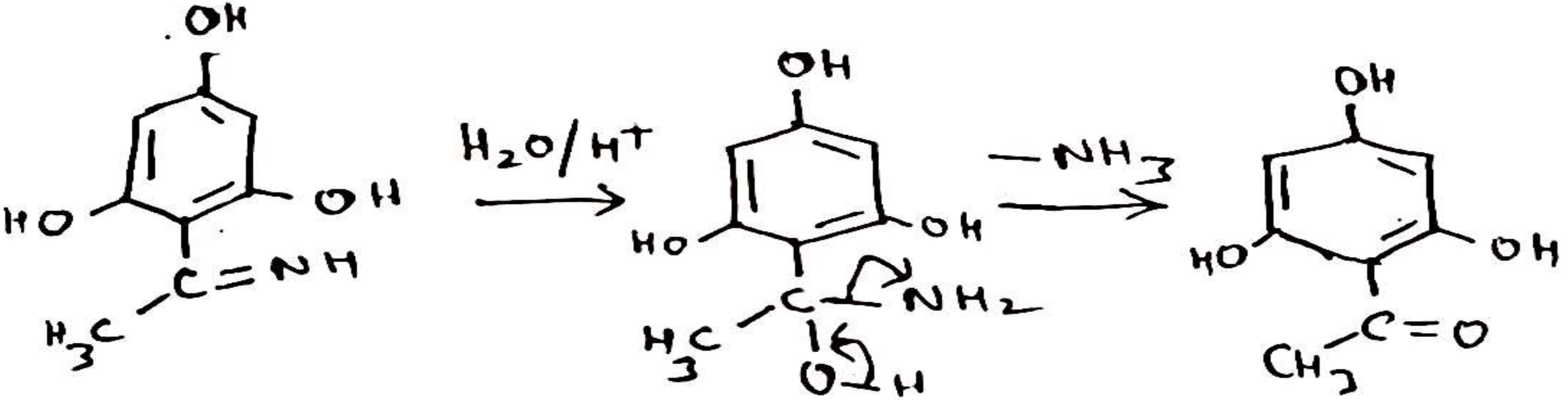


Chemical properties of Phenols

❑ Mechanism

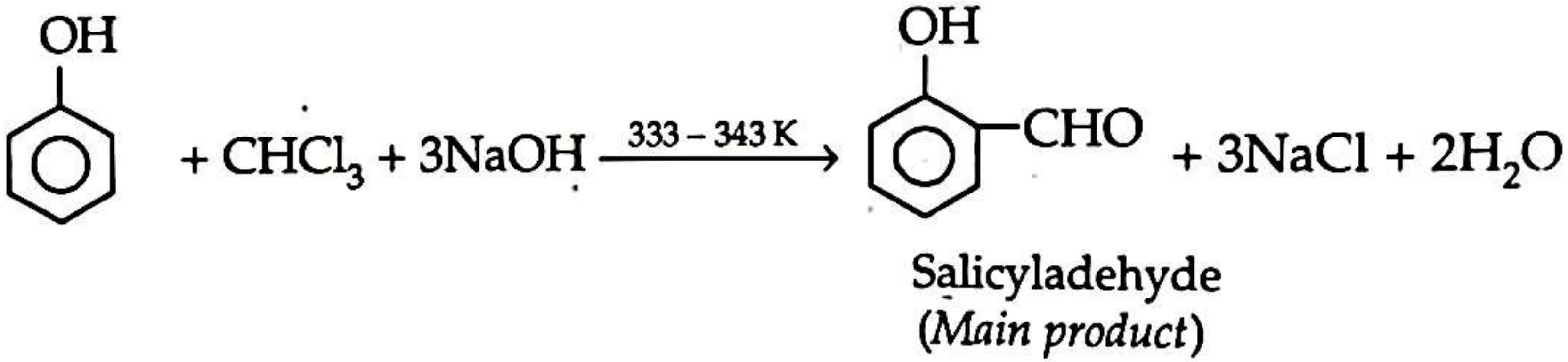
❖ Step 3

- ➢ **Hydrolysis of imine**



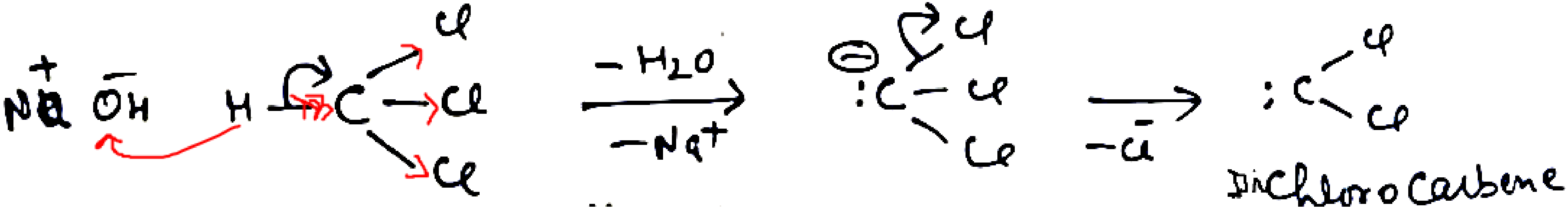
Chemical properties of Phenols

❑ Reimer Tiemann Reaction



❖ Mechanism

- **Step 1** Generation of electrophile

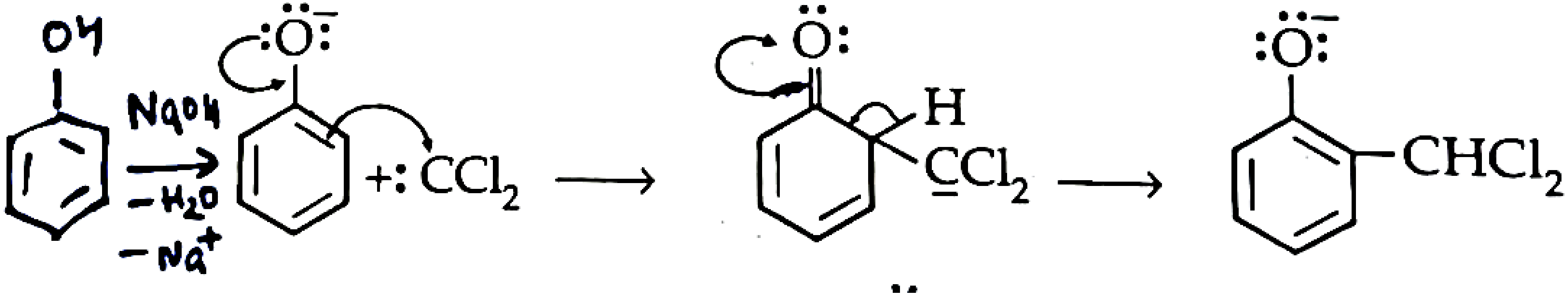


Chemical properties of Phenols

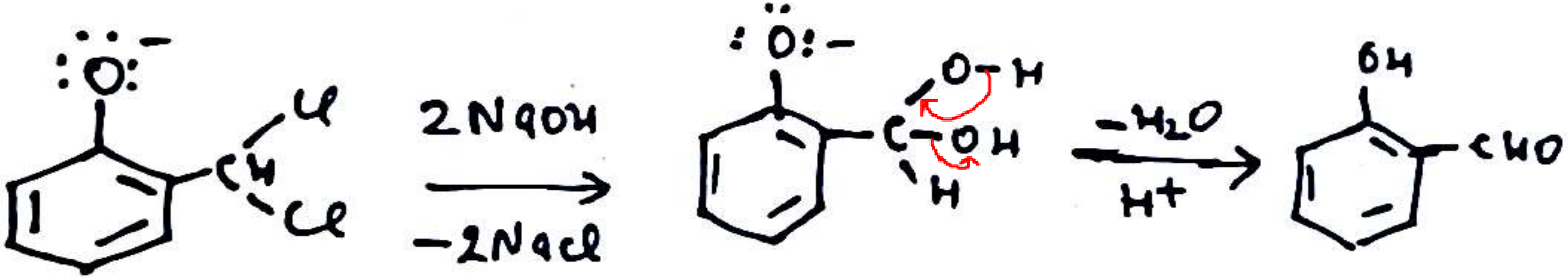
☐ Reimer Tiemann Reaction

❖ Mechanism

- **Step 2** Attack of electrophile on benzene ring

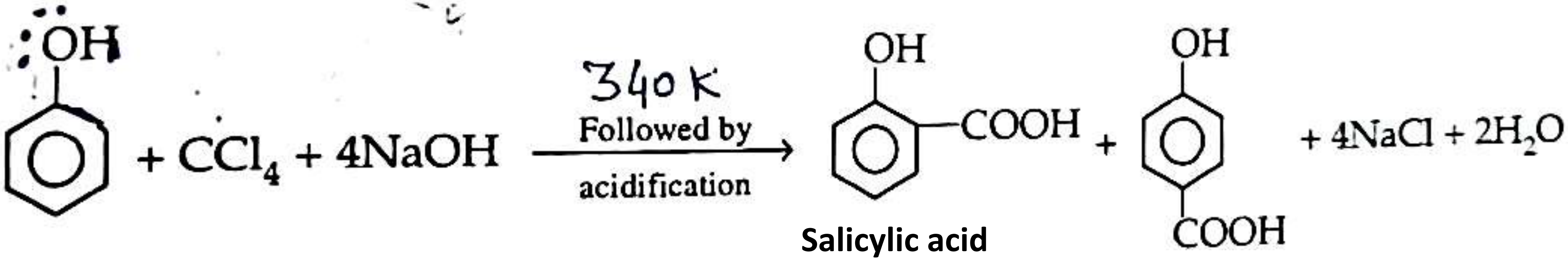


- **Step 3** Replacement of chlorine atoms with OH groups followed by loss of water



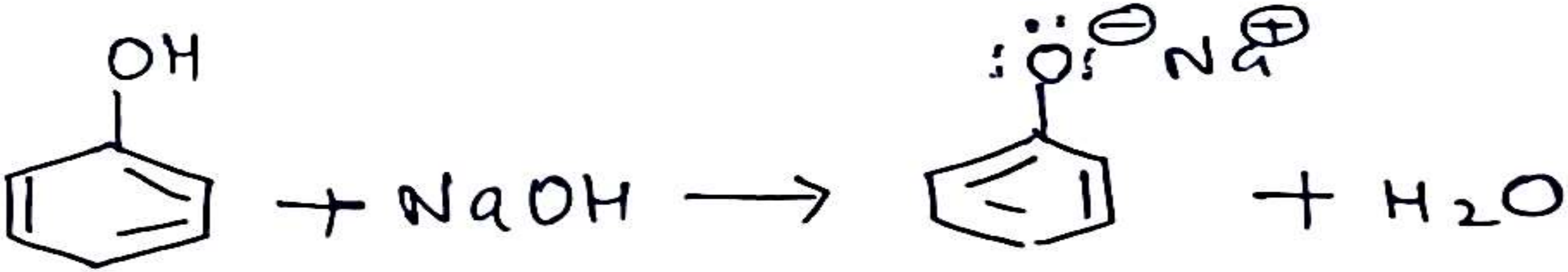
Chemical properties of Phenols

- ❑ **Reimer Tiemann Reaction can also be done with CCl_4**



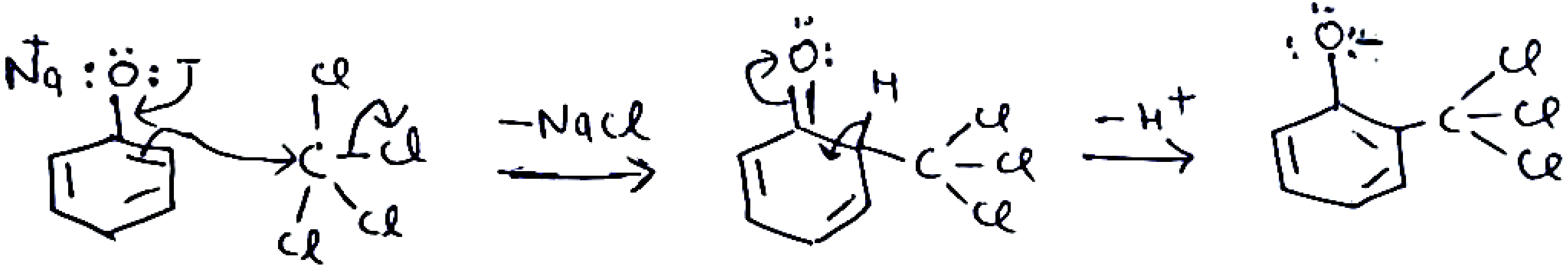
Salicylic acid

- ❖ **Mechanism**
- ❖ **Step 1**
- ➢ **Formation of Sodium phenoxide**

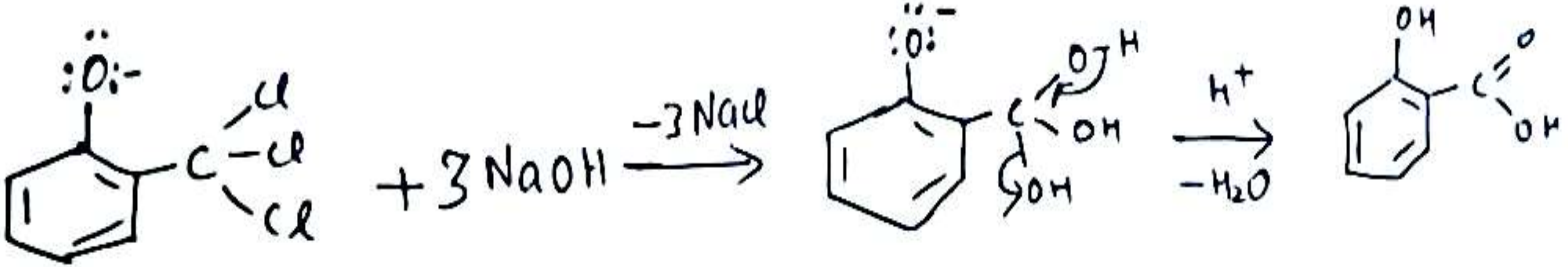


Chemical properties of Phenols

- ❑ **Reimer Tiemann Reaction can also be done with CCl_4 ……**
  - ❖ **Mechanism**
  - ➢ **Step 2** **Attack of Sodium phenoxide on CCl_4**

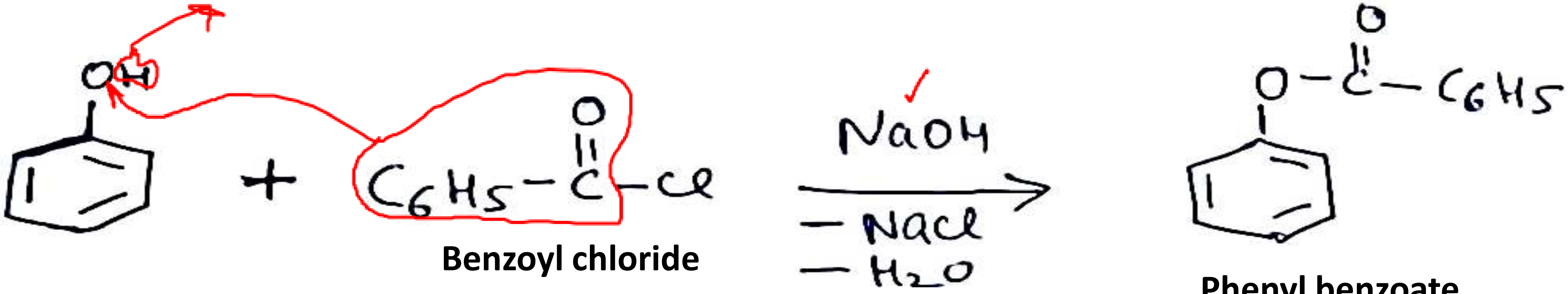


  - ➢ **Step 3** **Replacement of chlorine atoms with OH groups followed by loss of water and acidification**



Chemical properties of Phenols

❑ Schotten Baumann reaction

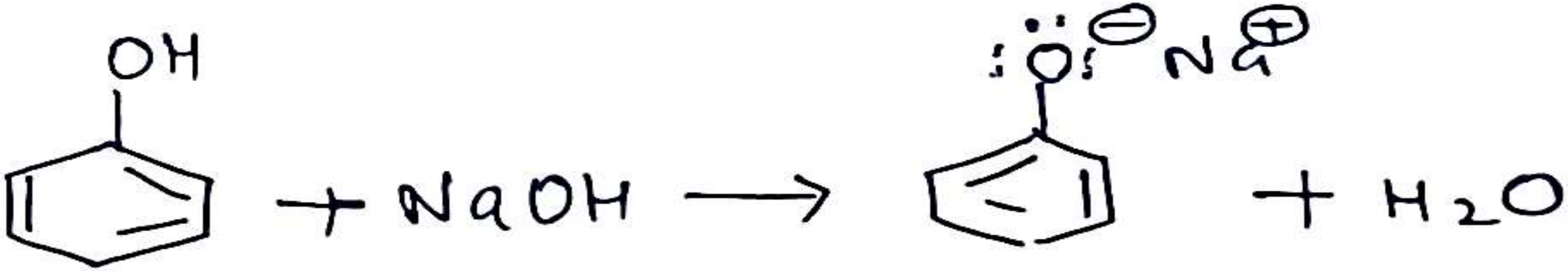


Benzoyl chloride

Phenyl benzoate

❖ **Mechanism**

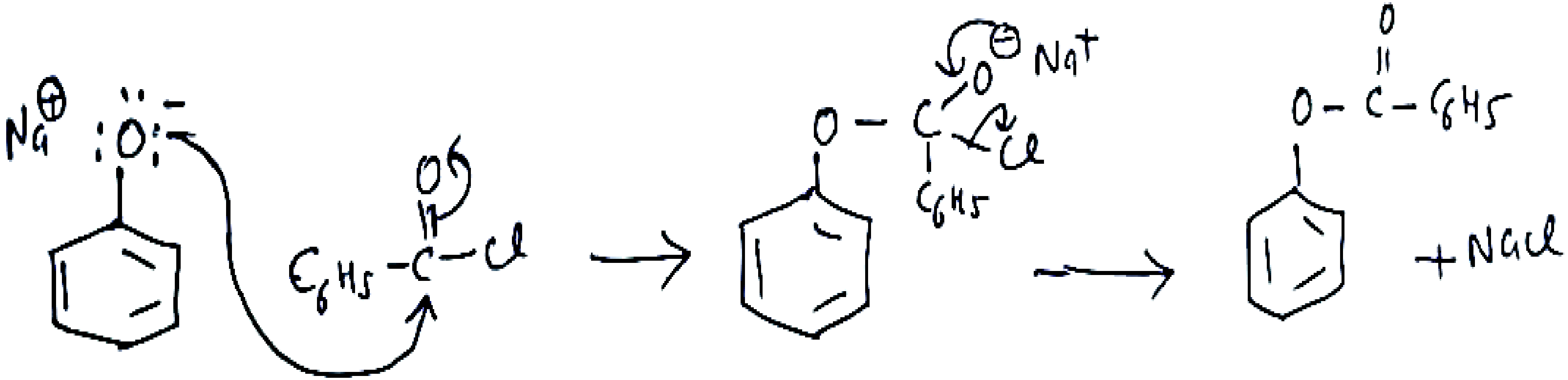
➢ **Step 1** **Formation of sodium phenoxide**



Chemical properties of Phenols

❑ Schotten Baumann reaction contd……..

- ❖ **Mechanism**
- ❖ **Step 2** **Attack of phenoxide ion on Benzoyl chloride followed by loss of Sodium chloride**



Questions

1. What happens when phenol is treated with $CHCl_3$ and aqueous NaOH solution at 343 K?
2. Name the reactive intermediate formed during Reimer Tieman reaction
3. How will you convert phenol in to salicylic acid? Name the reaction and give its mechanism?
4. C-O bond in phenols is shorter than in ethanol. Explain.
5. What is cumene? How can it be converted in to phenol? Give mechanism of the reaction involved.
6. Out of ortho and para nitrophenols which has greater boiling point and why?
7. What happens when phenol is treated with bromine water?