



PHENOLS

CHAPTER 18 XII FDC

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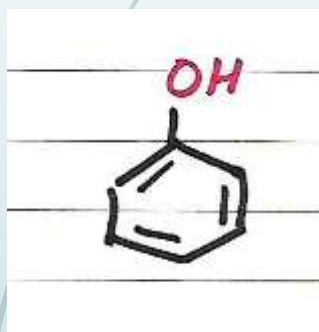
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PHENOLS

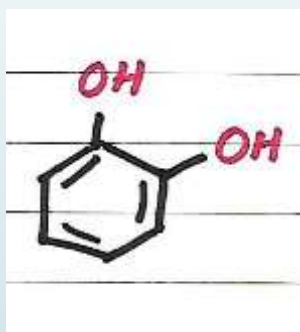
- Aromatic compounds containing one or more OH groups directly attached with carbon of benzene ring are called Phenols.
- Simplest phenol is Carboic Acid C_6H_5OH
- Term Phenol is derived from an old name of benzene – Phene
- Phenyl : C_6H_5

NOMENCLATURE OF PHENOLS

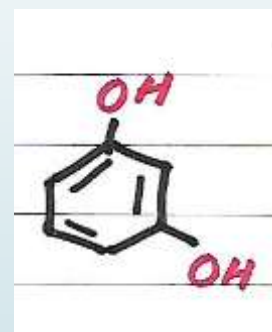
- In IUPAC –OH group is represented as hydroxyl. It is used as a prefix, while benzene part of the molecule is used as suffix.



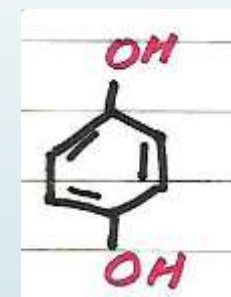
Phenol



1,2- dihydroxybenzene
O-hydroxyl phenol
(Catechol)

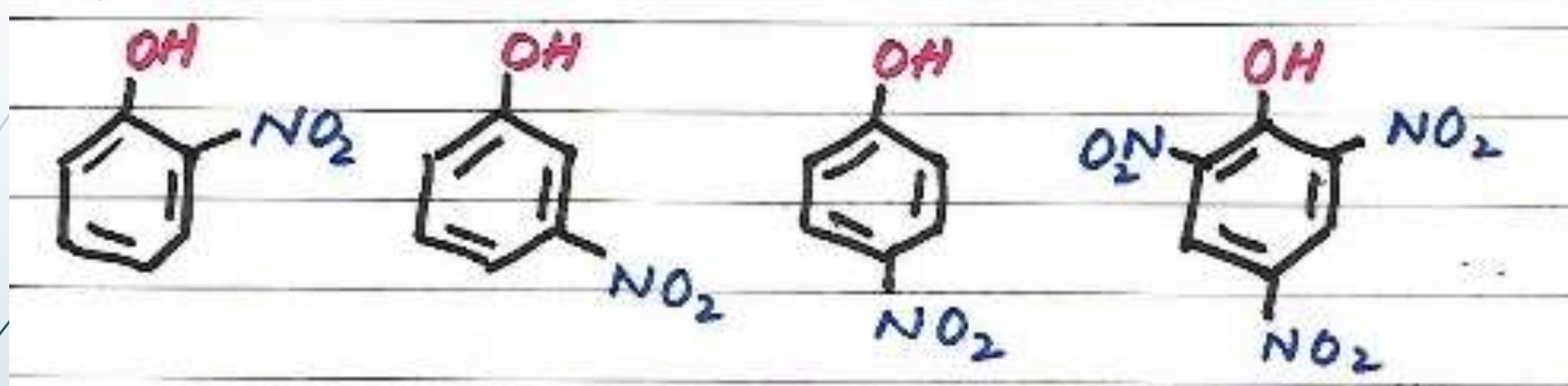


1,3- dihydroxybenzene
m-hydroxyl phenol
(Resorcinol)



1,4- dihydroxybenzene
p-hydroxyl phenol
(Hydroquinone)

NOMENCLATURE



2-nitrophenol
O-nitrophenol

3-nitrophenol
m-nitrophenol

4-nitrophenol
p-nitrophenol

2,4,6-trinitrophenol
Picric Acid

STRUCTURE OF PHENOLS

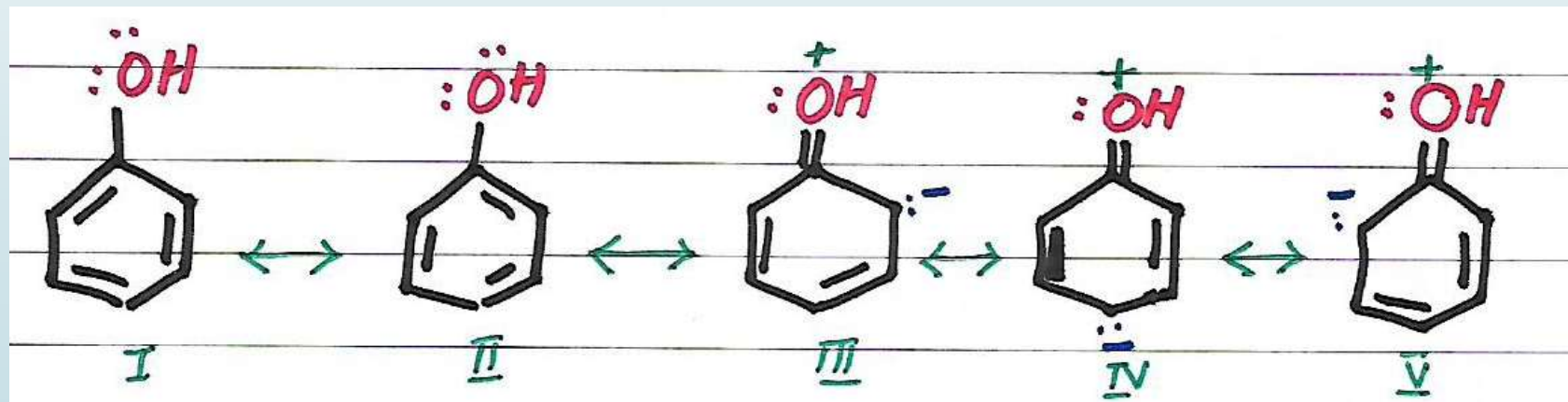
- The alcohol functional group consists of O atom bonded to sp^2 hybridized aromatic C atom and H atom via σ bond
- Both C-O and O-H bonds are polar
- Conjugation exist between an unshared electron pair of the O and Benzene Ring
- This results in, as compared to alcohols:
 - A shorter C-O bond
 - A more basic OH group
 - A more acidic OH proton

PHYSICAL PROPERTIES OF PHENOLS

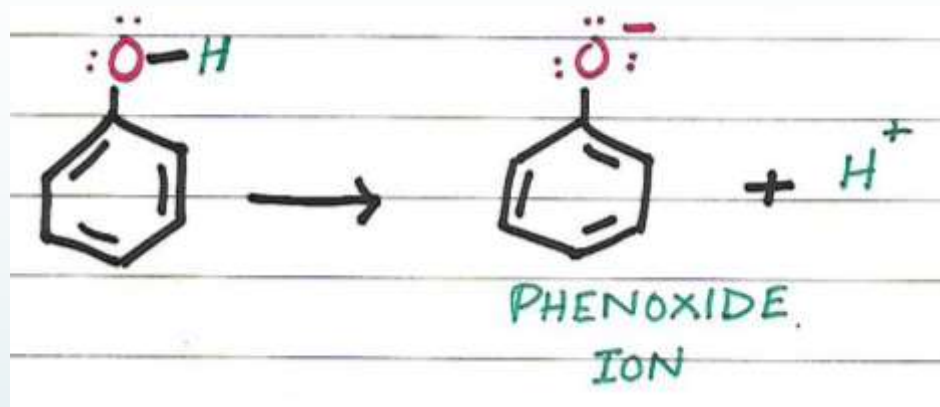
- Colorless, crystalline, poisonous solid with phenolic odor
- Melting point 41°C and Boiling Point 182°C
- Sparingly soluble in water forming pink solution at room temperature
- Completely soluble above 68.5°C
- Causes blisters on skin
- Used as disinfectants and in washrooms

ACIDITY OF PHENOLS

- Phenols are more acidic ($pK_a \approx 10$) than alcohol ($pK_a \approx 16-20$)
- Phenols are less acidic than **Carboxylic** acids ($pK_a \approx 5$)
- **COMPARISON OF ACIDITY OF PHENOLS AND ALCOHOLS**
 - Phenol exists as resonance hybrid of following structures



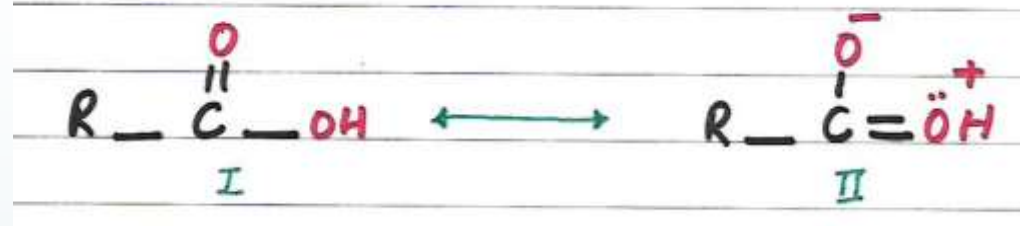
- Due to resonance O atom acquires a positive charge and hence attracts electron pair of O-H bond leading to the release of H^+



- Carbon atom of C-OH group of phenol (sp^2 hybridized) is more electrophilic than Carbon atom in Alcohols (sp^3 hybridized)
- In phenols, a greater inductive effect facilitated release of proton
- Thus phenols are more acidic than alcohols because resonance is impossible in alcohols
- Phenoxide is more resonance stabilized than phenol but in case of alcohol, alkoxide is not stable because there is no possibility for the delocalization of negative charge.

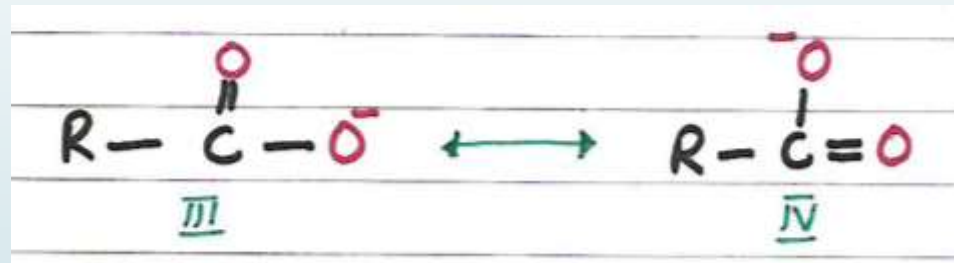
➤ COMPARISON OF ACIDITY OF PHENOLS AND CARBOXYLIC ACIDS

➤ Resonating structures of carboxylic acids:



➤ Carboxylic acids ionize as: $R-COOH \rightarrow R-COO^- + H^+$

➤ The carboxylate anion exhibits following resonating structures:

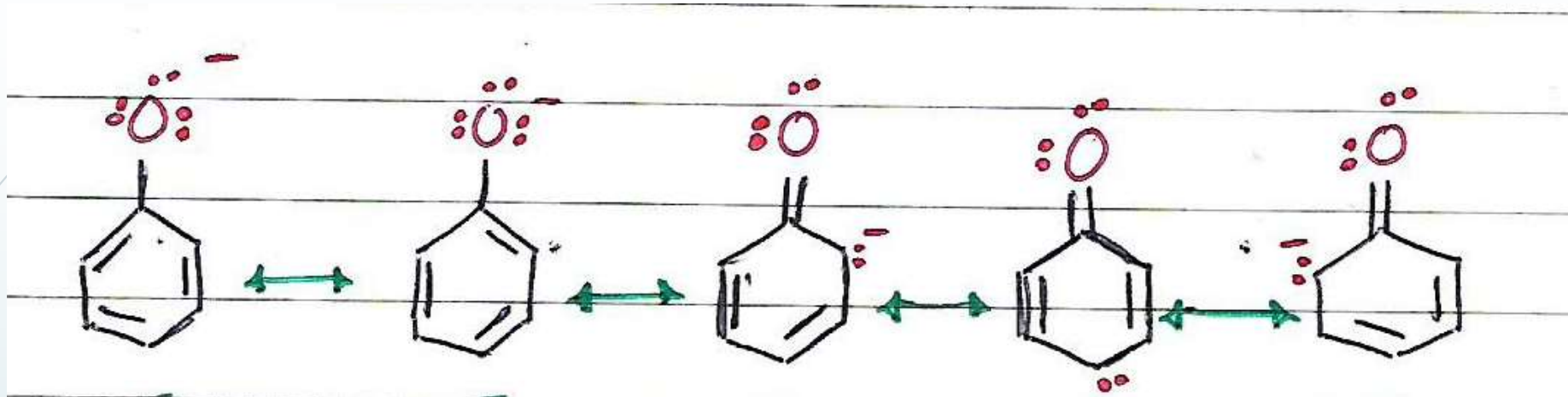


➤ The resonating structures of $RCOOH$ (I and II) are not equivalent and hence less stable

➤ The resonating structures of $RCOO^-$ ion (III and IV) are equivalent and hence more stable

➤ Thus $RCOOH$ have tendency to undergo ionization and form more stable carboxylate ion and proton

- The resonating structures of phenoxide ion are not equivalent as shown below:



- The resonating structures of RCOO^- ion are equivalent. Hence RCOO^- ion is relatively more resonance stabilized than Phenoxide ion.
- Thus a carboxylic acid is more acidic than a phenol.
- **RELATIVE ACIDITY ORDER OF SOME COMMON COMPOUNDS:**
 $\text{RCOOH} > \text{H}_2\text{CO}_3 > \text{C}_6\text{H}_5\text{OH} > \text{H}_2\text{O} > \text{ROH}$



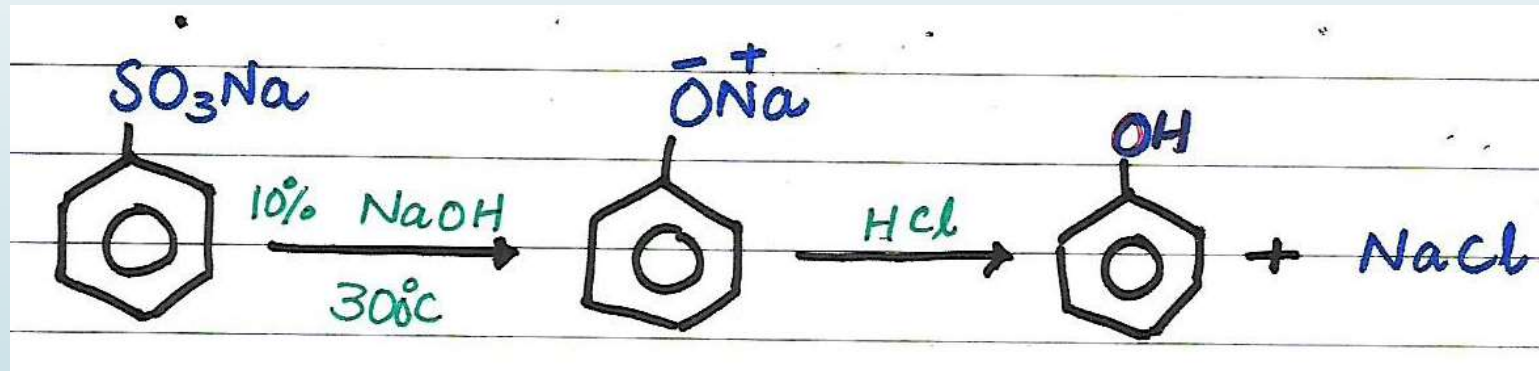
➤ EFFECT OF SUBSTITUENTS ON THE ACIDITY OF PHENOLS

- Electron attracting substituents tend to disperse negative charge of the phenoxide ion thus stabilize the ion and increase the acidity of phenols.
- Electron releasing substituents tend to intensify the charge, destabilize the ion, diminish the resonance and decrease the acidity.

PREPARATION OF PHENOL

► REACTION OF SODIUM SALT OF BENZENE SULFONIC ACID WITH NaOH:

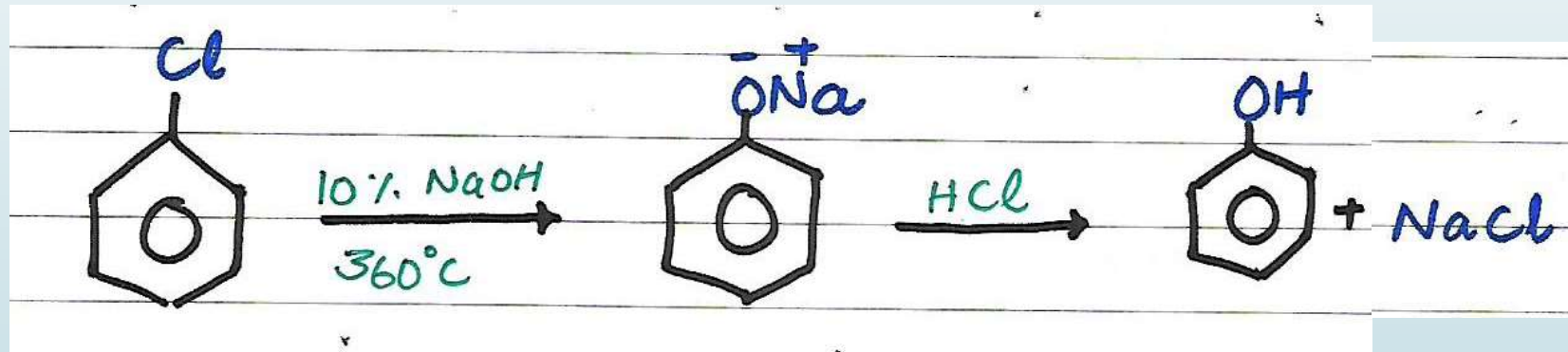
- Sodium benzene sulfonate on fusion with strong alkali like NaOH at 300°C give sodium phenoxide which on treatment with HCl gives phenol



PREPARATION OF PHENOL

► BASE HYDROLYSIS OF CHLOROBENZENE (DOW'S METHOD)

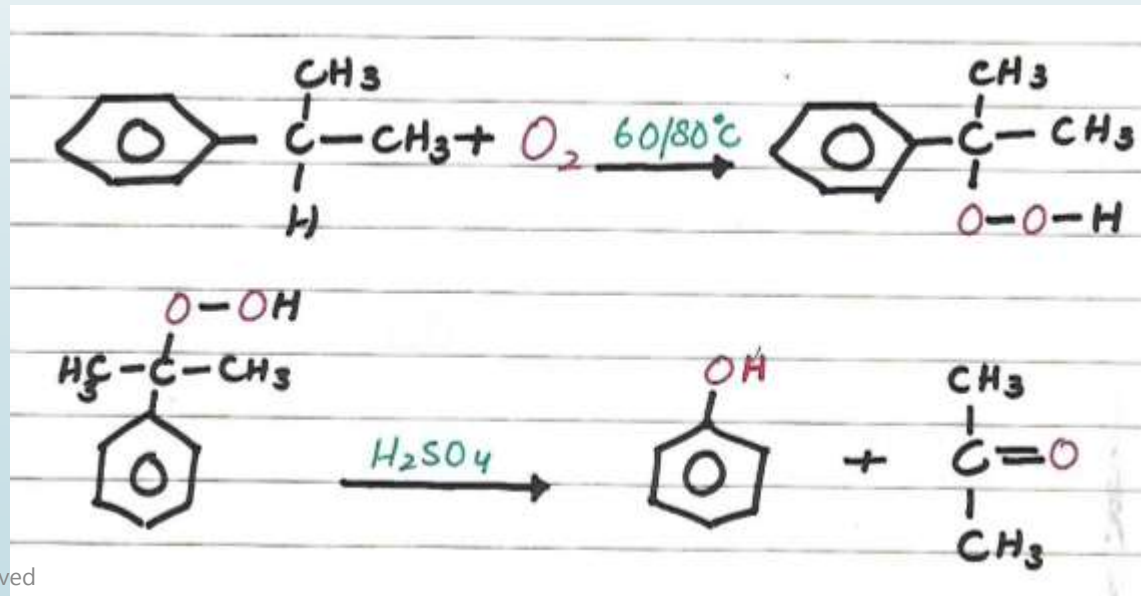
- Chlorobenzene is hydrolysed by heating with 10% NaOH at 360°C under high pressure to form sodium phenoxide which on treating with HCl gives phenol



PREPARATION OF PHENOL

► ACIDIC OXIDATION OF CUMENE

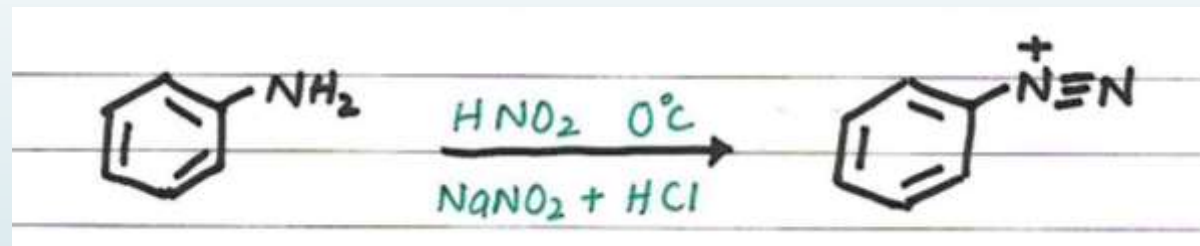
- It is recently developed commercial method for preparation of phenol. Cumene is oxidized by atmospheric oxygen in presence of metal catalyst into Cumene Hydroperoxide.
- The hydroperoxide is converted into phenol through acid catalyzed rearrangement



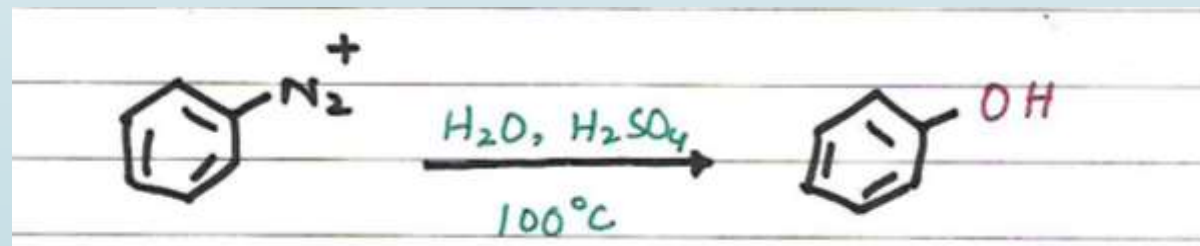
PREPARATION OF PHENOL

► Preparation of phenol from Aryl Diazonium salts

- Aryl diazonium salts are prepared by reaction of aryl amines with nitrous acid

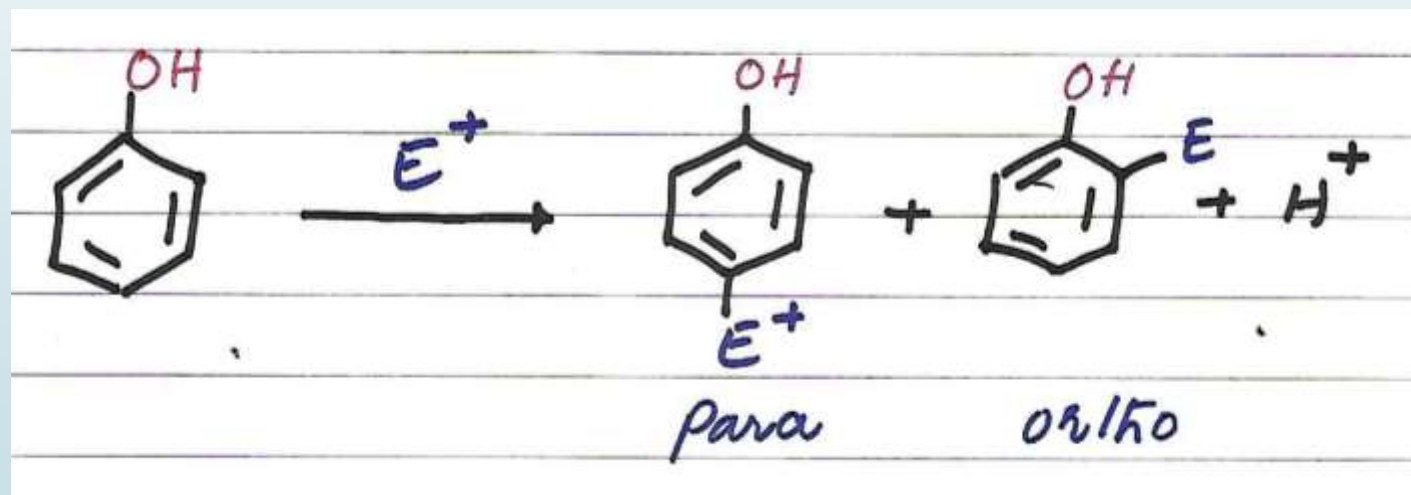


- Aryl diazonium salts can be converted into phenols using $\text{H}_2\text{O}/\text{H}_2\text{SO}_4/$ heat



REACTIVITY AND REACTIONS OF PHENOLS

- Phenols are very reactive towards electrophilic aromatic substitution.
- OH group is strongly activating ortho-/para- directing group.
- **ELECTROPHILIC AROMATIC SUBSTITUTION**

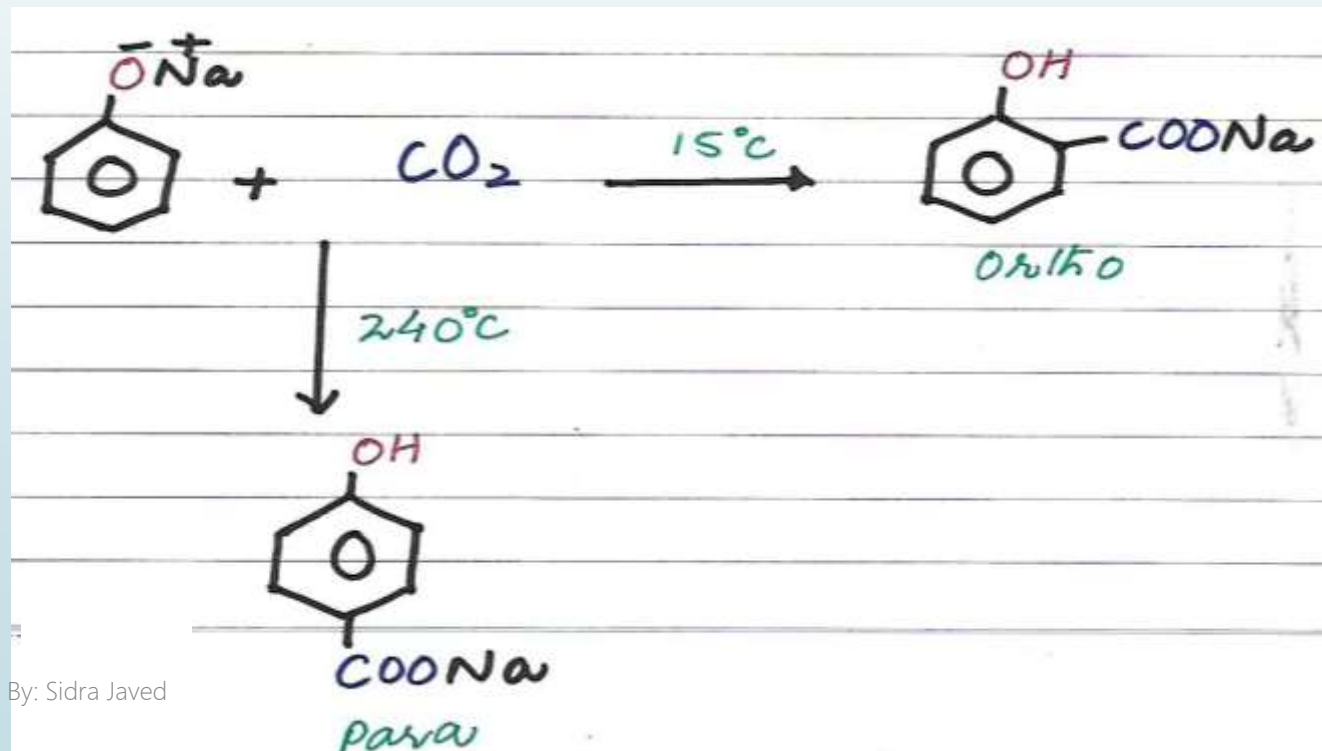


- Strong activation means milder reaction conditions than those used for benzene.

Reaction	Benzene	Phenol
Nitration	Conc. HNO_3 / H_2SO_4	Dil. HNO_3 in H_2O or CH_3COOH
Sulfonation	H_2SO_4 or $\text{SO}_3/\text{H}_2\text{SO}_4$	Conc. H_2SO_4
Halogenation	X_2/Fe or FeX_3	X_2
Alkylation	RCl/AlCl_3	ROH/H^+ or RCl/AlCl_3
Acylation	$\text{RCOCl}/\text{AlCl}_3$	$\text{RCOCl}/\text{AlCl}_3$
Nitrosation	-	Aq. NaNO_2/H^+

- Phenols are so activated that poly-substitution can be a problem.
- **OXIDATION OF PHENOLS**
- Phenols are very reactive towards oxidizing agent.
- The oxidation takes place through several steps eventually destroying the ring.

- REACTION WITH SODIUM METAL / CARBOXYLATION OF PHENOLS (KOLBE-SCHMITT REACTION)
- "The reaction of sodium salt of phenol with CO_2 is called Kolbe Reaction. It is carbonation of phenol."
- At low temperature Sodium salicylate (sodium-o-hydroxyl benzoate) is formed, at higher temperature o-product is isomerizes to p-isomer
- CO_2 act as electrophilic center in this reaction. Acidification of the salt gives corresponding hydroxyl acid.



DIFFERENCE BETWEEN ALCOHOLS AND PHENOLS

ALCOHOL

- OH group is attached to an alkyl group
- Hydroxyl derivatives of alkane
- The compounds in which one hydrogen of water is replaced by an alkyl group
- General formula ROH
- Lower alcohols are colorless liquids
- They characteristics sweet smell and burning taste
- $pK_a \approx 16 - 20$
- Readily soluble in water but solubility decreases in higher alcohols
- Alcohols react in two ways:
 - Reaction in C-O bond breaks
 - Reaction in O-H bond breaks

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PHENOL

- OH group is attached to an aryl group
- Hydroxyl derivatives of benzene
- The compounds in which one hydrogen of water is replaced by an aryl group
- General formula C_6H_5OH
- Colorless crystalline deliquescent solids (M.P $41^\circ C$)
- They have a characteristics phenolic odor
- $pK_a \approx 10$
- Sparingly soluble in water forming a pink solution but completely soluble above $68.5^\circ C$
- Phenolate ions have resonance structures but alcohols do not have resonance structures



The End

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