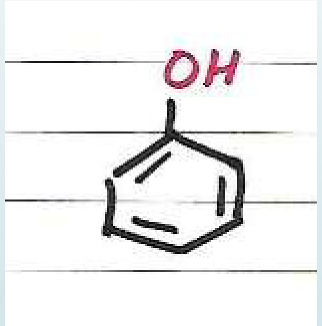
PHENOLS

PHENOLS

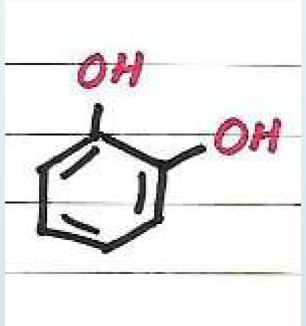
- Aromatic compounds containing one or more OH groups directly attached with carbon of benzene ring are called Phenols.
- Simplest phenol is Carbolic Acid C_6H_5OH
- Term Phenol is derived from an old name of benzene – Phene
- Phenyl : C_6H_5

NOMENCLATURE OF PHENOLS

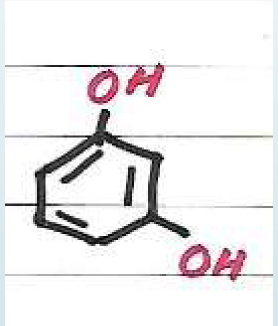
☐ In IUPAC –OH group is represented as hydroxyl. It is used as a prefix, while benzene part of the molecule is used as suffix.



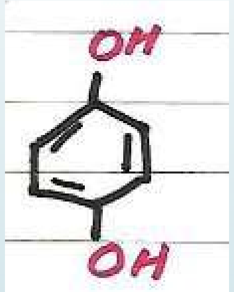
Phenol



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

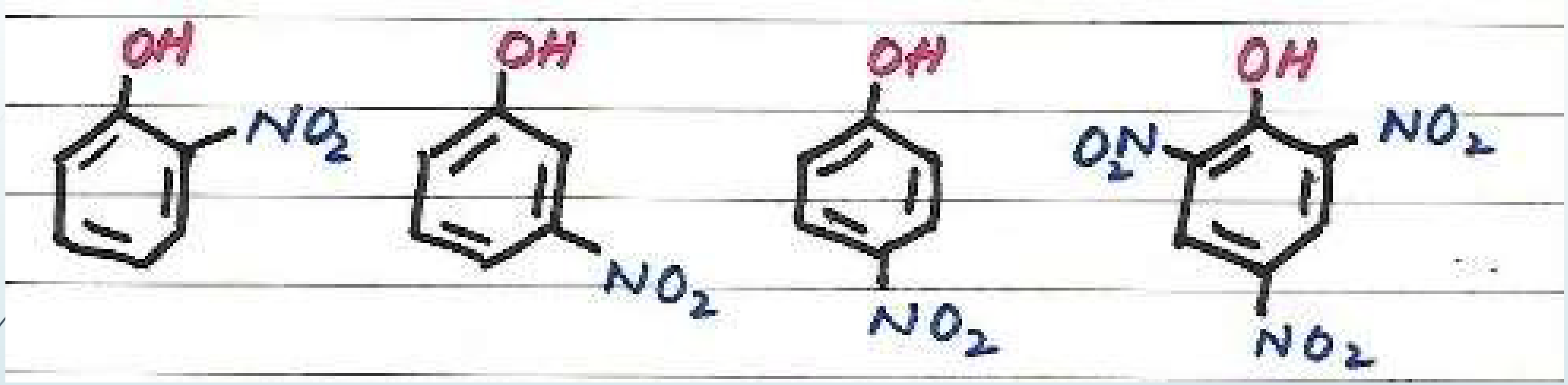


1,3- dihydorxybenzene
m-hydroxyl phenol
(Resorcinol)



1,4- dihydorxybenzene
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

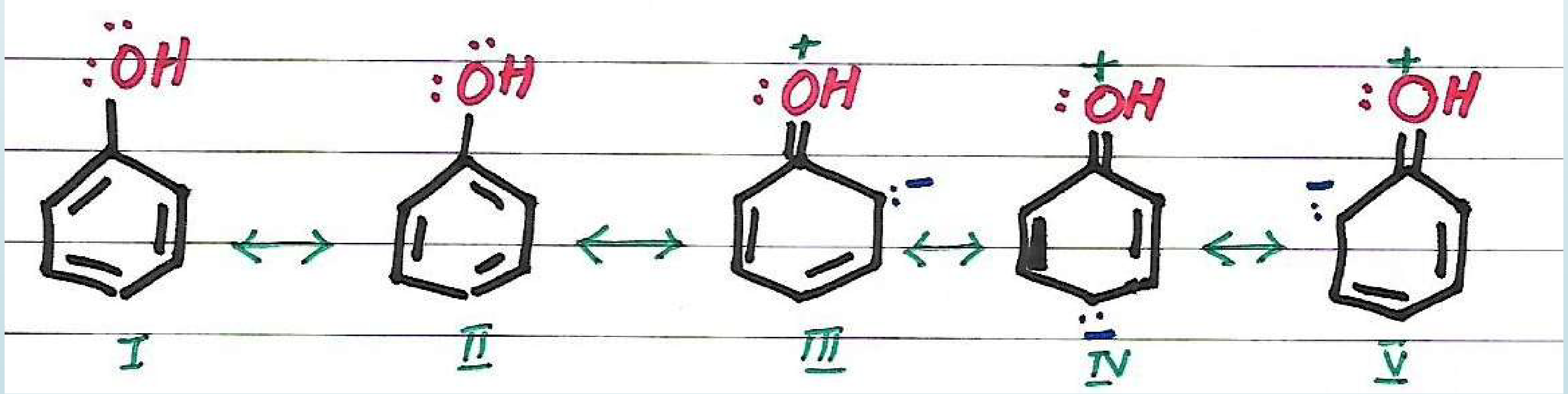
- ☐ The alcohol functional group consists of O atom bonded to sp^2 hybridized aromatic C atom and H atom via σ bond
- ☐ Both C-O and O-H bonds are polar
- ☐ Conjugation exist between an unshared electron pair of the O and Benzene Ring
- ☐ This results in, as compared to alcohols:
  - ☐ A shorter C-O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

PHYSICAL PROPERTIES OF PHENOLS

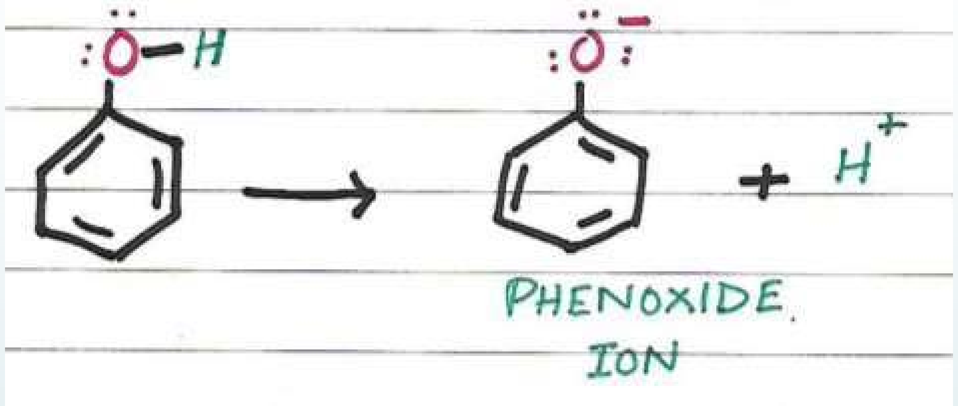
- Colorless, crystalline, poisonous solid with phenolic odor
- Melting point 41^{o}C and Boiling Point 182^{o}C
- Sparingly soluble in water forming pink solution at room temperature
- Completely soluble above 68.5^{o}C
- Causes blisters on skin
- Used as disinfectants and in washrooms

ACIDITY OF PHENOLS

- ☐ Phenols are more acidic (pKa ≈ 10) than alcohol (pKa ≈ 16-20)
- ☐ Phenols are less acidic than **Carboxylic** acids (pKa ≈ 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^+



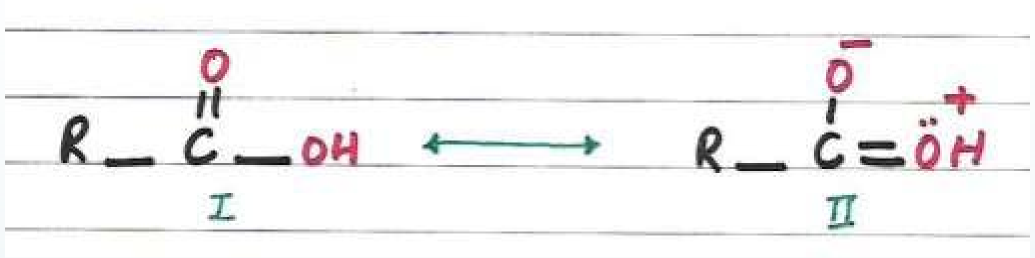
☐ Carbon atom of C-OH group of phenol (sp^2 hybridized) is more electrophilic than Carbon atom in Alcohols (sp^3 hybridized)

☐ In phenols, a greater inductive effect facilitated release of proton

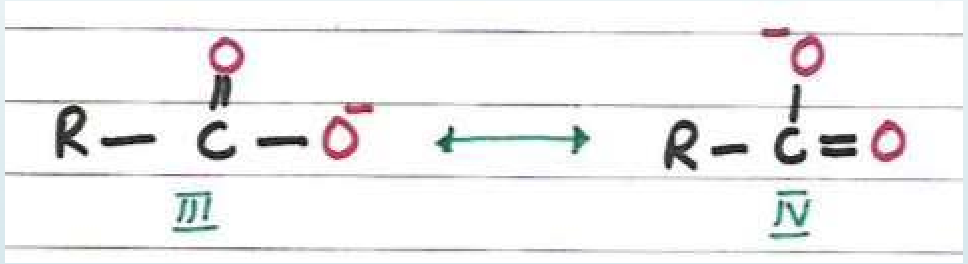
☐ Thus phenols are more acidic than alcohols because resonance is impossible in alcohols

☐ 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:

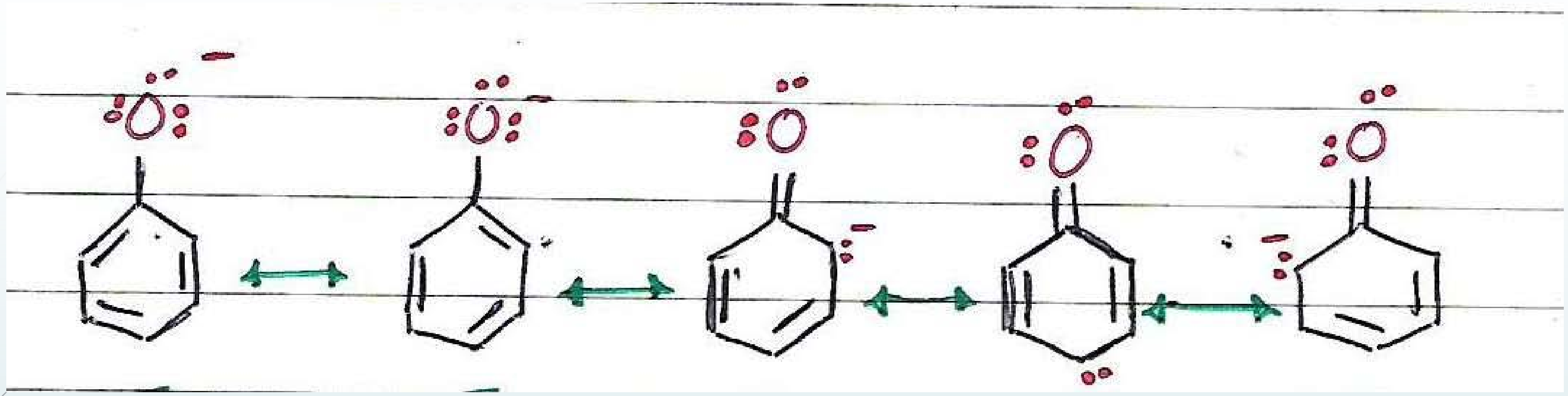


- Carboxylic acids ionize as: R-COOH → $R\text{-}COO^{-} + H^{+}$
- The carboxylate anion exhibits following resonating structures:



- 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:



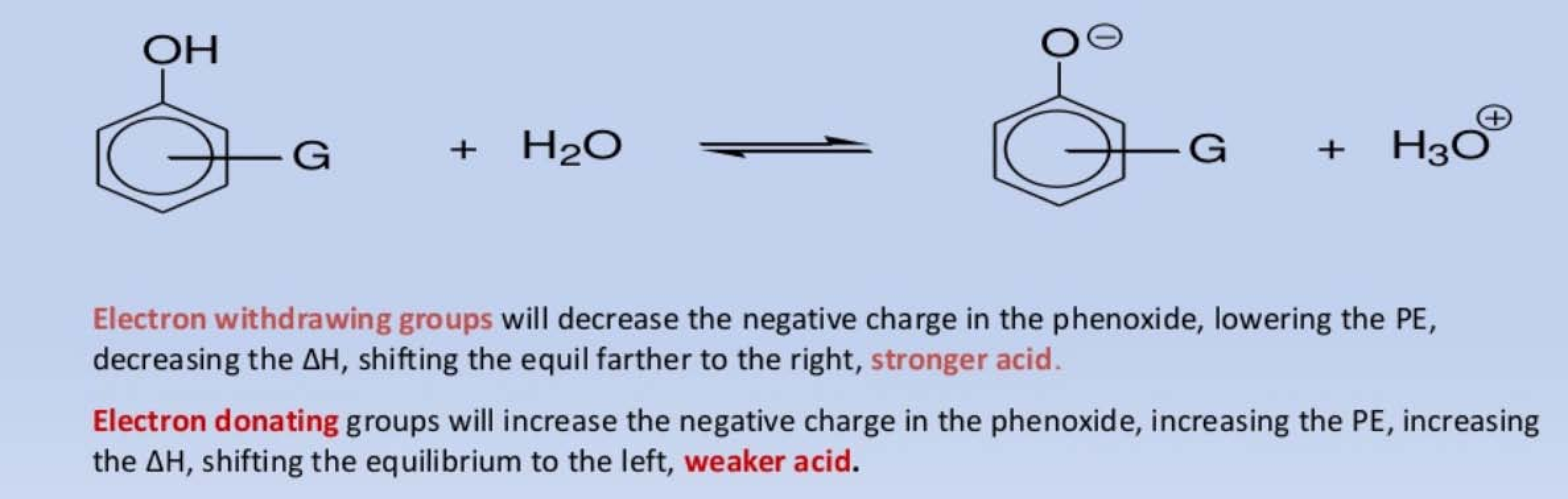
☐ The resonating structures of $RCOO^-$ ion are equivalent. Hence $RCOO^-$ ion is relatively more resonance stabilized that Phenoxide ion.

☐ Thus a carboxylic acid is more acidic than a phenol.

☐ **RELATIVE ACIDITY ORDER OF SOME COMMON COMPOUNDS:**

$RCOOH > H_2CO_3 > C_6H_5OH > H_2O > ROH$

- ☐ 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.

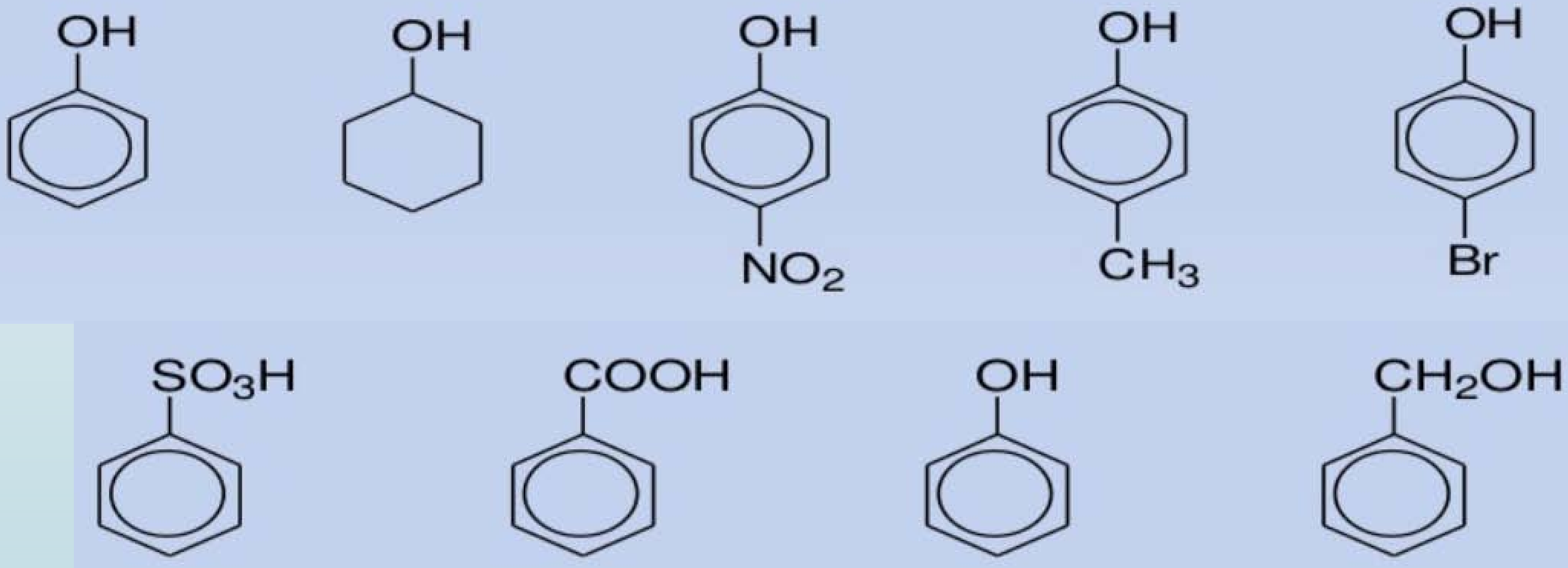


Electron withdrawing groups will decrease the negative charge in the phenoxide, lowering the PE, decreasing the ΔH, shifting the equil farther to the right, stronger acid.

Electron donating groups will increase the negative charge in the phenoxide, increasing the PE, increasing the ΔH, shifting the equilibrium to the left, **weaker acid.**

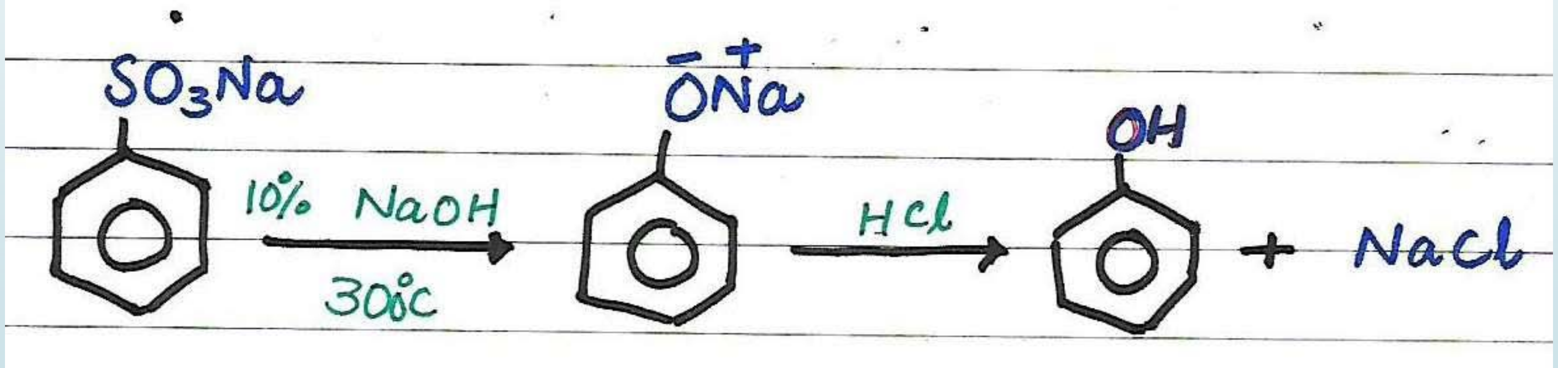
☐ EFFECT OF SUBSTITUENTS ON THE ACIDITY OF PHENOLS

Number the following acids in decreasing order of acid strength (let # 1 = most acidic, etc.)



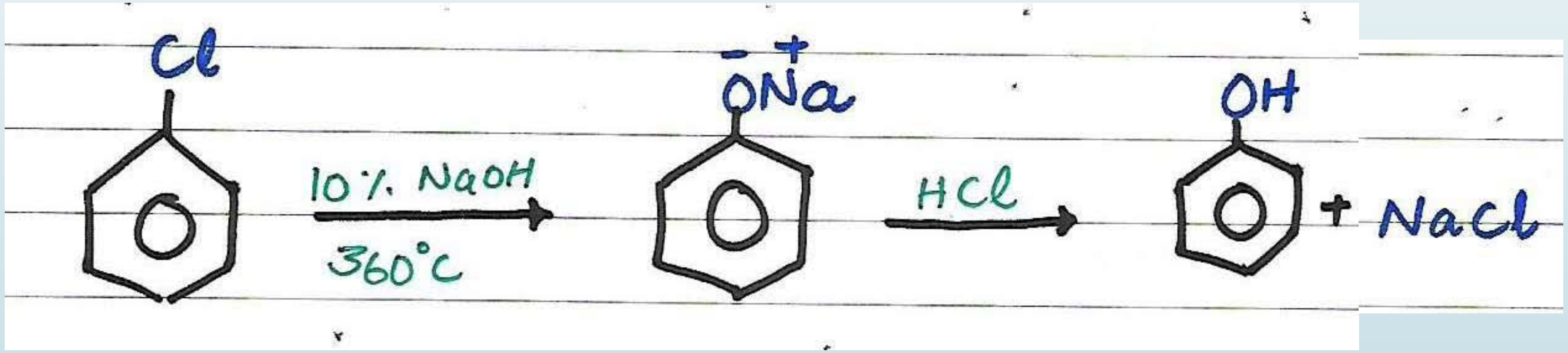
PREPARATION OF PHENOL

- ☐ **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



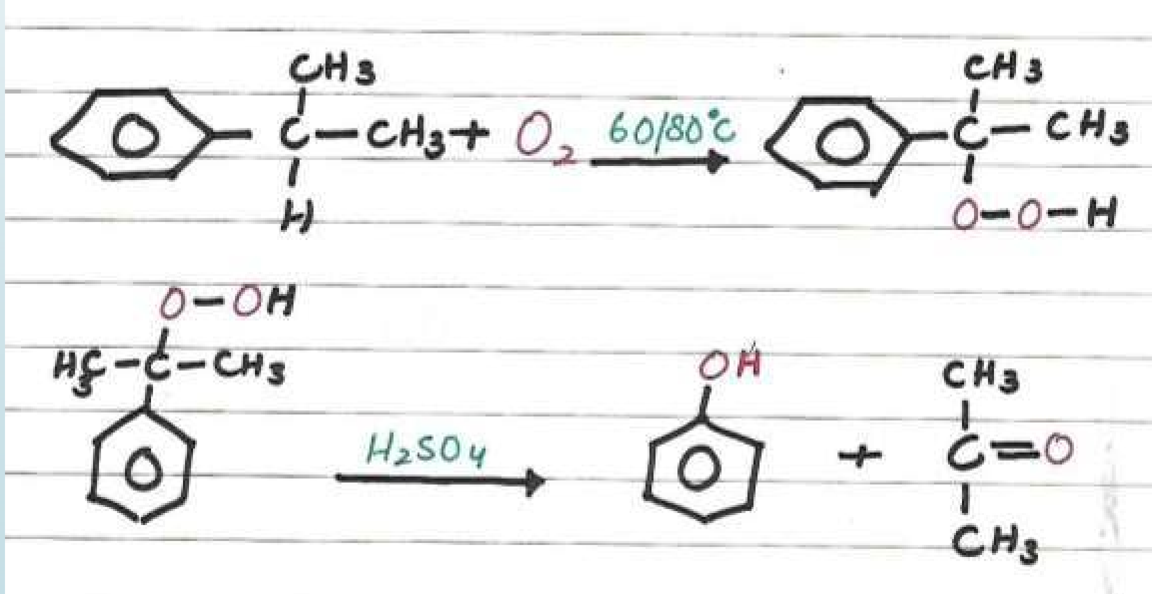
PREPARATION OF PHENOL

- **BASE HYDROLYSIS OF CHLOROBENZEN (DOW'S METHOD)**
  - Chlorobenzene is hydrolysed by heating with 10% NaOH at 360^{o}C under high pressure to form sodium phenoxide which on treating with HCl gives phenol



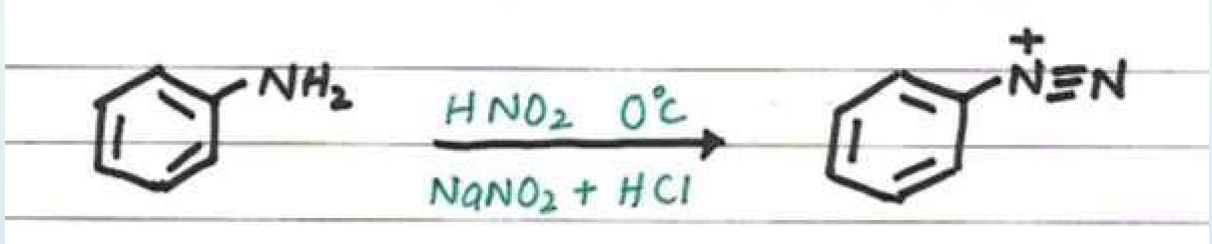
PREPARATION OF PHENOL

- ☐ **ACIDIC OXIDATION OF CUMENE**
  - ☐ It is recently developed commercial method for preparation of phenol. Cumene is oxidized by atmospheric oxygen is presence of metal catalyst into Cumene Hydroperoxide.
  - ☐ The hydroperoxide is converted into phenol through acid catalyzed arrangement

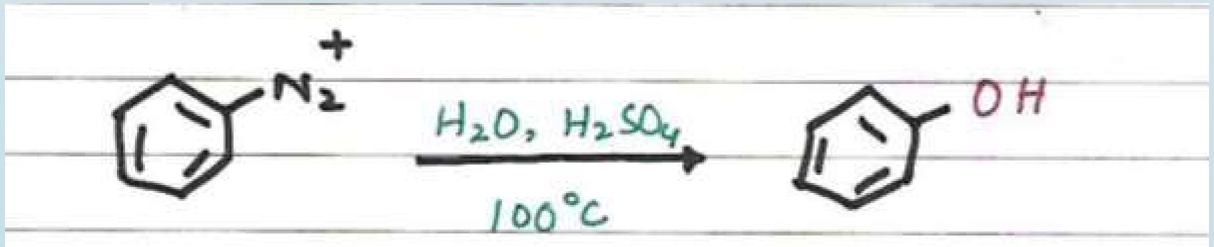


PREPARATION OF PHENOL

- **Preparation of phenol from Aryl Diazonium salts**
  - Aryl diazonium salts are prepared by reaction of aryl amines with nitrous acid

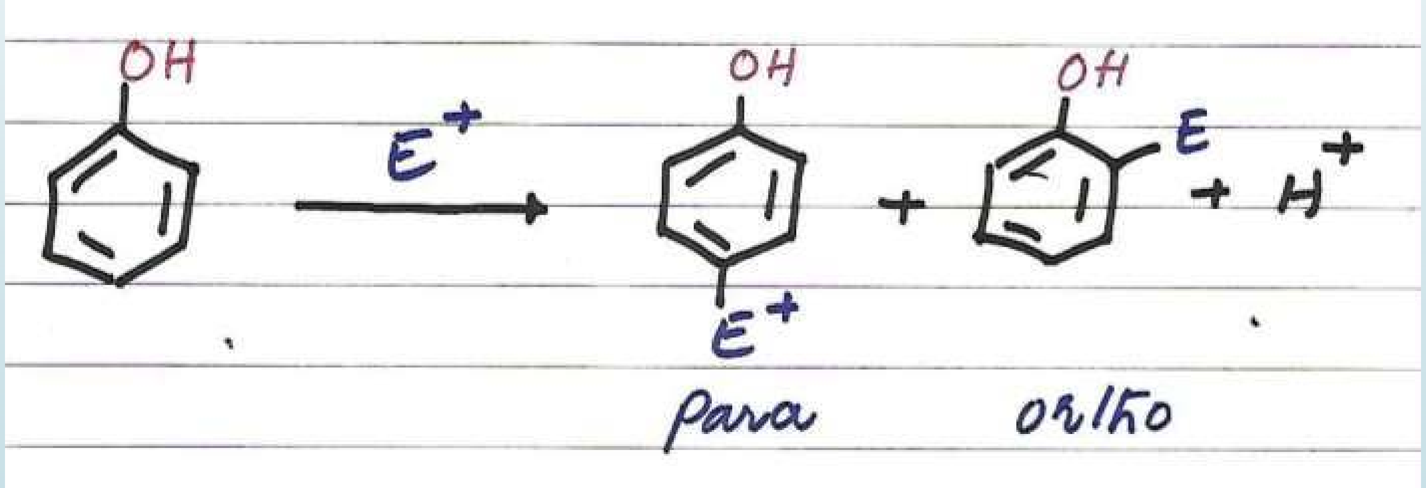


  - Aryl diazonium salts can be converted into phenols using H_2O/H_2SO_4/ heat



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 SO_3/H_2SO_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	$RCOCl/AlCl_3$	$RCOCl/AlCl_3$
Nitrosation	-	Aq. $NaNO_2/H^+$

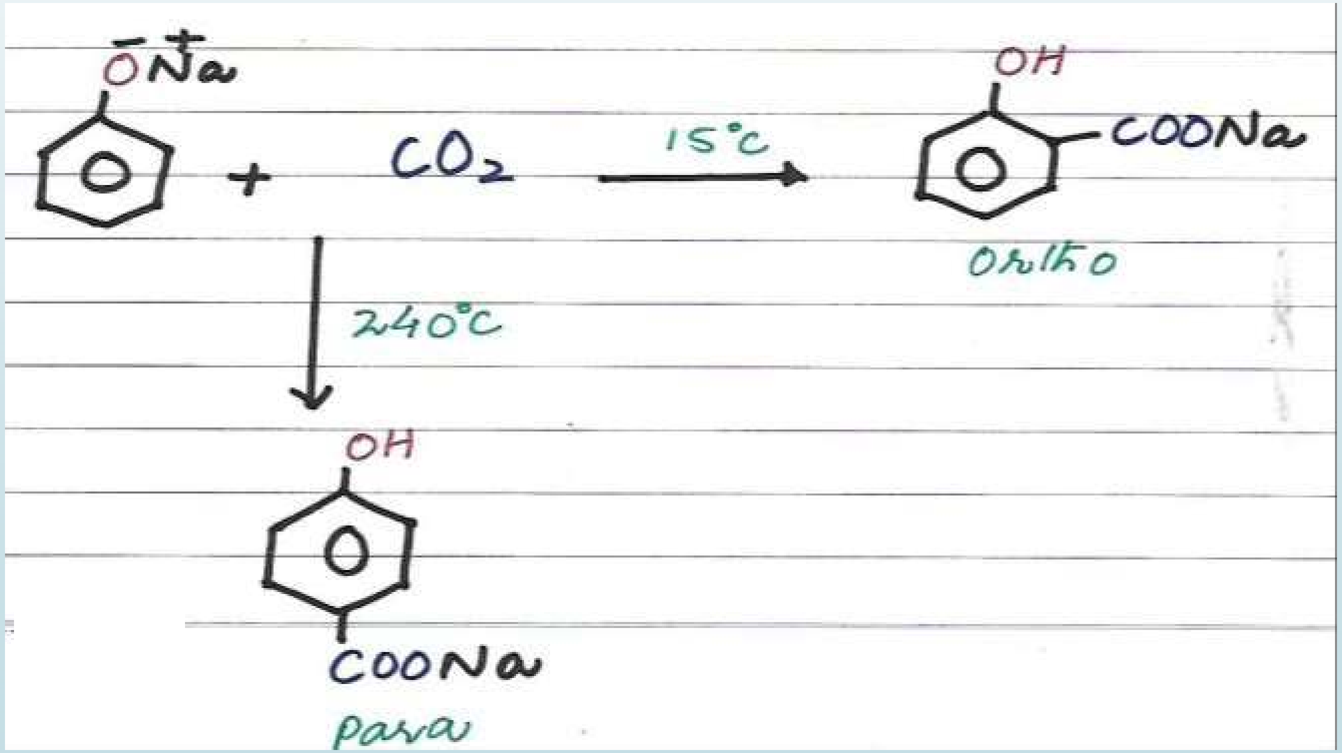
☐ Phenols are so activated that poly-substitution can be a problem.

☐ **OXIDATION OF PHENOLS**

☐ Phenols are very reactive towards oxidizing agent.

☐ The oxidation takes place through several steps eventually destroying the ring.

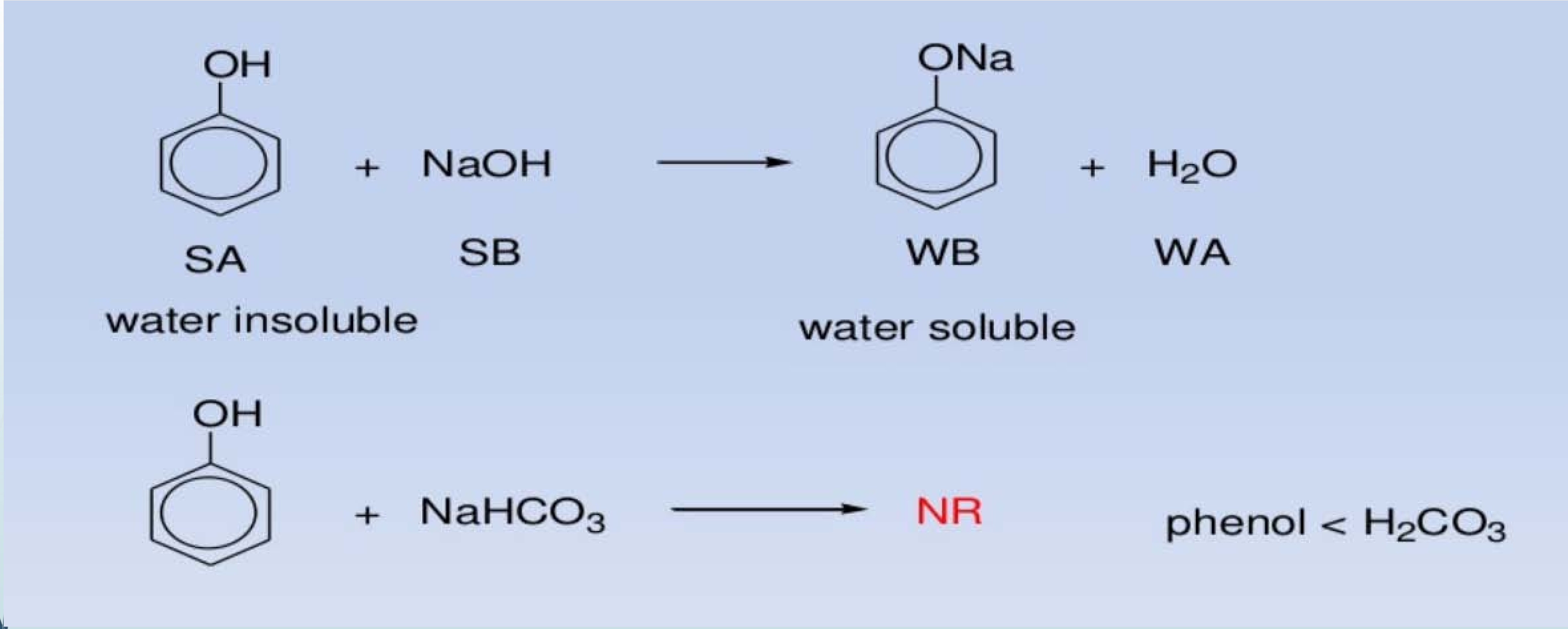
- REACTION WITH SODIUM METAL / CARBOXYLATION OF PHENOLS (KOLBE-SCHMITT REACTION)
- “The reaction of sodium salt of phenol with CO_2 is called Kolbe Reaction. It is carbonation of phenol.”
- At low temperature Sodium salicylate (sodium-o-hydroxyl benzoate) is formed, at higher temperature o-product is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



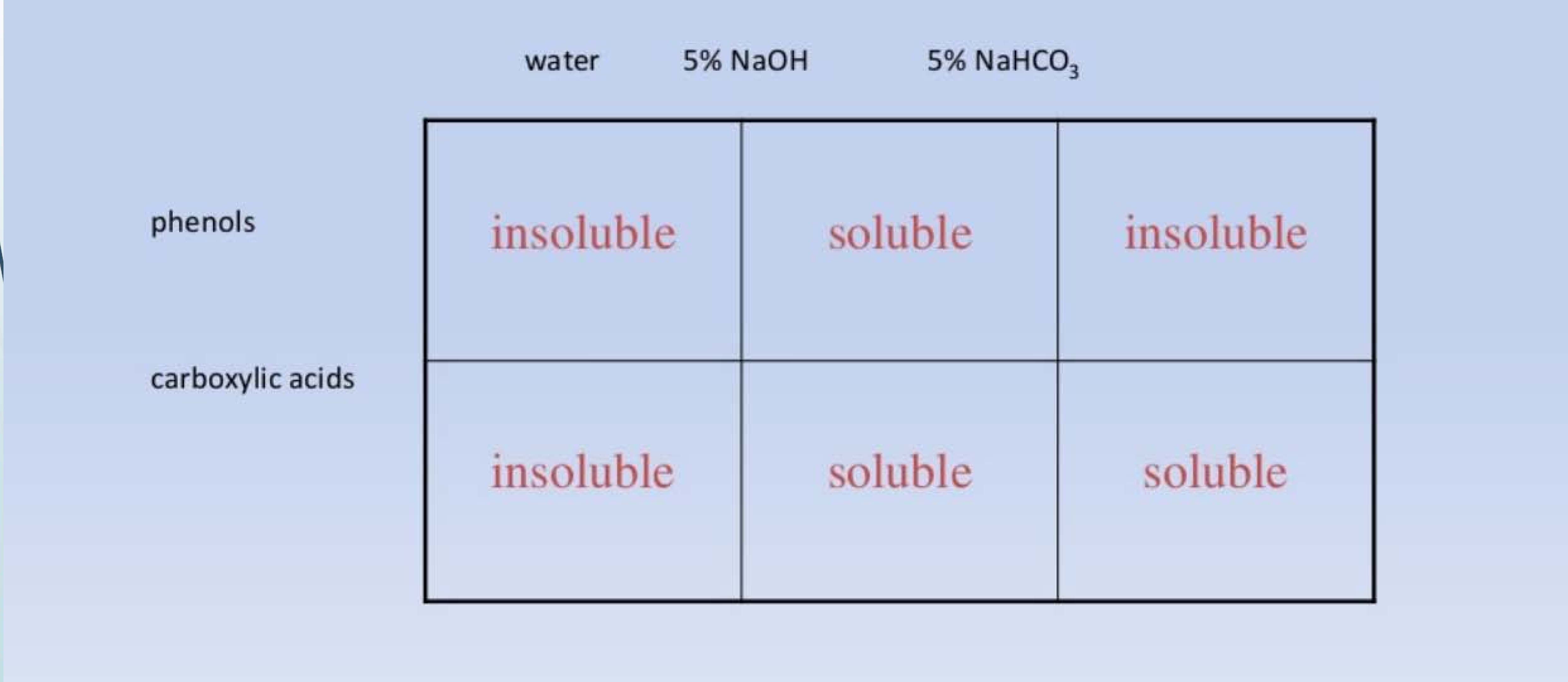
DIFFERENCE BETWEEN ALCOHOLS AND PHENOLS

ALCOHOL	**PHENOL**
☐ OH group is attached to an alkyl group	☐ OH group is attached to an aryl group
☐ Hydroxyl derivatives of alkane	☐ Hydroxyl derivatives of benzene
☐ The compounds in which one hydrogen of water is replaced by an alkyl group	☐ The compounds in which one hydrogen of water is replaced by an aryl group
☐ General formula ROH	☐ General formula C_6H_5OH
☐ Lower alcohols are colorless liquids	☐ Colorless crystalline deliquescent solids (M.P 41°C)
☐ They characteristics sweet smell and burning taste	☐ They have a characteristics phenolic odor
☐ pKa ≈ 16 - 20	☐ pKa ≈ 10
☐ Readily soluble in water but solubility decreases in higher alcohols	☐ Sparingly soluble in water forming a pink solution but completely soluble above 68.5°C
☐ Alcohols react in two ways: ☐ Reaction in C-O bond breaks ☐ Reaction in O-H bond breaks	☐ Phenolate ions have resonance structures but alcohols do not have resonance structures

QUALITATIVE TESTS



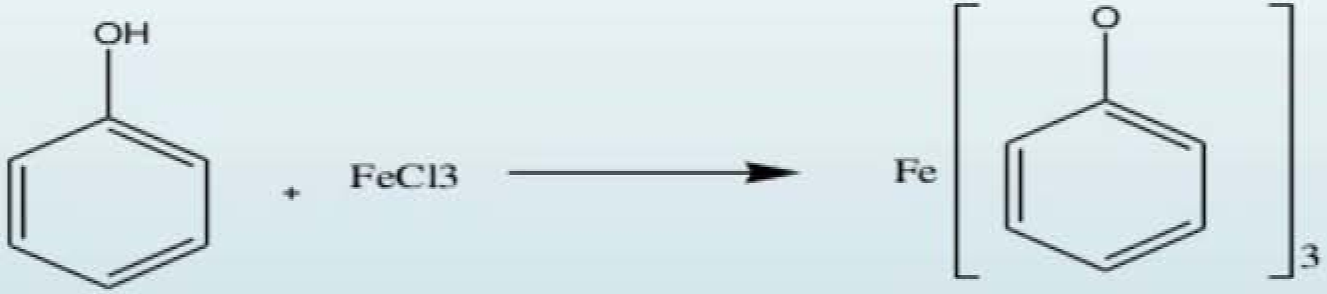
QUALITATIVE TESTS



	water	5% NaOH	5% $NaHCO_3$
phenols	insoluble	soluble	insoluble
carboxylic acids	insoluble	soluble	soluble

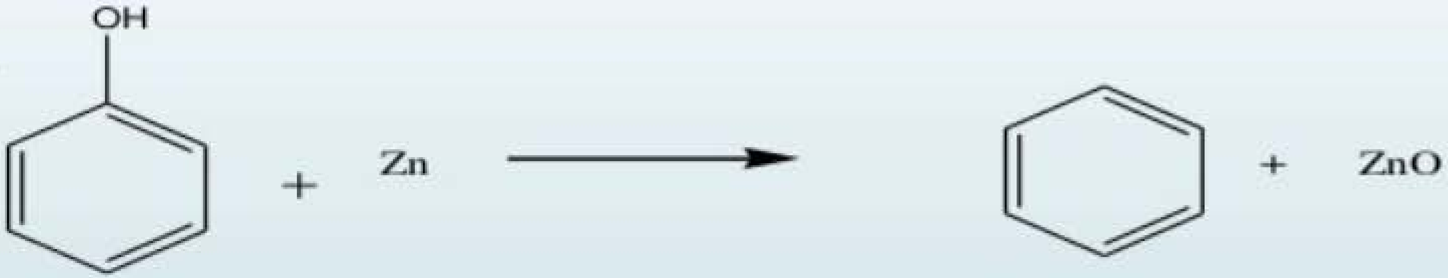
QUALITATIVE TESTS

Phenol gives purple color with one or two drops of ferric chloride due to formation of complex



QUALITATIVE TESTS

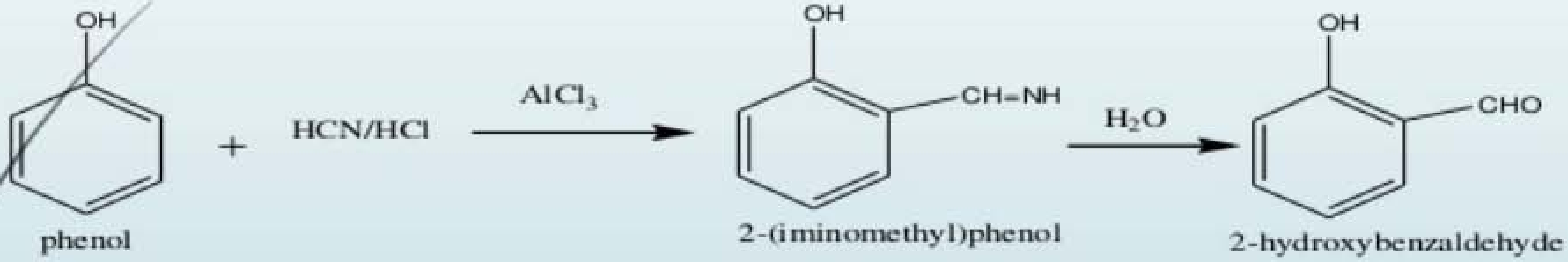
When phenol is distilled with zinc dust to produce benzene



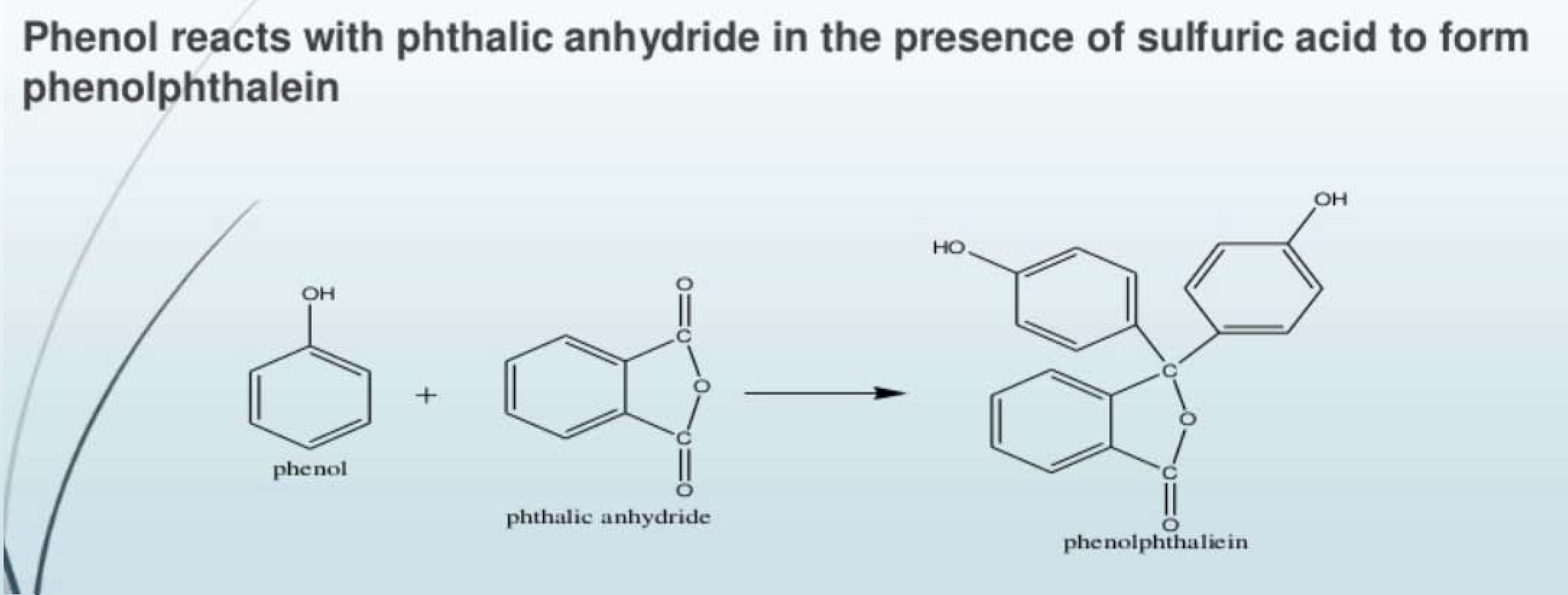
QUALITATIVE TESTS

Gatterman Reaction

This involves treatment of phenol with mixture hydrogen cyanide and hydrogen chloride



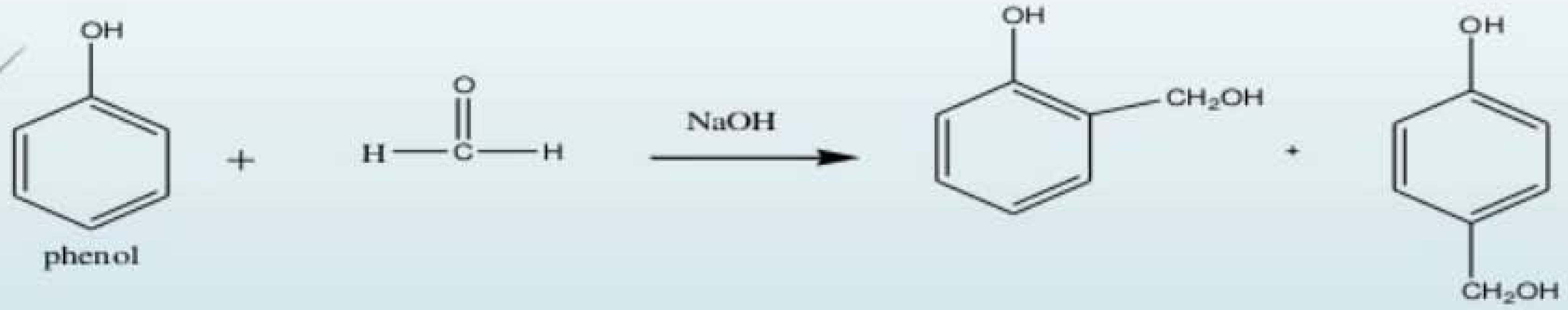
QUALITATIVE TESTS



Phenol reacts with phthalic anhydride in the presence of sulfuric acid to form phenolphthalein

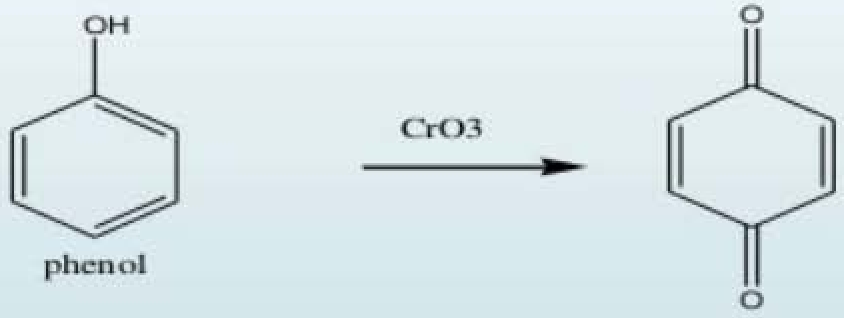
QUALITATIVE TESTS

Phenol treated with alkaline solution of formaldehyde to form o and p-hydroxy benzyl alcohol



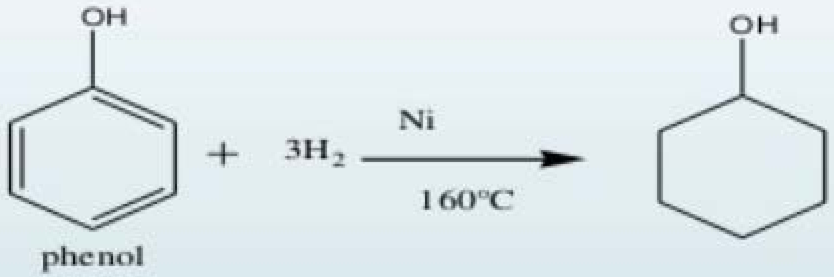
QUALITATIVE TESTS

Phenol undergoes oxidation with air or chromic acid to form p-benzoquinione

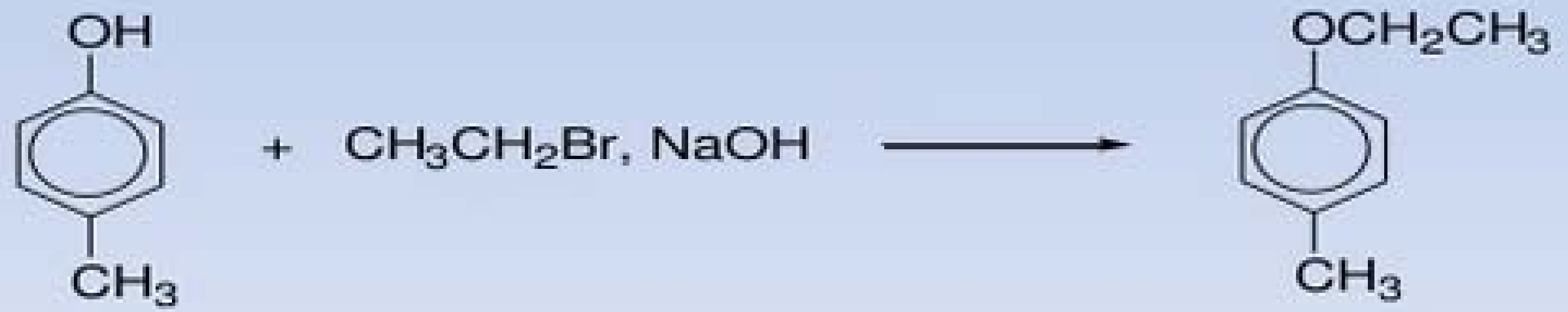


QUALITATIVE TESTS

Phenol passed over nickel catalyst to form cyclohexanol

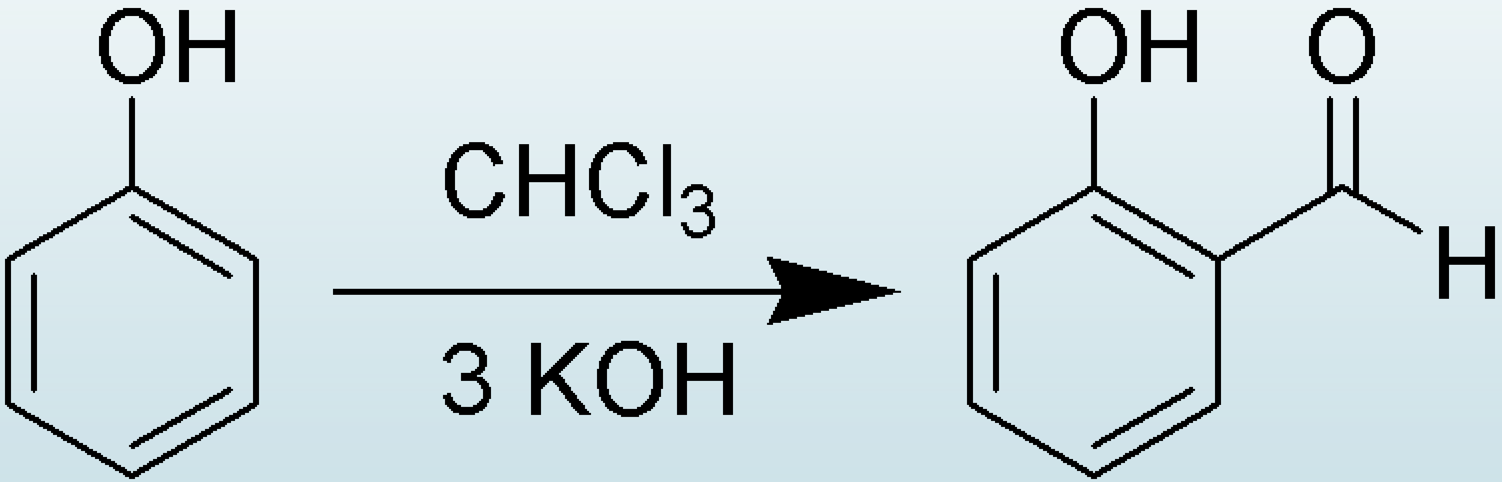


Phenols are often identified through bromination products and certain esters and ethers (Williamson ether synthesis).



QUALITATIVE TESTS

Reimer–Tiemann reaction



USES OF PHENOL

1. Medical uses

Phenol sprays are mostly used in medical industry. Phenol sprays work very well in the painful and irritating areas. They have anesthetic and analgesic combinations which help in getting instant relief from allergy also. Sore throat got immediate relief if phenol is used. It is also used in manufacturing if pesticides and insecticides in the pharma industry.

2.Plastic manufacturing industry

Two third of total phenol is used in preparing reagents. Reagents are used in plastic manufacturing industries. When phenol is condensed then it produces bisphenol with acetone.

3.Paint industry

Phenol is also used to produce epoxy resins for paints coatings and moldings. It is also used in polycarbonate plastics which can be seen in CDs and domestic electrical appliances.

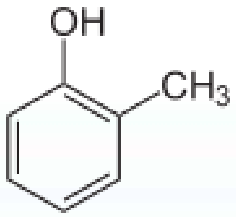
4. Cosmetic Industry

Phenol is also used in cosmetic industry in the manufacturing of sunscreens, skin lightening creams and hair coloring solutions. It is an ingredient that is used to kill microorganisms. It also prevents or inhibits the growth and reproduction of microorganisms.

5.Extraction Industry

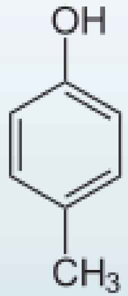
Extraction industry uses phenol in the study and extraction of bio-molecules. There is various application of phenol find by molecular biology in the extraction of nucleic acids from tissue samples for further investigations.

USES OF CRESOL



Cresols are precursors or synthetic intermediates to other compounds and materials, including plastics, pesticides, pharmaceuticals, and dyes.

Derivatives of *p*-cresol include:



1. Bupranolol, a non-selective beta blocker
2. Butylated hydroxytoluene, a common antioxidant
3. Indo-1, a popular calcium indicator

Derivatives of *m*-cresol include:

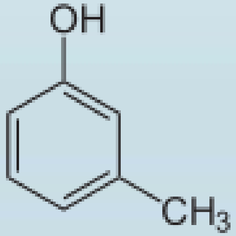
Amylmetacresol, an antiseptic

Bevantolol, (*RS*)-[2-(3,4-dimethoxyphenyl)ethyl][2-hydroxy-3-(3-methylphenoxy)propyl]amine

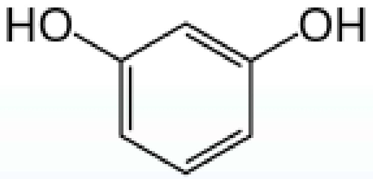
Bromocresol green

Chloro-*m*-cresol which is used as a household disinfectant

Tolimidone, 5-(3-methylphenoxy)pyrimidin-2(1*H*)-one

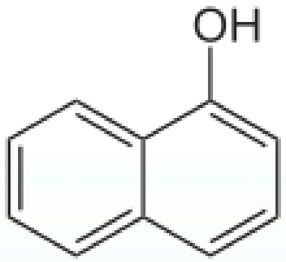


USES OF RESORCINOL

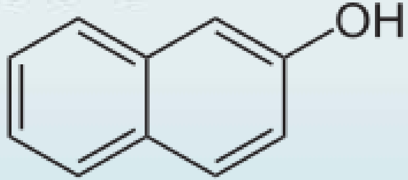


1. Used externally, it is an antiseptic and disinfectant, and is used 5 to 10% in ointments in the treatment of chronic skin diseases such as psoriasis, hidradenitis suppurativa, and eczema of a sub-acute.
2. A 2% solution used as a spray has been used with marked effect in hay fever and in whooping cough.
3. It can be included as an anti-dandruff agent in shampoo or in sunscreen cosmetics
4. It has also been employed in the treatment of gastric ulcers in doses of 125 to 250 mg in pills, and is said to be analgesic and haemostatic in its action.
5. In large doses, it is a poison, causing giddiness, deafness, salivation, sweating, and convulsions. It is also worked up in certain medicated soaps.
6. It is also worked up in certain medicated soaps

USES OF NAPTHOL



1. 1-Naphthol is a precursor to a variety of insecticides including carbaryl and pharmaceuticals including nadolol. It undergoes azo coupling to give various azo dyes,
2. In Molisch's test, 1-naphthol dissolved in ethanol, known as Molisch's reagent, is used as reagent for detecting the presence of carbohydrates. The test known as Molisch's test would give a red- or purple-colored compound to indicate the presence of carbohydrate.



3. The Sakaguchi test uses 1-naphthol with sodium hypobromite to detect the presence of arginine in proteins.
4. The Voges–Proskauer test uses 1-naphthol in potassium hydroxide (KOH) solution to detect the breakdown of glucose into acetoin which is used by bacteria for external energy storage. A positive test will be indicated by the appearance of a red color of the original yellow solution.

The End