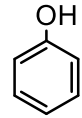
11. PHENOLS

INTRODUCTION

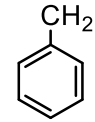
Phenols are a class of organic compounds with the general formula Ar-OH, where Ar- is aryl group (most commonly C_6H_5- group). When –OH group is attached to the side chain alkyl group of the Benzene it is an aromatic alcohol.

CH_3OH

Methanol
(Methyl alcohol)
An Aliphatic alcohol

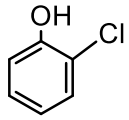


Phenol

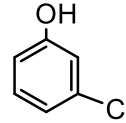


Phenyl methanol
(Benzyl alcohol)
An Aromatic alcohol

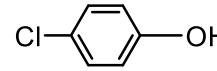
Following are the other examples of Phenols.



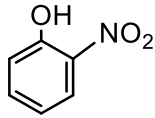
2-chlorophenol
o-chlorophenol



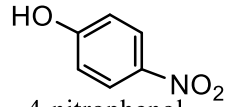
3-chlorophenol
m-chlorophenol



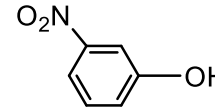
4-chlorophenol
p-chlorophenol



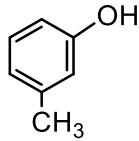
2-nitrophenol
o-nitrophenol



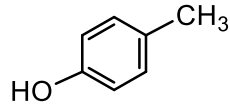
4-nitrophenol
p-nitrophenol



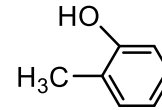
3-nitrophenol
m-nitrophenol



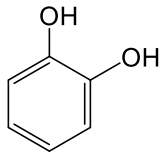
3-hydroxytoluene
m-hydroxytoluene



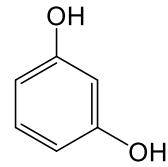
4-hydroxytoluene
p-hydroxytoluene



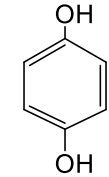
2-hydroxytoulene
o-hydroxytoulene



1,2-dihydroxybenzene
o-dihydroxybenzene
(Catechol)



1,3-dihydroxybenzene
m-dihydroxybenzene
(Resorcinol)

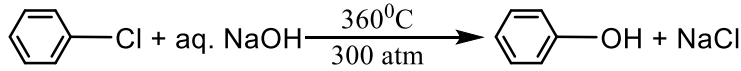


1,4-dihydroxybenzene
p-dihydroxybenzene
(Dihydroquinone)

Preparations

1. From Chlorobenzene (Dow process) (studied in Haloarenes)

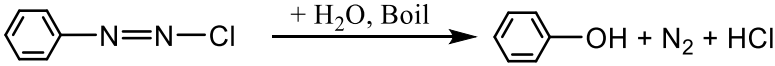
Phenols can be prepared by nucleophilic substitution reaction of Chlorobenzene with aqueous NaOH at 350°C temperature and 300 atmosphere pressures. This method was first used by Dow chemical industries, so is called Dow process.



Chlorobenzene Phenol

2. From Diazonium salt

Benzene diazonium salt can be change into Phenol by simply boiling with water.

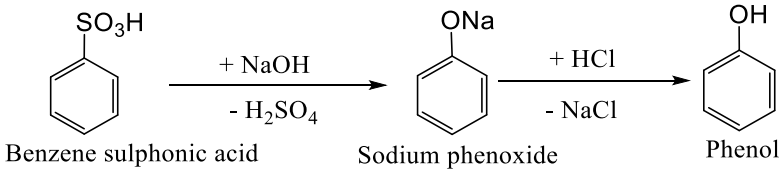


Benzene diazonium chloride Phenol

1. If benzene diazonium salt is warmed with water, what major product will it form?
   a. Acetone b. phenol
   b. Benzene d. chlorobenzene

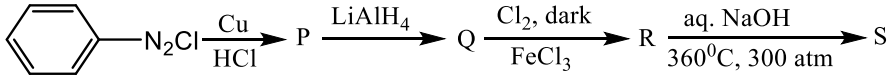
3. From Benzene sulphonic acid

Benzene sulphonic acid gives sodium phenoxide when heated with NaOH. The product on acidic hydrolysis results Phenol.



Conversions

1. Identify P, Q, R and S in following reaction sequence,



Physical Properties

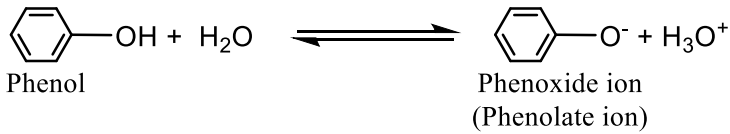
- Simplest Phenols are colourless liquids or low melting solids.
- They have a characteristic Phenolic odour.
- They have quite high boiling points due to intermolecular hydrogen bonding.
- Phenol is somewhat soluble in water (solubility-9) because of hydrogen bonding with water.

Chemical Properties

1. Acidic nature

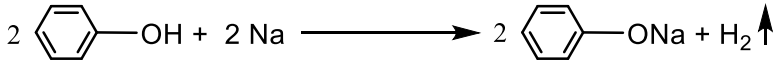
a. Ionization and action of litmus

Phenol ionises in aqueous solution into phenoxide ion and hydronium ion. Therefore, it turns litmus red.



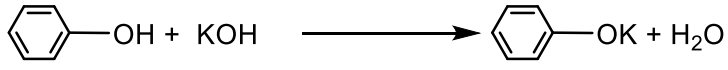
b. Reaction with active metals:

Phenol reacts with active metals such as sodium or potassium forming phenoxide (Phenolate) salt and hydrogen gas is liberated.



c. Reaction with caustic alkalis (NaOH, KOH)

Phenol dissolves in solutions of strong alkalis to form Phenolate salt and water.

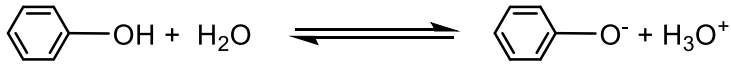


d. Reaction with carbonates and bicarbonates

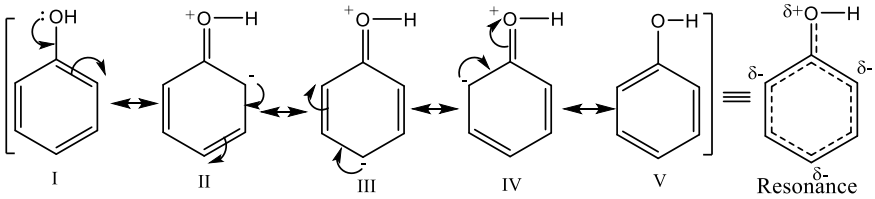
Phenols being weak acids do not react with metal carbonates and bicarbonates which are weak bases.

2. Why is Phenol more acidic than alcohol? 3

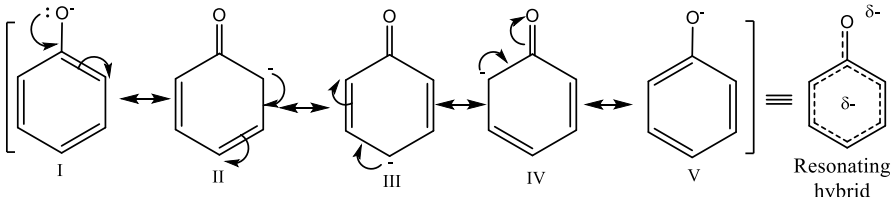
Solution: Phenol ionizes in aqueous solutions as:



Now Phenol is resonance hybrid of following five structures.



Similarly, phenoxide ion is a resonance hybrid of these five structures.



Resonating structures of Phenoxide ion

From the resonating structures, it can be seen that, the phenoxide ion is more stable. This is due to the fact that there is no charge separation. However, resonating structures of Phenol involve charge separation hence it is less stable. Thus, the above equilibrium lies considerably towards the right, producing more hydronium ions. Thus, Phenol is more acidic than alcohol. Both alcohol and alkoxide ions involve no resonance stabilization hence the following equilibrium lies considerably to the left as alcohol is more stable than alkoxide ions.

$$\underset{\text{Alkanol}}{R\text{-}OH} + H_2O \rightleftharpoons \underset{\text{Alkoxide ion}}{RO^-} + H_3O^+$$

Comparison of acidic strength of Phenol with water

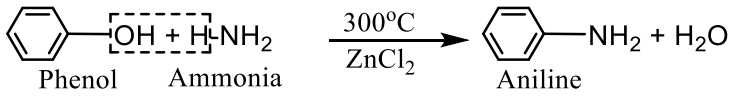
Phenol is more acidic than water. Because, when Phenol ionizes, it forms phenoxide ion, which is resonance stabilized. But water forms hydroxide ion which is not resonance stabilized.

Hence the order of acidity is

Carboxylic acids > Phenol > water > alcohols

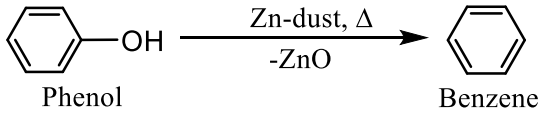
2. Action with Ammonia

On drastic conditions like high temperature, high pressure and the presence of zinc chloride as a catalyst, Phenol reacts with ammonia producing aniline.



3. **Action with Zn**

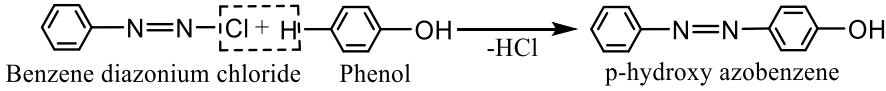
Phenol gives benzene when heated with Zn-dust.



3. What happens when Phenol is heated with zinc dust? 1
4. How would you obtain benzene from Phenol? 1

4. **Action with Benzene dizonium chloride** (coupling reaction)

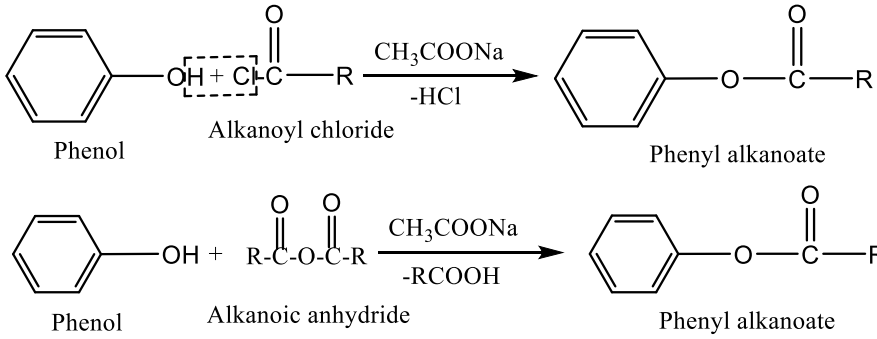
Phenols undergo coupling with Benzene diazonium chloride to form p-hydroxy azobenzene, which is a useful **dye.**



5. What happens when Phenol is treated with Benzene diazonium chloride?
6. Write the chemical equation with conditions for the following reaction: Phenol is coupled with benzene diazonium chloride. 2

5. **Acylation reaction**

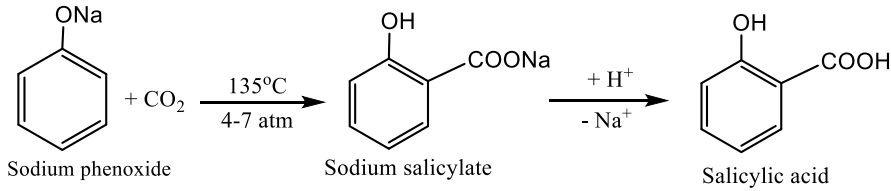
Phenol reacts with acid chlorides (Alkanoyl chloride) or acid anhydrides (Alkanoic anhydride) **in presence of Sodium ethanoate (sodium acetate)** to form phenyl ester.



7. What action takes place when Phenol reacts with Ethanoyl chloride? 1

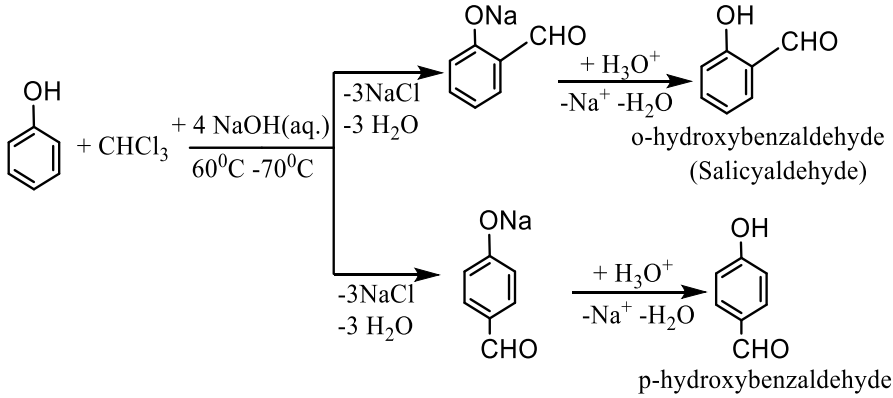
6. Kolbe's reaction (Carboxylation reaction)

When sodium phenoxide is heated with carbon dioxide at 135°C and under 4-7 atmospheric pressure, sodium salicylate is formed as the major product. This on acidification yields salicylic acid and the reaction is known as Kolbe's reaction. Introduction of –COOH group in molecule is called carboxylation.



7. Reimer Tiemann's reaction

When chloroform is heated with Phenol in presence of aqueous NaOH or KOH at 60°C -70°C temperature, followed by acidification, a mixture of o-hydroxybenzaldehyde (o-salicyaldehyde) and p-hydroxybenzaldehyde is obtained. The former i.e., ortho isomer is the major product.

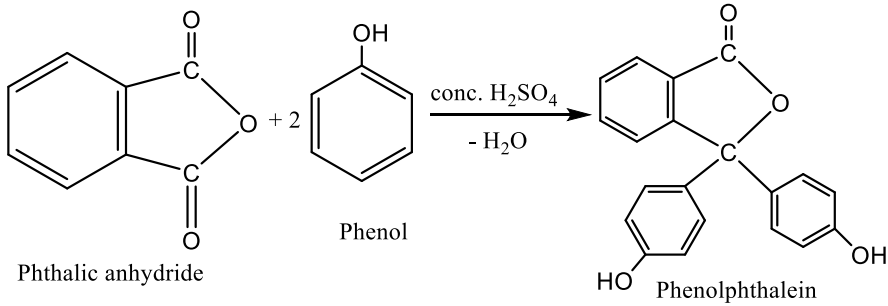


8. **What happens when Trichloromethane reacts with Phenol?** **1**

9. Write the action of monohydroxy benzene with Trichloromethane in presence of alcoholic NaOH. 2
10. Show your acquaintance with Riemer-Tiemann's reaction. 2
11. Give an example of Riemer-Tiemann's reaction. 1

8. Action with Phthalic anhydride

Phenol and Phthalic anhydride condense together in presence of conc. H_2SO_4 and form Phenolphthalein, a famous indicator.



Phthalic anhydride Phenol Phenolphthalein

8. Electrophilic substitution:

- -OH is an **activating group** in electrophilic aromatic substitution so these reaction occur faster in Phenol than in Benzene.
- The products are ortho and para substituted as –OH behaves as **o, p-directing group** in these reactions.

I. Halogenation

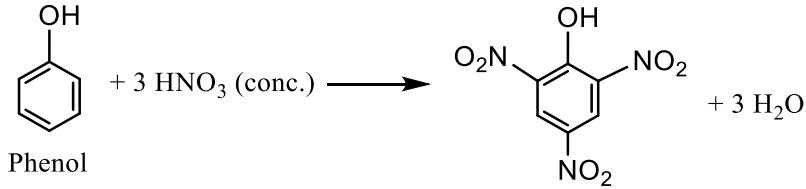
Phenol reacts with aq. bromine resulting 2,4,6-tribromophenol, which is a white precipitate. Hence this reaction is used as a ***test of Phenol***.

12. **How does Phenol react with aqueous bromine?** **1**
13. Write the action of monohydroxy Benzene with aqueous bromine. 1
14. Write the reaction between Phenol and aq. Br_2. 2

But in the presence of non-polar solvents, like CS_2, CCl_4 etc. Phenol forms a mixture of o-bromophenol and p-bromophenol with bromine.

II. Nitration

Phenol reacts with conc. nitric acid forming 2,4,6-trinitrophenol also called Picric acid, used as an explosive, medicine, and yellow dye.



Phenol

2,4,6-trinitrophenol(TNP)
(Picric acid)

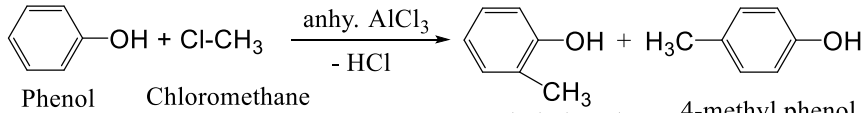
Mononitrophenol can be obtained in low temperatures with dilute Phenol.

15. How is picric acid prepared? Write its one use. 2

III. Sulphonation

Phenol on sulphonation gives different products depending upon the temperature of the reaction. Sulphonation mainly occurs at ortho positions at low temperatures and para positions at high temperatures. *(Practice writing the reactions.)*

IV. Friedel Craft's alkylation and acylation



Phenol Chloromethane

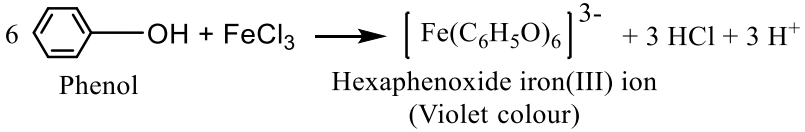
2-methyl phenol
o-cresol

4-methyl phenol
p-cresol

How do you explain that the –OH group of Phenol is ortho/para directing group? 2

Laboratory test of Phenol

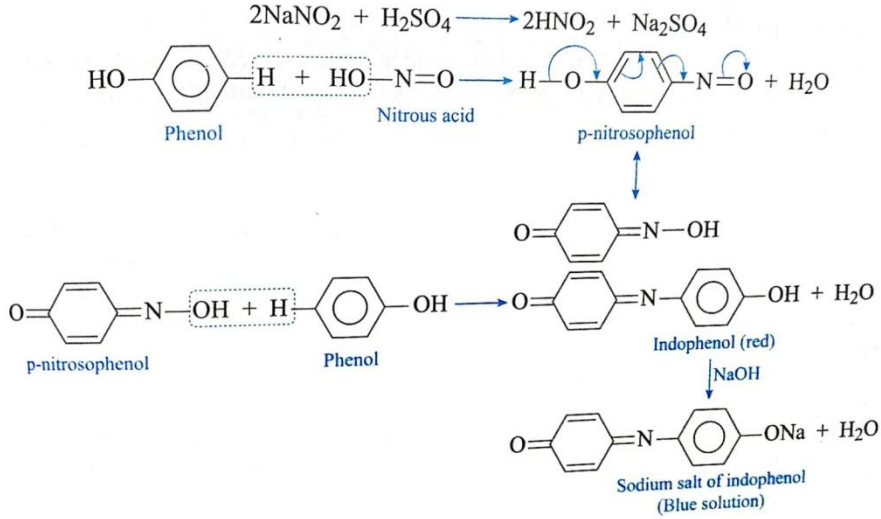
1. **$FeCl_3$ (Ferric chloride) test**: Phenol reacts with $FeCl_3$ solution to give green, blue, violet or red coloured water soluble complex.



2. **Aqueous bromine test** (studied earlier in the chemical properties)

3. **Libermann's test**

Phenols give red/brown colouration on warming with **sodium nitrite dissolved in conc. H_2SO_4**. The red or brown colouration thus obtained changes into *intense blue or green* on addition of **NaOH**.

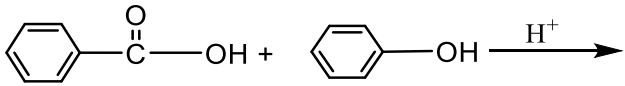


Uses of Phenol

- Production of Bakelite - a thermosetting plastic.
- Manufacture of dyes, explosives (e.g. picric acid) etc.

- Manufacture of drugs (e.g. aspirin, Phenacetin, salicylic acid etc)
- Preparation of Phenolphthalein, an indicator.
- As disinfectant and germicide.
- Manufacture of Cyclohexanol used as solvent for rubber.

16. Complete the following equation



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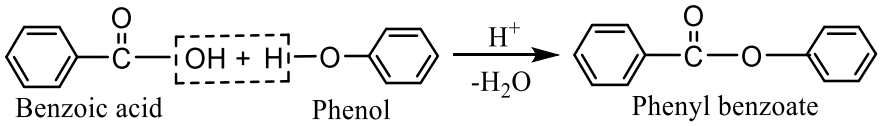
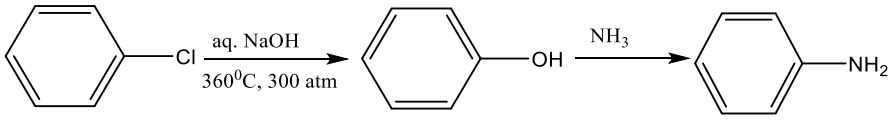
Solution: This is Esterification reaction like that between an aliphatic alcohol and carboxylic acid. This results an aromatic ester.



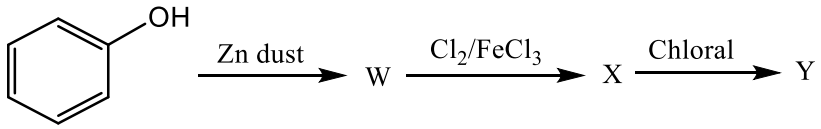
Conversions

17. How is Phenol prepared from Benzene? 2
18. How could you synthesize Toluene from Phenol?# 2.5
19. Convert Chlorobenzene into Aniline. 2

Solution: *(always write IUPAC names and side products)*



20. Make the following conversions:



2. Which of the following aromatic compounds is capable of hydrogen bonding
   a. Benzene

b. Chlorobenzene
c. Phenol
d. Nitrobenzene

3. When Benzene sulphonic acid is fused with NaOH and hydrolyzed it forms
   a. Phenol
   b. Sodium salicylate
   c. Salicylic acid
   d. Benzene
4. When Benzene diazonium chloride is hydrolyzed it gives
   a. Alcohol
   b. Benzene
   c. Chlorobenzene
   d. Phenol
5. Dow process is used for the preparation of
   a. Benzene
   b. Chlorobenzene
   c. Phenol
   d. Nitrobenzene
6. Phenol is
   a. Slightly acidic
   b. Strongly acidic
   c. Slightly basic
   d. Strongly basic
7. Phenol does not react with
   a. KOH
   b. Na
   c. NaOH
   d. $NaHCO_3$
8. When Phenol is reacted with zinc dust we get
   a. Phenol
   b. Benzaldehyde
   c. Benzene

d. Chlorobenzene

9. When Phenol reacts with $CHCl_3$ and NaOH, it gives
   a. Benzaldehyde
   b. Salicyldehyde
   c. Salicylic acid
   d. Benzoic acid
10. Reimer Tiemann's reaction yields
   a. Salicylaldehyde
   b. Benzaldehyde
   c. Benzoic acid
   d. Aspirin
11. When phenol is heated with $CHCl_3$ and aq. KOH produces salicylaldehyde. This reaction is called
   a. Friedel-Craft's reaction
   b. Rosenmund reaction
   c. Riemer-Tiemann's reaction
   d. Carbyl amine reaction
12. When Phenol is reacted with Benzene diazonium chloride in alkaline medium at cold condition, it gives an orange dye, the reaction is called
   a. Kolbe's carboxylation reaction
   b. Diazotization reaction
   c. Riemer Tiemann's reaction
   d. Coupling reaction
13. When sodium phenoxide is heated with CO_2 at about 125-135^{0}C and 4-7 atm pressure followed by acidification gives salicylic acid, the reaction is
   a. Kolbe's carboxylation reaction
   b. Diazotization reaction
   c. Riemer Tiemann's reaction
   d. Friedel Craft's reaction
14. Phenol on treatment with conc. HNO_3 in the presence of conc. H_2SO_4 gives

a. m-nitroPhenol
b. o-nitroPhenol
c. p-nitroPhenol
d. Picric acid

15. Which of the following contains -OH functional group
    a. Picric acid
    b. Acetic acid
    c. Formic acid
    d. Oxalic acid
16. Picric acid is
    a. 2,4,6-trinitro toluene
    b. 2,4,6-trinitro Phenol
    c. 2,4-dinitro Phenol
    d. 2,4,6-tribromoPhenol
17. Picric acid is an example of
    a. Azo dye
    b. Phthalein dye
    c. Nitro dye
    d. Anthracene dye
18. Picric acid is a nitro substiuent of
    a. Aniline
    b. Phenol
    c. Nitrolic acid
    d. Salicylic acid
19. Rate of substitution in Phenol is
    a. Less than in Benzene
    b. Same as in Benzene
    c. Greater than in Benzene
    d. Could not be known
20. The -OH group in the Phenol is
    a. Both o-, p- directing and deactivating
    b. Both o-,p- directing and activating
    c. Both m-directing and activating

d. Both m-directing and deactivating

21. Which of the following decreases the electron density in the Benzene ring to maximum extent?
    a. -OH
    b. -Cl
    c. $-NH_2$
    d. $-CH_3$
22. When Phenol is treated with aqueous Br_2, it gives white ppt. of
    a. 2,4,6-trinitro toluene
    b. 2,4,6-trinitro phenol
    c. 2,4-dinitro phenol
    d. 2,4,6-tribromophenol
23. Phenol reacts with bromine in CS_2 at low temperature to give
    a. 2,4,6-tribromophenol
    b. o-bromophenol
    c. o- bromophenol and p-bromophenol
    d. p-bromophenol
24. $FeCl_3$ gives violet colour with
    a. Alcohols
    b. Amines
    c. Phenols
    d. Aldehydes
25. Which of the following is not a test for Phenol?
    a. $FeCl_3$ test
    b. Aq. Br_2 test
    c. Fehling's test
    d. Libermann's test
26. Which of the compound used in formation of Bakellite, which gives positive $FeCl_3$ test
    a. Formaldehyde
    b. Benzaldehyde
    c. phenol
    d. benzoic acid

This is not a complete note. It is just to guide you. It is recommended to study prescribed textbooks along with this material.