

# 11. PHENOLS

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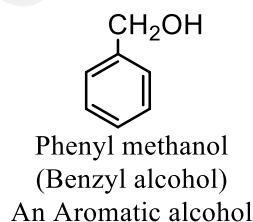
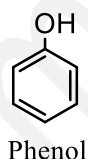
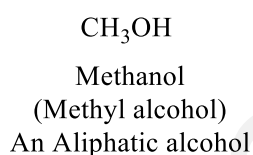
## Learning outcomes

By the end of the chapter, students should be able to:

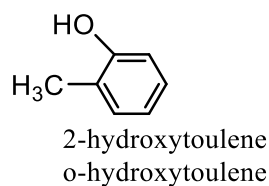
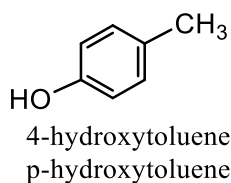
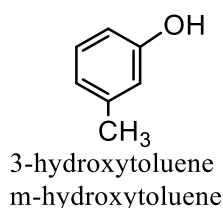
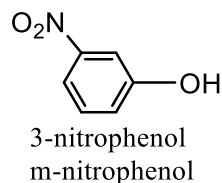
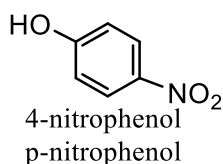
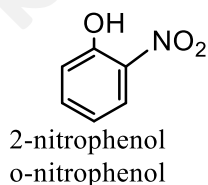
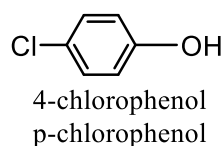
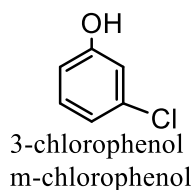
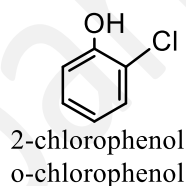
- Describe the nomenclature of phenols briefly.
- Show the preparation of phenol from chlorobenzene, Diazonium salt and benzene sulphonic acid
- State the physical properties of phenol.
- Describe the acidic nature of phenol (comparison with alcohol and water).
- Explain the chemical properties of phenol
  - with  $\text{NH}_3$ ,
  - $\text{Zn}$ ,
  - $\text{Na}$ ,
  - benzene diazonium chloride and
  - phthalic anhydride,
  - Acylation reaction,
  - Kolbe's reaction and
  - Reimer-Tiemann reaction
- Electrophilic substitution (nitration, sulphonation, bromination, and Friedel-Crafts alkylation).
- Describe the test of phenol ( $\text{FeCl}_3$  test, aq. Bromine test & Libermann test).
- State important uses of phenol.

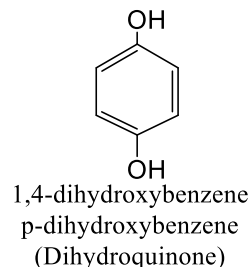
## INTRODUCTION

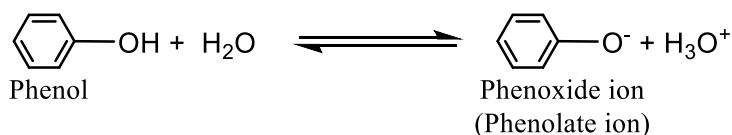
Phenols are a class of organic compounds with the general formula  $\text{Ar-OH}$ , where  $\text{Ar-}$  is an aryl group (most commonly the  $\text{C}_6\text{H}_5\text{-}$  group). When an  $\text{-OH}$  group is attached to the side chain alkyl group of benzene, it is an aromatic alcohol.



The following are other examples of Phenols.

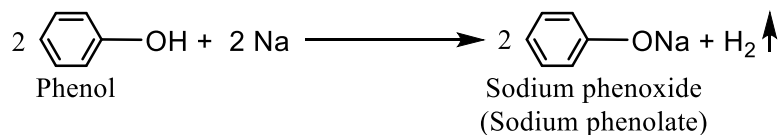






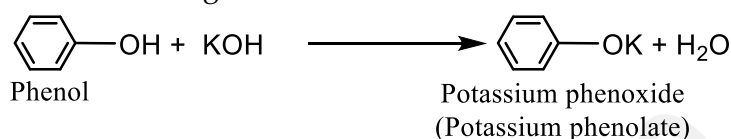
**b. Reaction with active metals:**

Phenol reacts with active metals such as sodium or potassium, forming a 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.



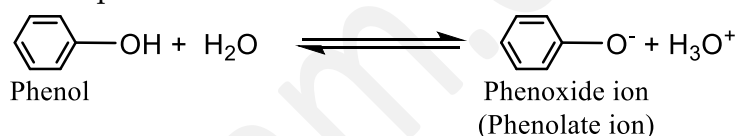
**d. Reaction with carbonates and bicarbonates**

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

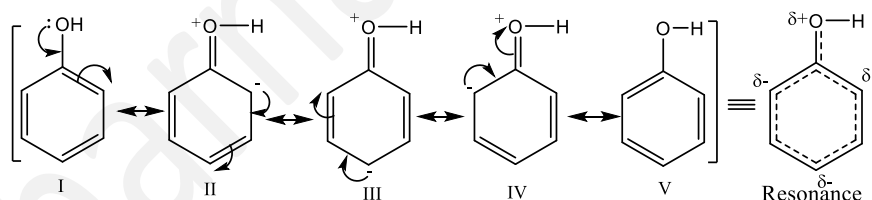
1. Why is Phenol more acidic than alcohol?

3

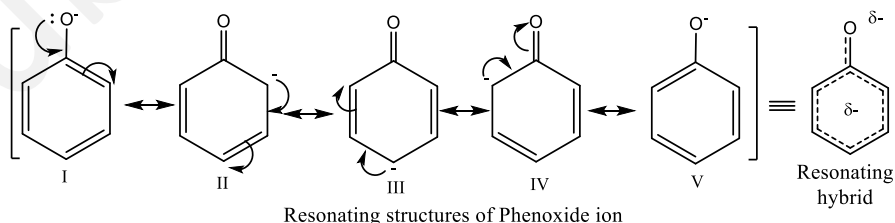
Solution: Phenol ionises in aqueous solutions as:



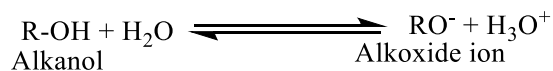
Now Phenol is a resonance hybrid of the following five structures.



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



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, the 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 stabilisation; hence, the following equilibrium lies considerably to the left, as alcohol is more stable than alkoxide ions.



### Comparison of the acidic strength of Phenol with water

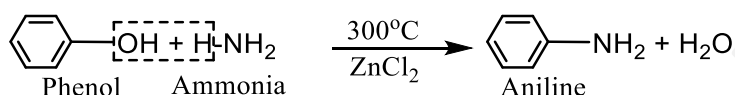
Phenol is more acidic than water. Because when Phenol ionizes, it forms the phenoxide ion, which is resonance-stabilised. But water forms a hydroxide ion, which is not resonance-stabilised.

Hence, the order of acidity is

Carboxylic acids > Phenol > water > alcohols

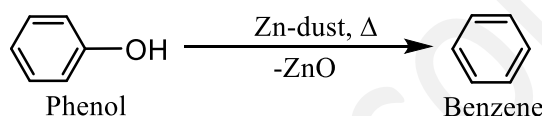
### 2. Action with Ammonia

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



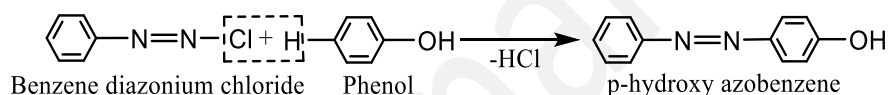
### 3. Action with Zn

Phenol gives benzene when heated with Zn dust.



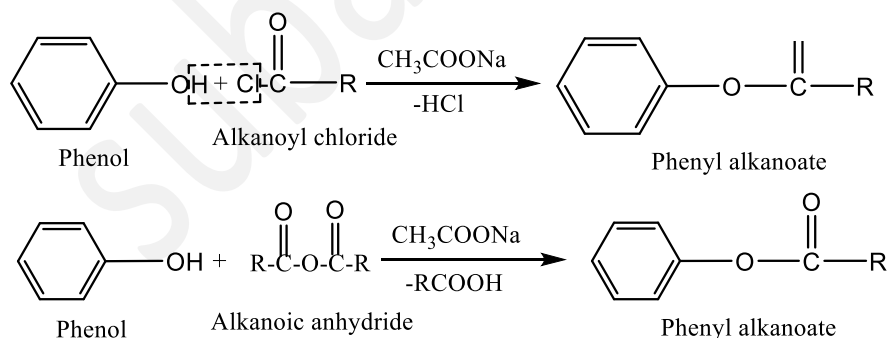
### 4. Action with Benzene diazonium chloride (coupling reaction)

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



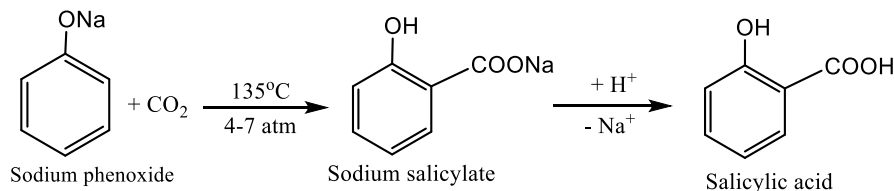
### 5. Acylation reaction

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



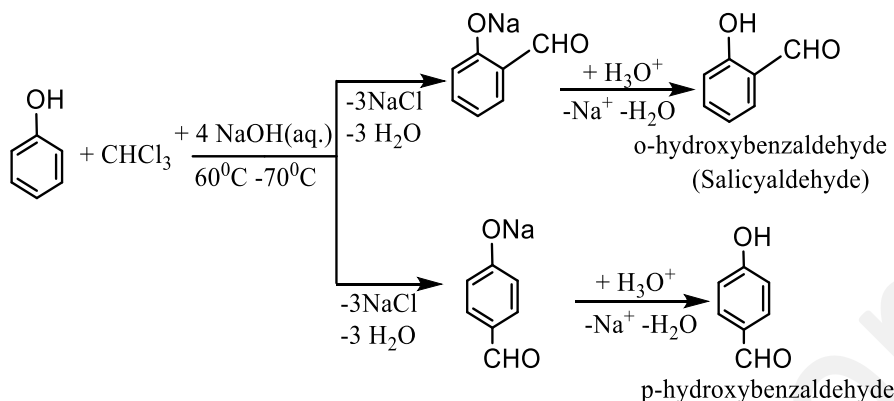
### 6. Kolbe's reaction (Carboxylation reaction)

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, upon acidification, yields salicylic acid, and the reaction is known as Kolbe's reaction. Introduction of a -COOH group in a molecule is called carboxylation.



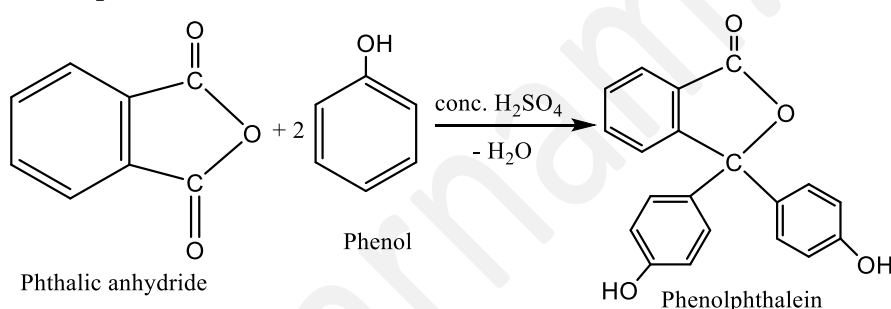
## 7. Reimer Tiemann's reaction

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



## 8. Action with Phthalic anhydride

Phenol and Phthalic anhydride condense together in the presence of conc. H2SO4 and form Phenolphthalein, a famous indicator.



## 8. Electrophilic substitution:

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

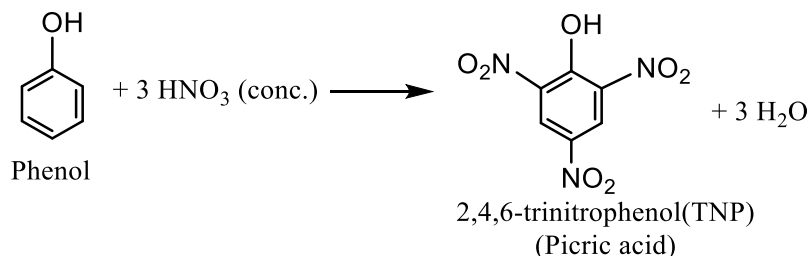
### I. Halogenation

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

But in the presence of non-polar solvents, like CS2, CCl4, etc. Phenol forms a mixture of o-bromophenol and p-bromophenol with bromine.

### II. Nitration

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

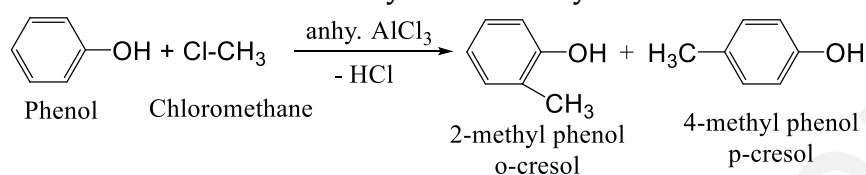


Mononitrophenol can be obtained at low temperatures with dilute Phenol.

### III. Sulphonation

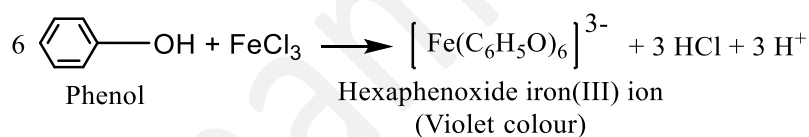
Phenol on sulphonation gives different products depending upon the temperature of the reaction. Sulphonation mainly occurs at ortho positions at low temperatures and para positions at high temperatures. *(Practice writing the reactions.)*

### IV. Friedel-Crafts alkylation and acylation



### Laboratory test of Phenol

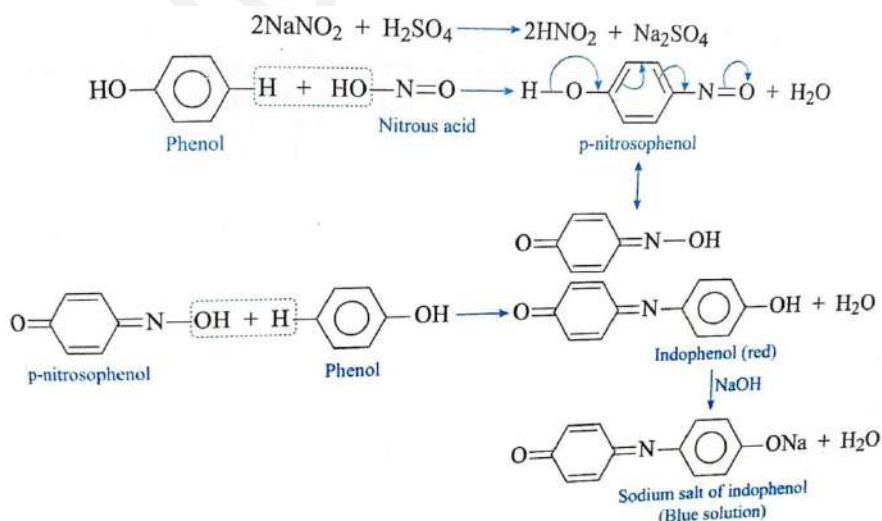
- 1. FeCl<sub>3</sub> (Ferric chloride) test:** Phenol reacts with FeCl<sub>3</sub> solution to give a green, blue, violet or red coloured, water-soluble complex.



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

- 3. Libermann's test**

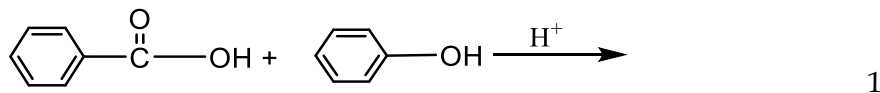
Phenols give red/brown colouration on warming with **sodium nitrite dissolved in conc. H<sub>2</sub>SO<sub>4</sub>**. The red or brown colouration thus obtained changes into *intense blue or green* on the addition of **NaOH**.



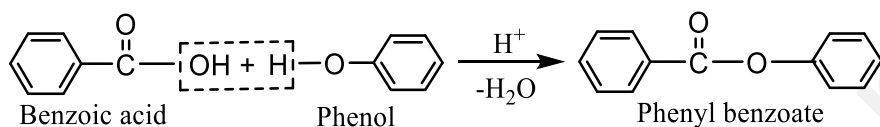
## Uses of Phenol

- 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 a disinfectant and germicide.
- Manufacture of Cyclohexanol used as a solvent for rubber.

2. Complete the following equation



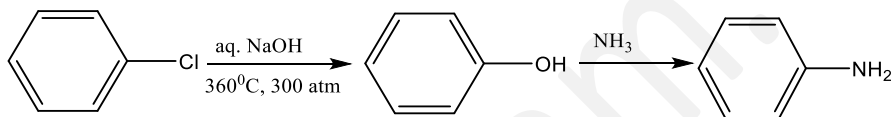
*Solution:* This is an esterification reaction like that between an aliphatic alcohol and a carboxylic acid. This results in an aromatic ester.



## Conversions

3. Convert Chlorobenzene into Aniline.

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



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