HYDROXY COMPOUND

Organic Hydroxyl Compounds

Organic hydroxyl compounds are a class of organic compounds that contain one or more **hydroxyl groups (-OH)** attached to a carbon atom.
The presence of a hydroxyl group greatly influences the **physical properties** (like solubility and boiling point) and **chemical reactivity** of these compounds.

Organic hydroxyl compounds can be classified into several categories based on the type of carbon atom to which the hydroxyl group is attached.

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1. Alcohols

Alcohols are the simplest type of organic hydroxyl compounds in which the hydroxyl group is attached to a **saturated carbon atom (sp^3 hybridized)**.

Examples:

- **Methanol (CH_3OH):** The simplest alcohol, used as a solvent and antifreeze.
- **Ethanol (C_2H_5OH):** Found in alcoholic beverages; also used as a solvent and fuel.
- **Isopropanol (C_3H_7OH):** Commonly known as isopropyl alcohol; used as a disinfectant and solvent.

2. Phenols

Phenols are compounds in which the hydroxyl group is attached **directly to an aromatic ring (benzene ring)**.

Uses:
Phenols are widely used in the manufacture of **plastics, medicines, antiseptics, and disinfectants**.

Example:

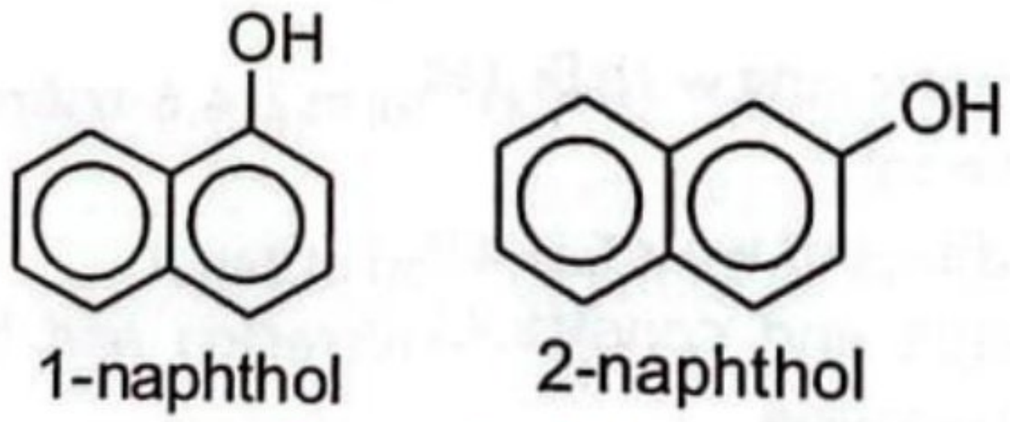
- **Phenol (C_6H_5OH)** — also known as carbolic acid.

phenol

3. Naphthols

Naphthols are derivatives of **naphthalene ($C_{10}H_8$)** containing a hydroxyl group. Their general formula is **$C_{10}H_7OH$**.
They exist in two **isomeric forms** depending on the position of the hydroxyl group:

- **1-Naphthol (α-naphthol):** The -OH group is attached to the **first carbon atom** of the naphthalene ring.
- **2-Naphthol (β-naphthol):** The -OH group is attached to the **second carbon atom** of the naphthalene ring.



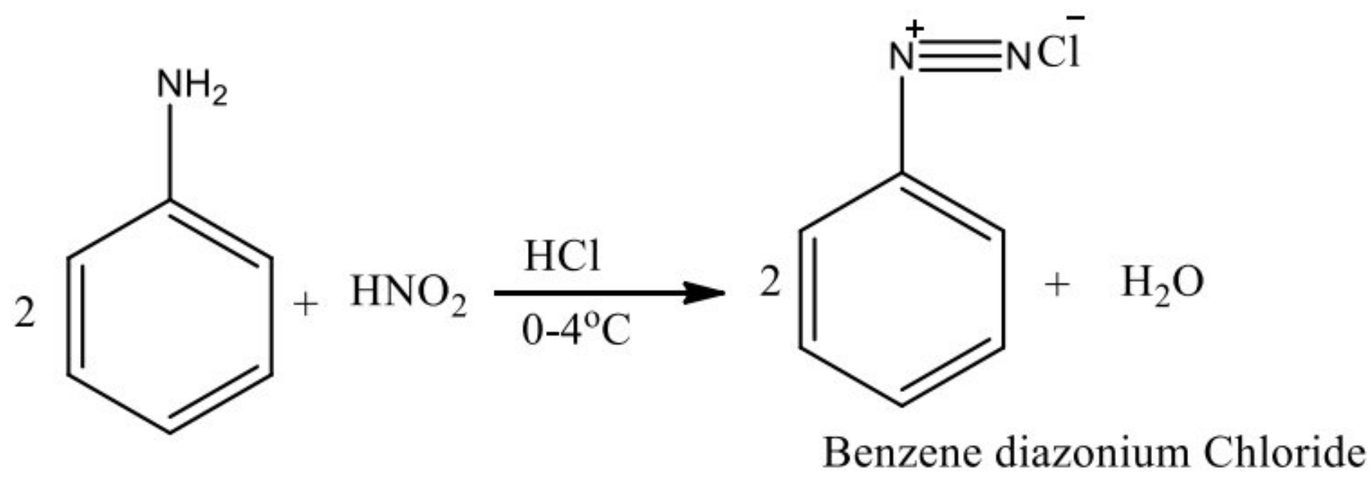
Uses:
Naphthols are used in the synthesis of **dyes, pigments, pharmaceuticals, and agrochemicals**, and serve as **intermediates** in various organic reactions.

Preparation of Phenol

Phenol can be prepared from aniline (phenylamine) through the formation and subsequent hydrolysis of a benzene diazonium salt.

Step 1: Formation of Benzene Diazonium Chloride

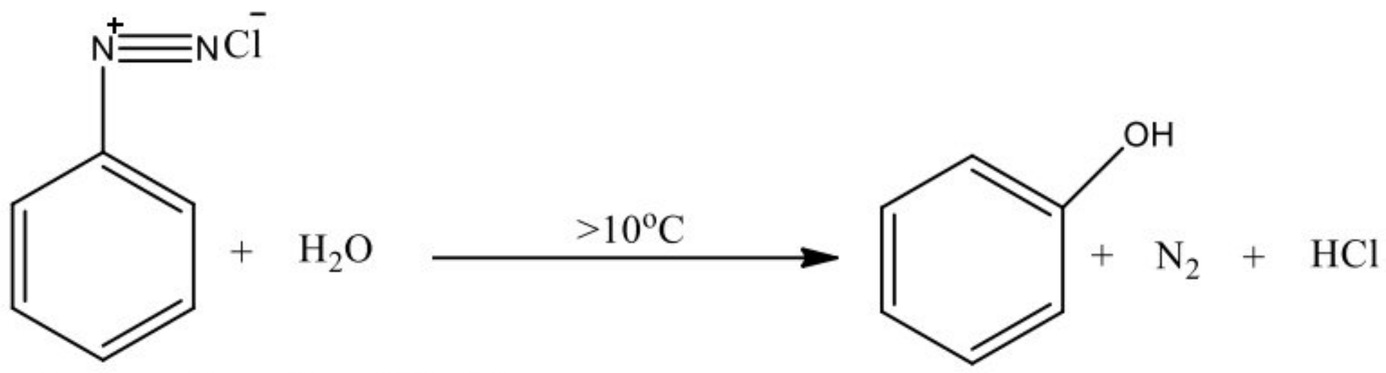
Aniline reacts with nitrous acid (HNO_2) in the presence of hydrochloric acid (HCl) at a temperature below 10°C to form benzene diazonium chloride.
Nitrous acid is usually prepared *in situ* by reacting sodium nitrite ($NaNO_2$) with dilute hydrochloric acid:



Benzene diazonium Chloride

Step 2: Hydrolysis of Benzene Diazonium Chloride

When the temperature is raised above 10°C, the benzene diazonium chloride undergoes hydrolysis, forming phenol.
The diazonium group ($-N_2^+$) is replaced by a hydroxyl group (-OH), and nitrogen gas is liberated.



Benzene diazonium Chloride Phenol

Acidity of Water, Phenol, and Ethanol

Acidity refers to the ability of a compound to donate a proton (H^+) and the stability of the **conjugate base** formed after proton donation.

1. Water (H_2O)

Water acts as both an acid and a base. It undergoes autoionization:

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

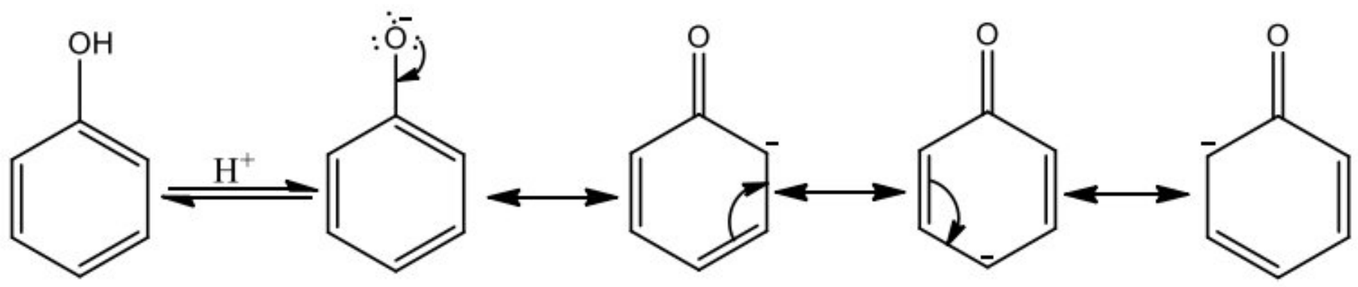
However, the autoionization constant ($K_w = 1 \times 10^{-14}$) is very small, showing that water is a **weak acid**.

2. Phenol (C_6H_5OH)

Phenol is **more acidic than water**. When phenol loses a proton, it forms the **phenoxide ion ($C_6H_5O^-$)**:

$$C_6H_5OH \rightleftharpoons C_6H_5O^- + H^+$$

The phenoxide ion is stabilized by **resonance** — the negative charge on the oxygen atom is delocalized over the aromatic ring. This resonance stabilization makes the conjugate base more stable, thus increasing acidity.
The acid dissociation constant (K_a) of phenol is 1.3×10^{-10}, which is much higher than that of water (1.8×10^{-16}).



Phenoxide ion

3. Ethanol (CH_3CH_2OH)

Ethanol is **less acidic than both water and phenol**. Its conjugate base, the **ethoxide ion ($CH_3CH_2O^-$)**, is not resonance-stabilized — the negative charge remains localized on the oxygen atom.
The K_a value of ethanol ($\mathbf{1.26 \times 10^{-16}}$) is smaller than that of both water and phenol, confirming its weak acidity.

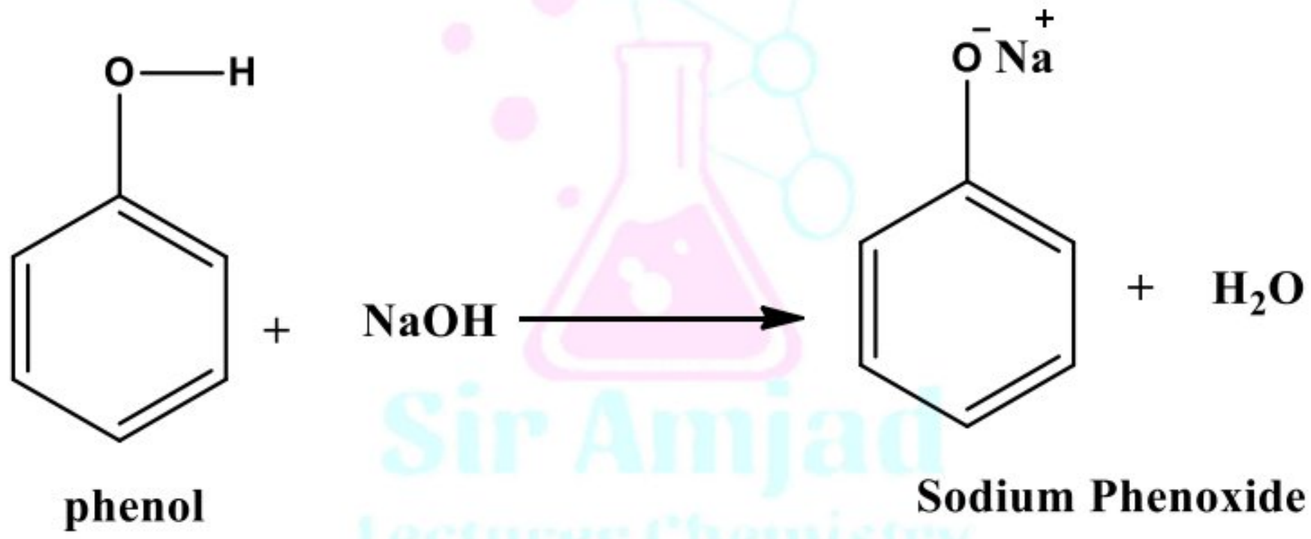
Relative Acidity Order

Phenol > Water > Ethanol

Reactions of Phenol

1. Reaction with Sodium (Na)

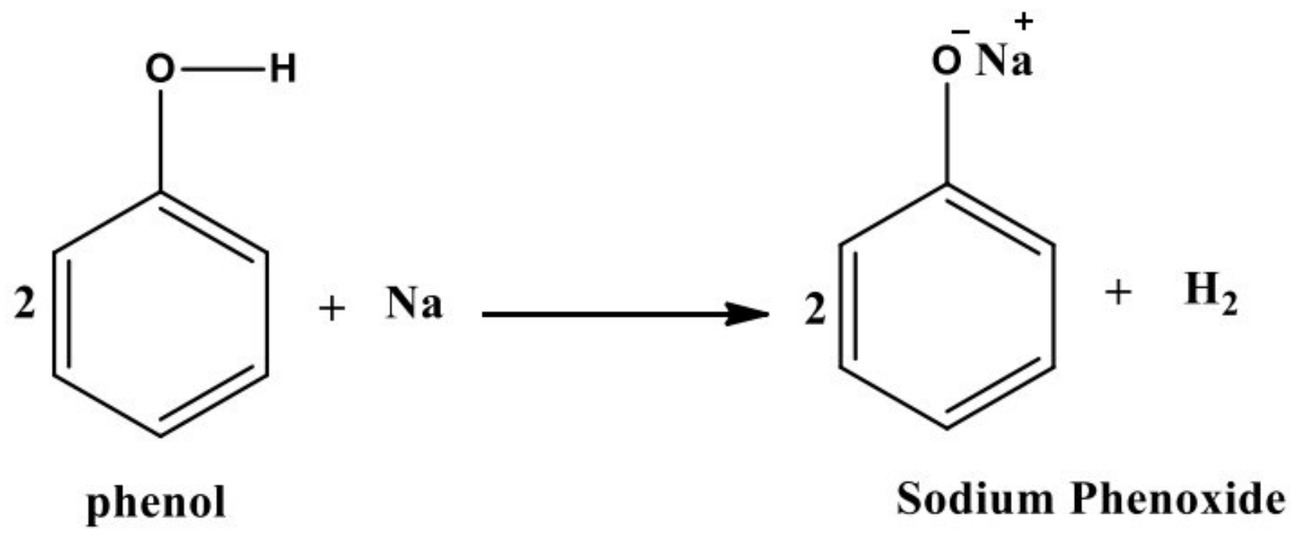
Phenol is acidic in nature and reacts with sodium to form salts.



phenol **Sodium Phenoxide**

2. Reaction with sodium hydroxide (NaOH)

Phenol is acidic in nature and reacts with sodium hydroxide to form salts.



phenol **Sodium Phenoxide**

3. Electrophilic Substitution Reactions in Phenol

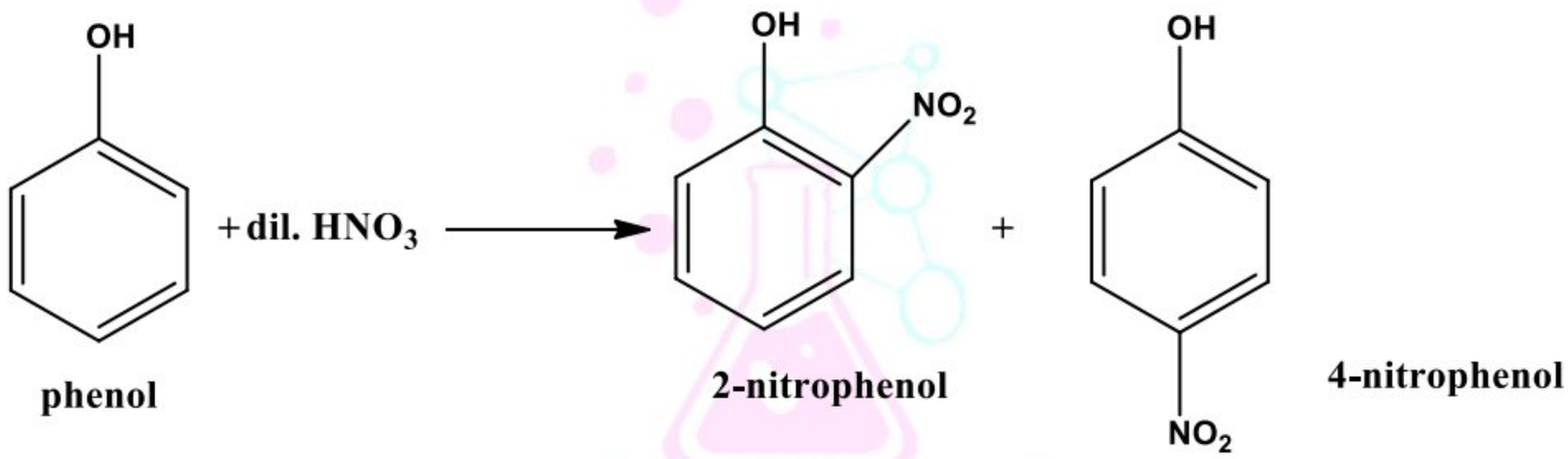
The **electrophilic substitution reactions** of phenol occur more readily than those of benzene. This is because of the **activating effect** of the **hydroxyl (-OH) group** attached to the benzene ring.

Activating Effect of the –OH Group

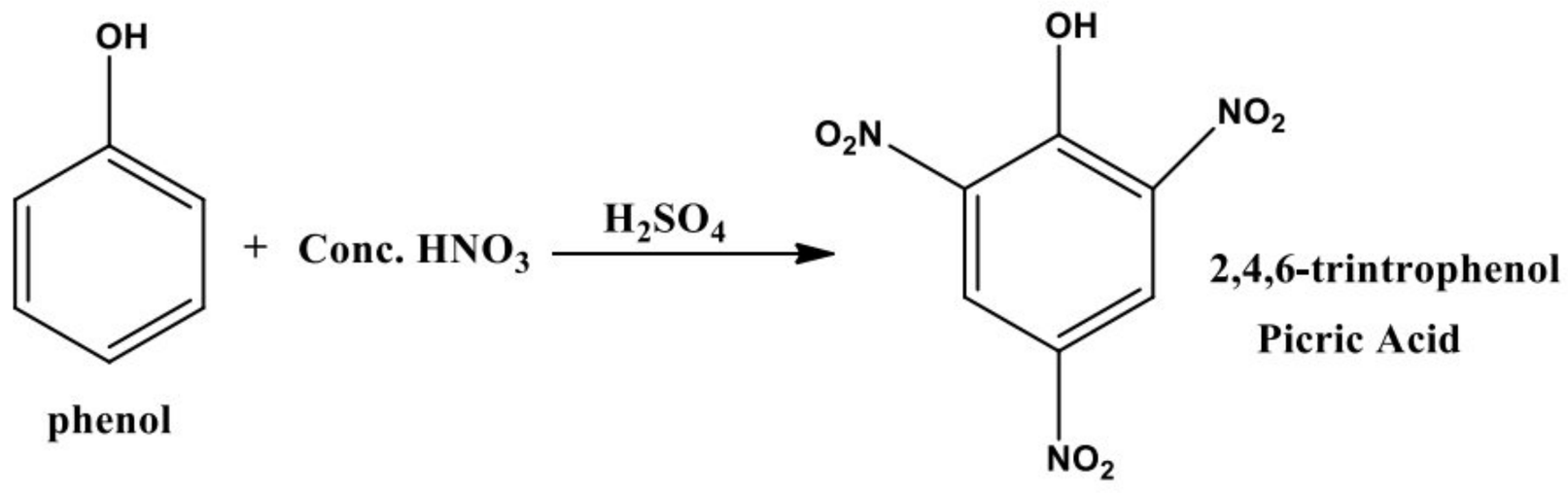
The hydroxyl group in phenol donates electrons to the aromatic ring through **resonance** and **inductive effects**.
This **increases the electron density** in the ring, particularly at the **ortho (2,6)** and **para (4)** positions.
As a result, phenol is **more reactive toward electrophilic attack** than benzene, and incoming electrophiles preferentially substitute at the ortho and para positions.

(a) Nitration of phenol

Phenol on treatment with dilute nitric acid undergoes nitration at room temperature to give a mixture of 2- and 4-nitrophenols.

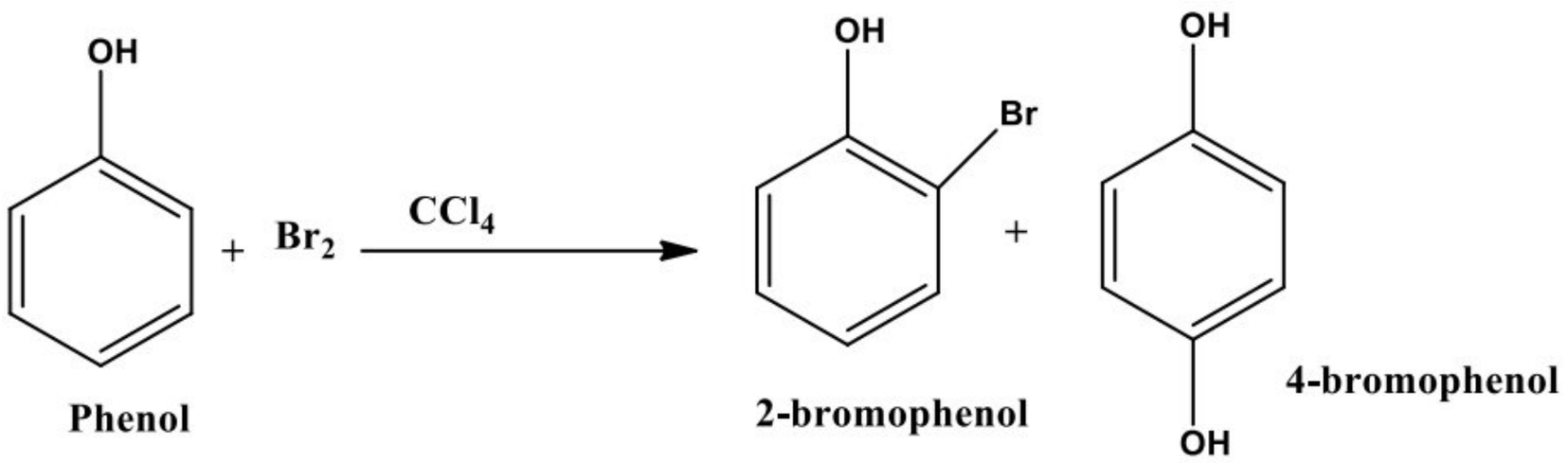


With concentrated nitric acid more nitro groups substitute the ring to give 2,4,6-trinitrophenol (picric acid).

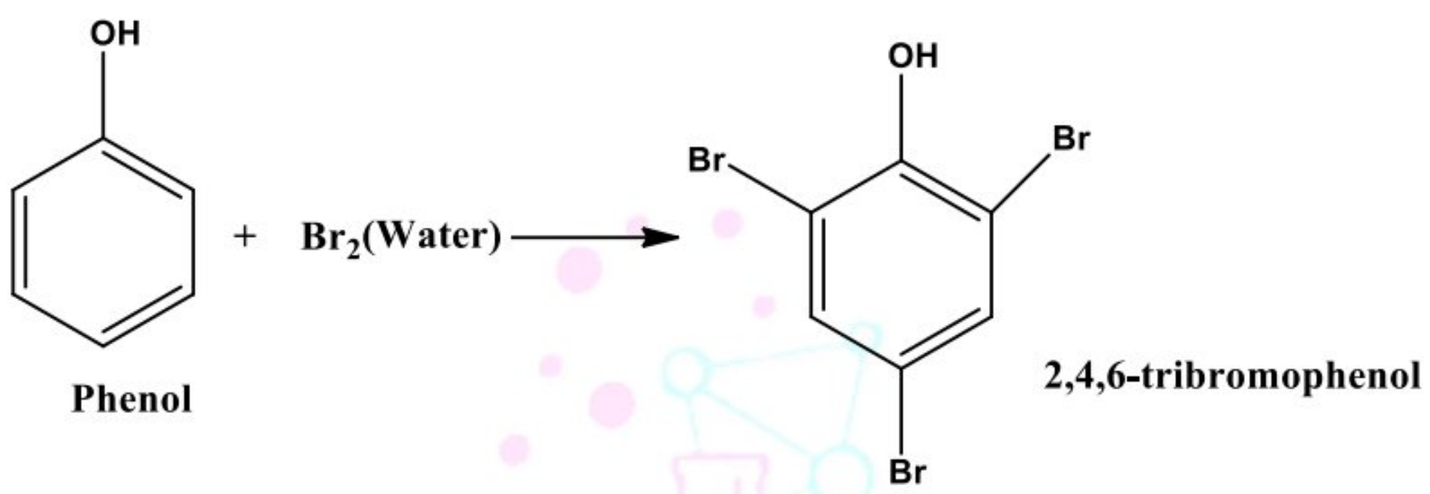


(b) Bromination of phenol

Phenol on reaction with bromine in the presence of a non-polar solvent (CCl_4, or CS_2) gives a mixture of 2- and 4- bromo phenol.



When bromine water is added to an aqueous solution of phenol, the reddish-brown colour of bromine is decolourized and a white precipitate of 2,4,6-tribromophenol is produced. This reaction is used to identify phenol.

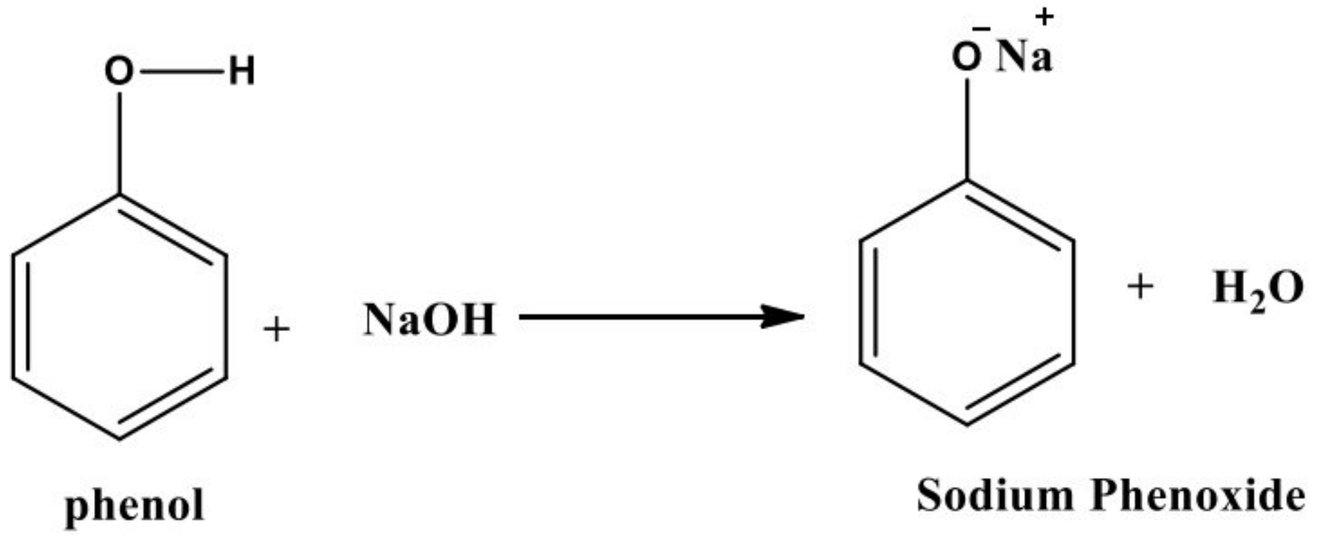


4. Reaction of Phenol with Diazonium Salt

Phenol reacts with **benzene diazonium chloride** in an **alkaline medium** to form an **azo compound**, which is an important type of **synthetic dye**.

Step 1: Formation of Sodium Phenoxide

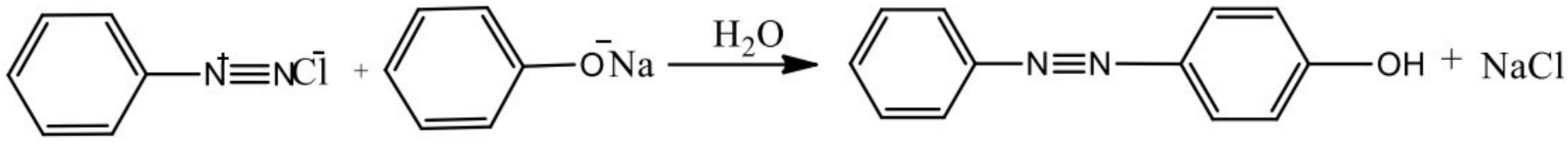
Phenol is first dissolved in **sodium hydroxide (NaOH)** solution:



This produces **sodium phenoxide**, which is more reactive than phenol itself.

Step 2: Coupling Reaction

When the solution of sodium phenoxide is **cooled in ice** and treated with a **cold solution of benzene diazonium chloride ($C_6H_5N_2^+Cl^-$)**, a **yellow-orange precipitate or solution** is formed.



Benzene diazoniumchloride

yellow- orange

The product is **p-hydroxyazobenzene**, one of the simplest **azo compounds**.

About Azo Compounds

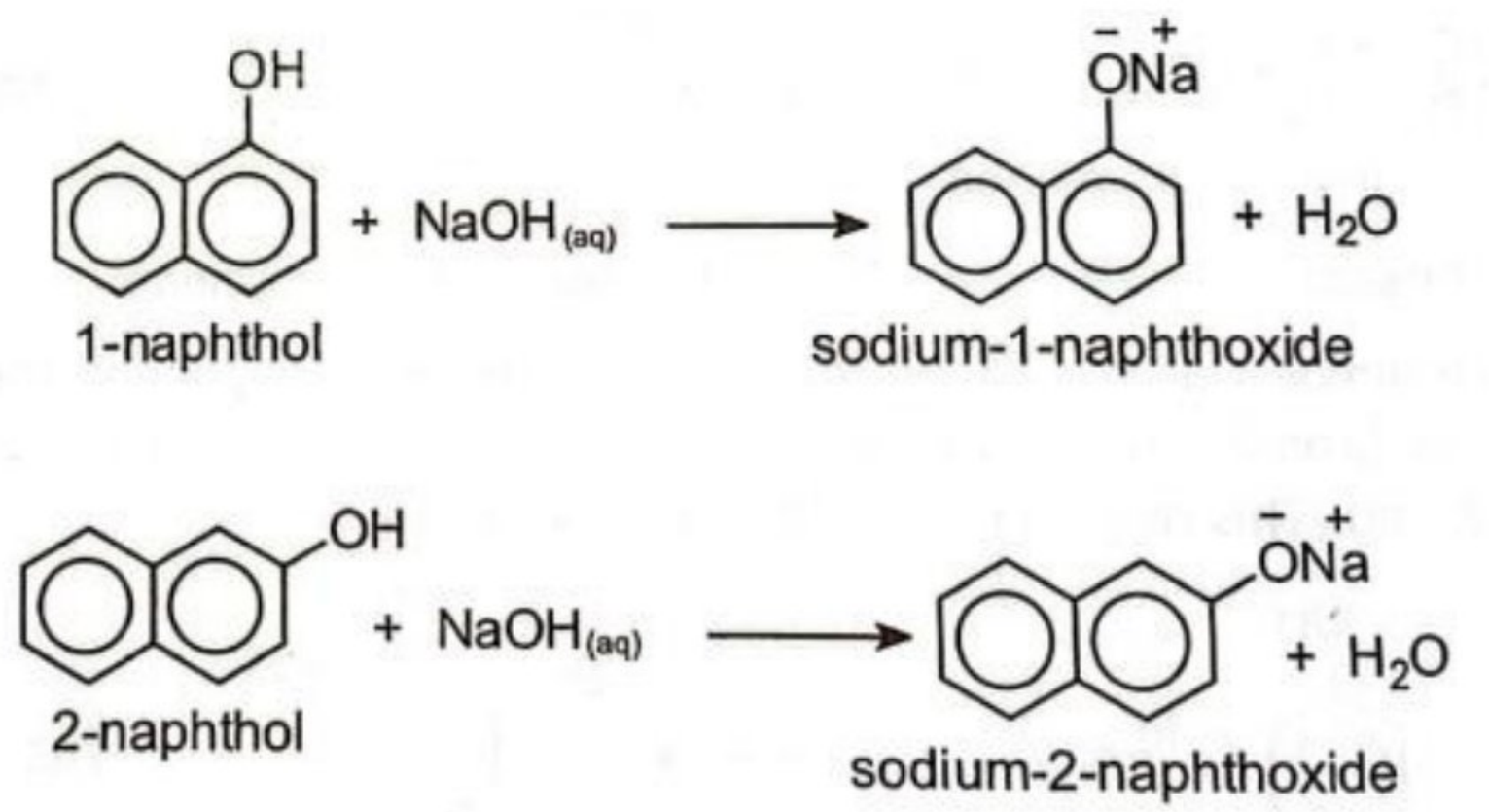
- **Azo compounds** contain the **–N=N– (azo)** linkage connecting two aromatic rings.
- These compounds are **highly colored** and form the basis of **azo dyes**, which are **synthetic dyes** (not found naturally).
- Azo dyes are widely used in **textile**, **printing**, and **food coloring** industries.

Naphthol

Reactions of Naphthols

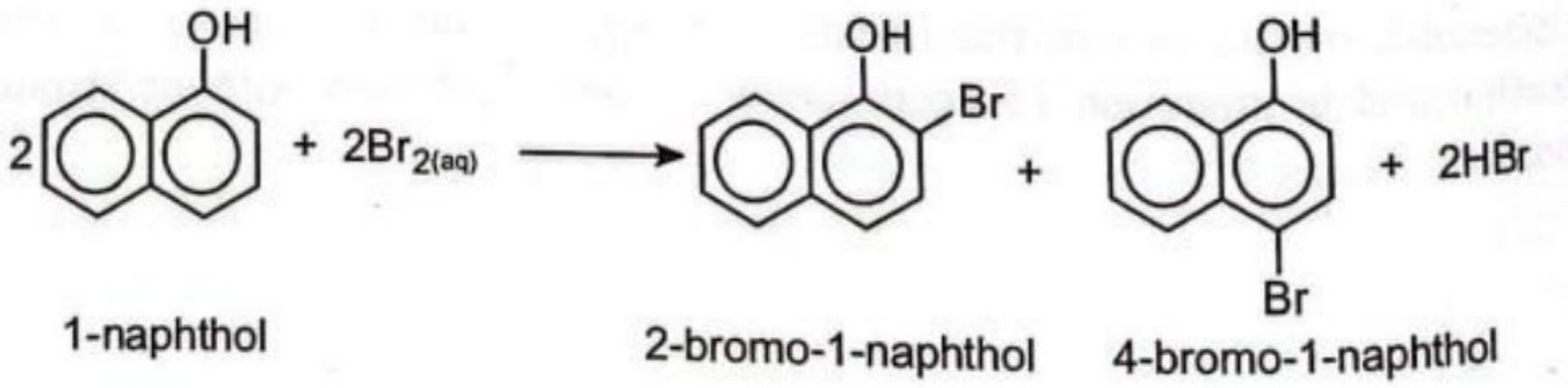
General reactions of simple phenol can also be applied to other phenolic compounds such as naphthols. Naphthols behave like simple phenols in chemical reactions.

1. **Reaction with sodium hydroxide**
   Naphthols dissolve in sodium hydroxide solution producing naphthoxide.

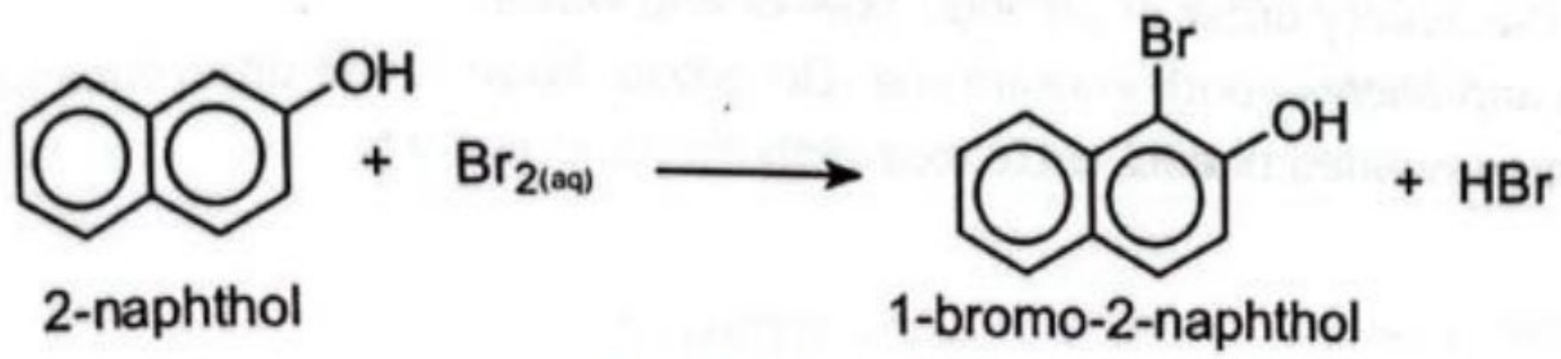


2.Reaction with bromine water

1-Naphthol decolourizes bromine water with a substitution of bromine at 2- and 4-positions.

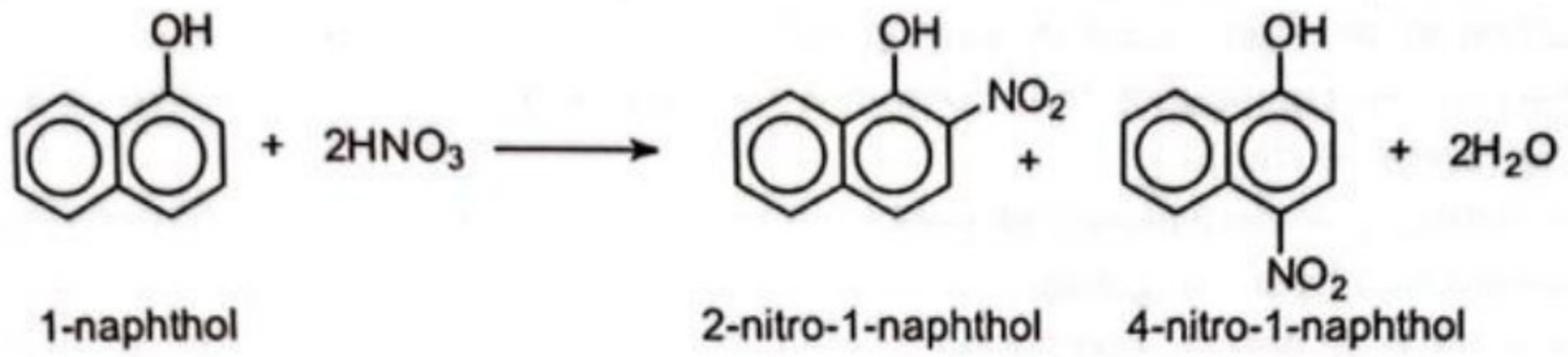


2-naphthol decolourizes bromine water with a substitution at the position between the OH group and the other ring. Position 4 is cluttered with the other ring.

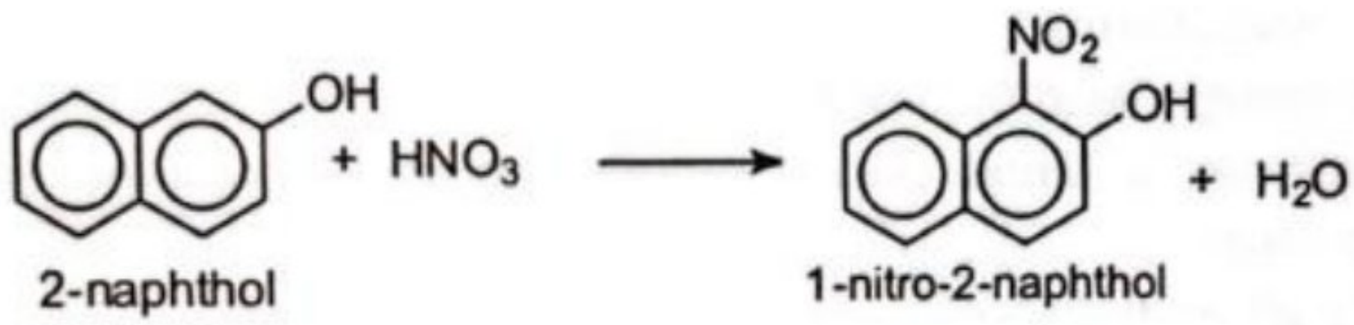


3. Reaction with nitric acid

1-naphthol gives substitution at 2- and 4-positions.



Niration of 2 naphthol

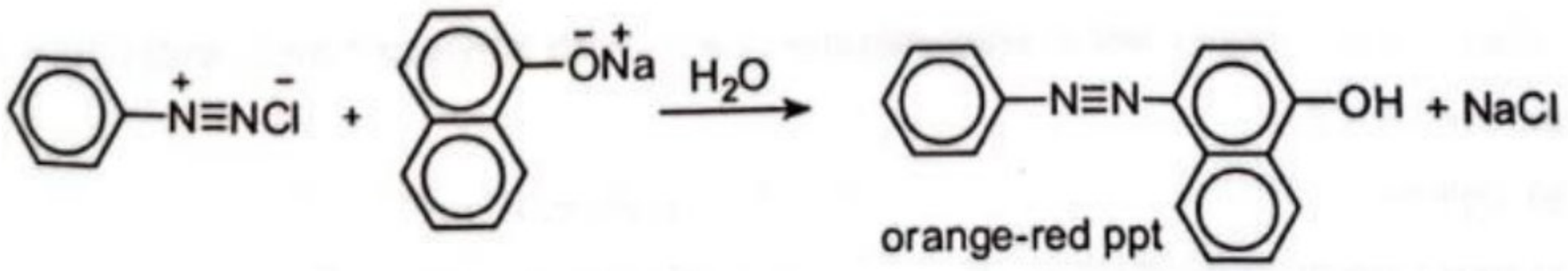


4. Reaction of Naphthols with Diazonium Chloride

Naphthols (1-naphthol and 2-naphthol) react with **diazonium salts** to form **azo compounds**, similar to the reaction of phenol with diazonium salts.

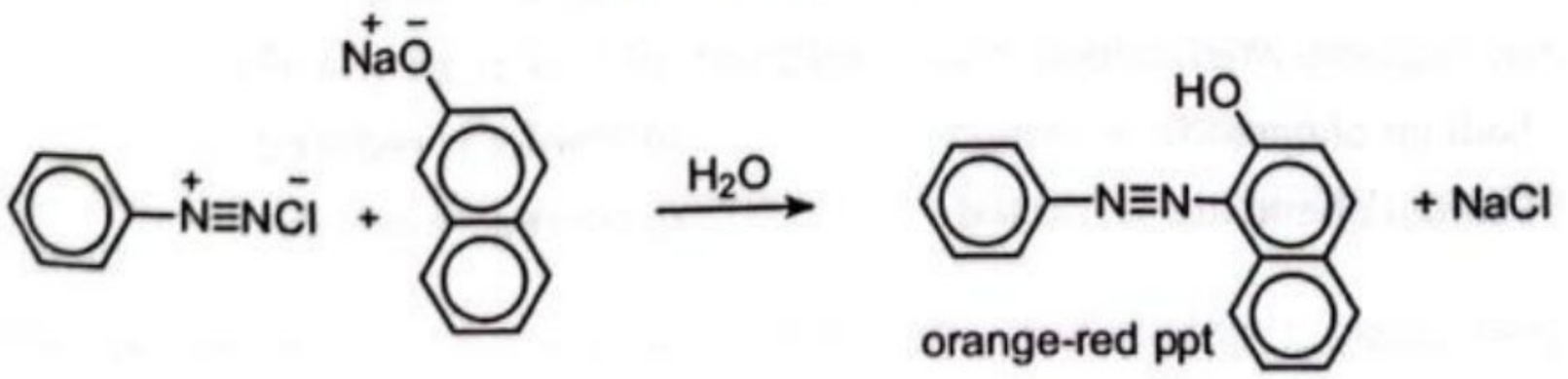
Step 1: Formation of Sodium Naphthoxide

1-naphthol or 2-naphthol is first dissolved in **sodium hydroxide (NaOH)** solution to form the **naphthoxide ion**, which is more reactive toward electrophilic substitution.



Step 2: Coupling Reaction

The alkaline solution of the naphthoxide ion is **cooled in ice** and then mixed with a **cold solution of benzene diazonium chloride ($C_6H_5N_2^+Cl^-$)**.
This results in the formation of a **brightly colored azo compound**.



An **intense orange-red precipitate** of the **azo dye** is produced.

Position of Substitution

- **1-Naphthol:** Coupling occurs mainly at the **4-position**.
- **2-Naphthol:** Coupling occurs at a position **between the –OH group and the second ring** (usually at the **1-position** relative to the hydroxyl group).

For More Information:

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