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 significantly affects the properties and reactivity of these compounds. Organic hydroxy compounds can be classified into several categories based on the nature of the carbon atom to which the hydroxyl group is attached. The main categories of hydroxy organic *organic* compounds are as follows:

1. Alcohols

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

For example;

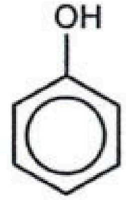
Methanol (CH_3OH): The simplest alcohol, often used as a solvent and antifreeze.

Ethanol (C_2H_5OH): Found in alcoholic beverages, used as a solvent and fuel.

Isopropanol (C_3H_7OH): Also known as isopropyl alcohol, used as a disinfectant and solvent.

2. Phenols

Phenols have a hydroxyl group attached directly to an aromatic ring (benzene ring). They are used in the manufacture of plastics, medicines, and as antiseptics and disinfectants.

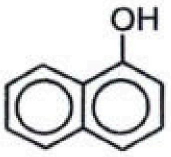


phenol

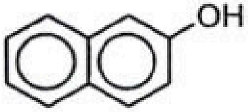
3. Naphthols

Naphthols are a set of organic compounds with the chemical formula $C_{10}H_7OH$. They are derivatives of naphthalene and consist of a naphthalene ring system bonded to a hydroxyl group. Naphthols exist in two isomeric forms:

1. **1-Naphthol:** Also known as α-naphthol, the hydroxyl group is attached to the first carbon atom of the naphthalene ring.
2. **2-Naphthol:** Also known as β-naphthol, the hydroxyl group is attached to the second carbon atom of the naphthalene ring.



1-naphthol



2-naphthol

These compounds are commonly used in the synthesis of dyes, pigments, and other organic chemicals. They also have applications in the manufacture of pharmaceuticals, agrochemicals, and in various chemical reactions as intermediates.

10.1 Preparation of Esters

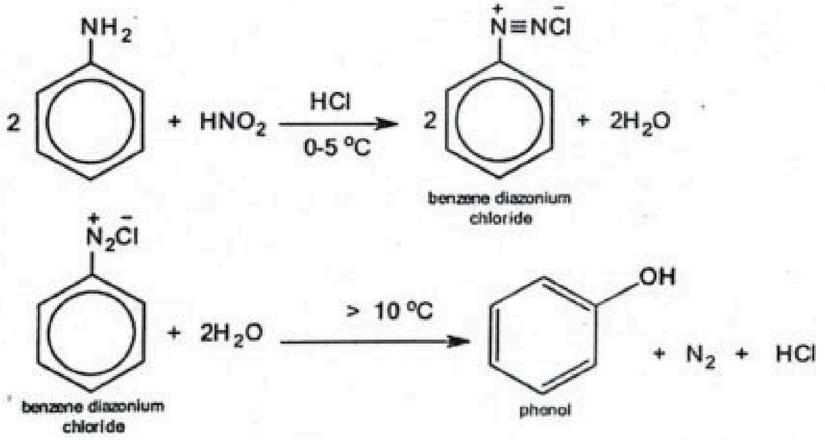
An ester is an organic compound formed by the addition of an acid to an alcohol. Esters are used in a variety of applications, such as the production of fragrances, flavourings, and pharmaceuticals. Esters can be prepared directly by reacting acyl halides with alcohols. Ethanoyl chloride, for example, reacts immediately with cold ethanol to form ethyl ethanoate. The reaction is very exothermic. A steamy acidic gas, (hydrogen chloride), is released. The oxygen atom of the alcohol, which has one lone pair of electrons, attacks electrophilic carbonyl carbon (acyl chloride). This attack results in the formation of the tetrahedral intermediate. In the subsequent step, the chloride ion (a good leaving group) departs and rapidly loses a proton to yield the ester.

$$CH_3COCl + CH_3CH_2OH \longrightarrow CH_3COOCH_2CH_3 + HCl$$

10.2 Preparation of Phenol

Phenol can be produced by the reaction of phenylamine with HNO_3 or $NaNO_3$ and dilute acid below 10°C to produce the diazonium salt.

Benzene diazonium chloride can be prepared by the reaction of aniline with nitrous acid (HNO_2) in the presence of hydrochloric acid. If the temperature is greater than 10°C, hydrolysis of benzene diazonium chloride takes place and phenol is formed.



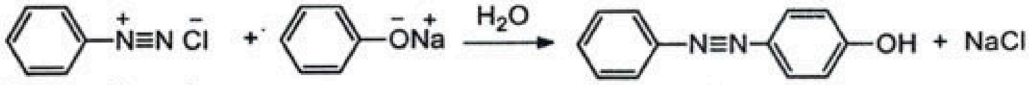
10.3 Acidity of water, phenol and ethanol

Acidity refers to the stability of the conjugate base formed by proton donation. Water is an acid and base. It is autoionized, but the autoionization constant of water is very low ($k_w = 1 \times 10^{-14}$). Therefore, water is a weak acid. Phenol is a stronger acid than water. The reason for this is that the phenoxide ion which is formed after the proton is lost, undergoes resonance stabilization. The negative charge of the phenoxide ion is delocalized into the ring. Therefore, phenoxide ions are stable. So, K_a of phenol (1.3×10^{-10}) is higher than that of water (1.8×10^{-16}).

(c) Reaction of phenol with diazonium salt

Phenol is dissolved in sodium hydroxide solution to give a solution of sodium phenoxide. When this solution is cooled in ice, and cold benzene diazonium chloride solution is added, a yellow-orange solution or precipitate is formed. The product is one of the simplest azo-compounds which are used as azo dyes. Azo-dyes are synthetic dyes that do not occur naturally. In azo-dyes, two benzene rings are linked by a nitrogen bridge.

phenol sodium phenoxide



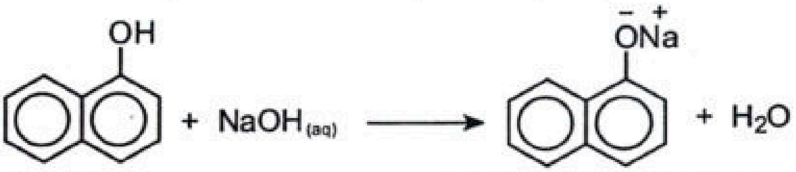
benzenediazonium chloride yellow-orange ppt

10.5 Reactions of Naphthols

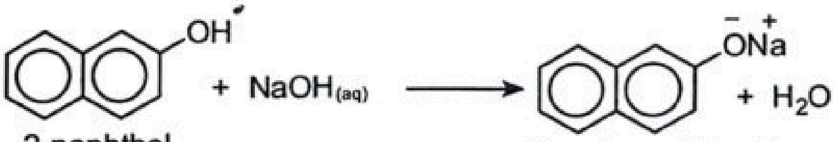
General reactions of simple phenol can also be applied to other phenolic compounds such as naphthols. Naphthols behave like simple phenols in chemical reactions.

1. Reaction with sodium hydroxide

Naphthols dissolve in sodium hydroxide solution producing naphthoxide.



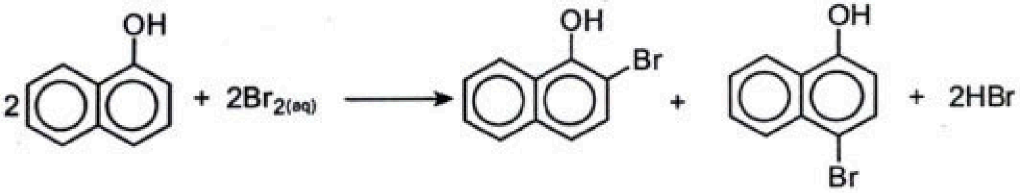
1-naphthol sodium-1-naphthoxide



2-naphthol sodium-2-naphthoxide

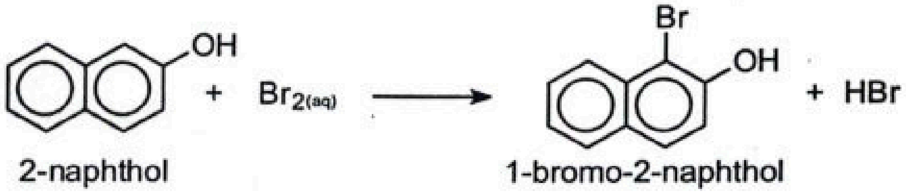
2. Reaction with bromine water

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



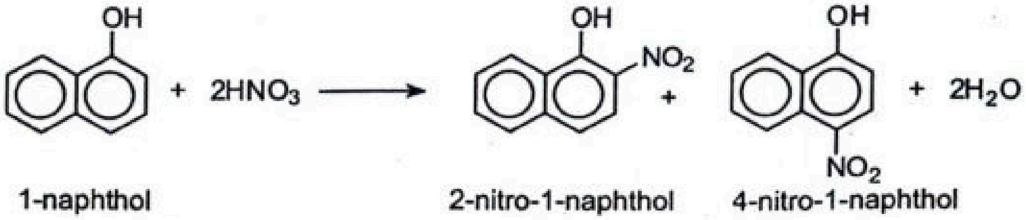
1-naphthol 2-bromo-1-naphthol 4-bromo-1-naphthol

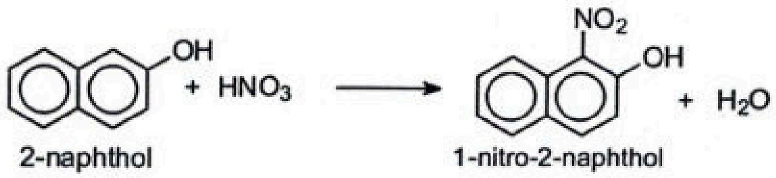
2-naphthol decolourizes bromine water with a substitution at the position between the OH group and the other ring. Position 4 is cluttered with the other ring.



3. Reaction with nitric acid

Nitration occurs like bromination. 1-naphthol gives substitution at 2- and 4-positions.

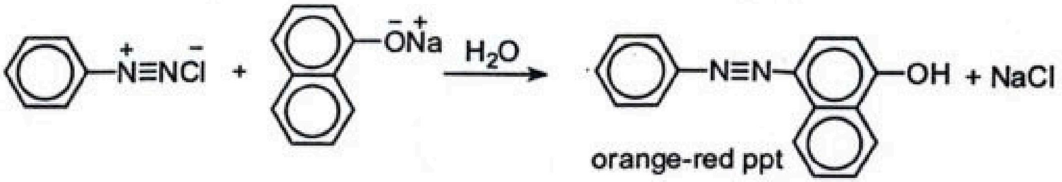


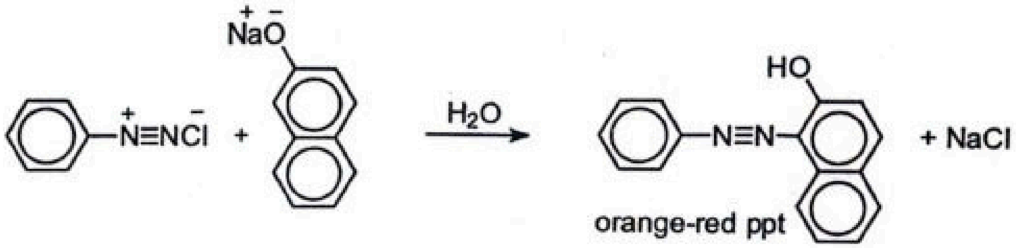


4. Reaction with diazonium chloride

Naphthols react with diazonium salt to give azo compounds. 1-naphthol reacts with diazonium salt in exactly the same conditions as with phenol. The 1-naphthol is dissolved in NaOH solution to produce an ion like the phenol. This solution is ice-cooled and mixed with the diazonium salt solution. An intense orange-red precipitate of an azo compound is produced. With 1-naphthol reaction occurs at position 4.

With 2-naphthol reaction occurs at a position between the OH group and the other ring.





ix. Explain the resonance stabilization of the phenoxide ion and how it contributes to the acidity of phenol.

x. Compare the acidities of phenol, ethanol, and water. Provide a brief explanation for the differences in their acid strengths.

xi. Predict the products of the reaction of 1-naphthol with NaOH and bromine water. Provide the balanced chemical equations and indicate the positions of the substituents.

3. Long Answer Questions

1. Compare and contrast the reactivity of phenol, benzene, and ethanol in electrophilic aromatic substitution reactions. Explain the role of the hydroxyl group in phenol and its influence on these reactions.
2. Describe the acidity of phenol in terms of its ability to donate protons. Compare its acidity to that of water and ethanol and explain the molecular basis for the differences observed.
3. Describe how 2-naphthol will undergo a reaction with bromine water and nitric acid.
4. Predict the products if methanol is used instead of ethanol in the reaction with ethanoyl chloride. Provide the balanced chemical equation.
5. Write the balanced chemical equations for the reactions of phenol with NaOH and sodium metal. Describe the products formed in each reaction.
6. Explain the reaction of phenol with bromine water
7. Describe the reaction of phenol with dilute nitric acid at room temperature. What are the products, and why do they form in the observed positions on the aromatic ring?
8. Discuss the similarities and differences in the directing effects of the hydroxyl group in phenol and 1-naphthol.
9. Phenol is more acidic than ethanol. Analyze the structure of phenol to explain this difference in acidity.
10. Phenol reacts with bromine water to form a white precipitate without needing a catalyst. What does this suggest about the electron density of the aromatic ring in phenol?