Organic chemistry for 2nd stage by Asst. Prof. Amjed Taher / Chemistry Department) 2024-2025

PHENOLS

By: Asst. Prof. Amjed Taher Battor

Structure

- Alcohols contain an OH group bonded to an sp^3-hybridized carbon.
- Phenols contain an OH group bonded to an sp^2-hybridized carbon of a benzene ring

Phenol

Nomenclature

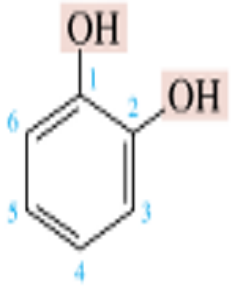
1. Monohydric phenols

-Functional group suffix = *-common -phenol*

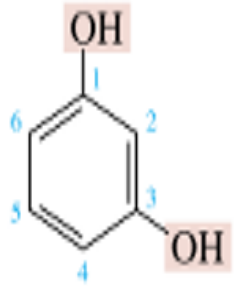
-Functional group prefix = *hydroxy*

-Numbering of the ring begins at the hydroxyl-substituted carbon and proceeds in the direction of the next substituted carbon that possesses the lower number.

-Ortho, meta or para : **Mono-substituted phenols are characterized using the prefix ortho (*o*-), meta (*m*-) or para (*p*-) depending on the placement of the substituent from the hydroxyl group or the hydroxyl group from a higher priority functional group.**

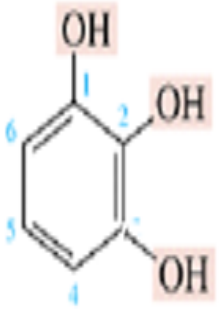


1,2-Benzenediol
(pyrocatechol)

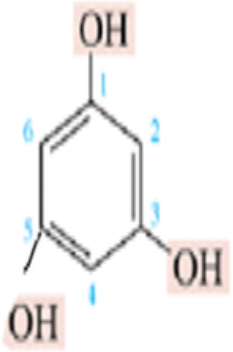


1,3-Benzenediol
(resorcinol)

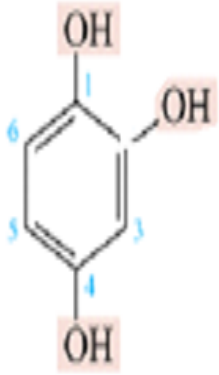
1,4-Benzenediol
(hydroquinone)



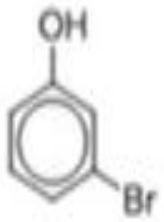
1,2,3-Trihydroxybenzene
or (pyrogallol)



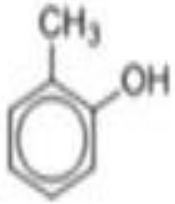
1,3,5-Trihydroxybenzene
or (phloroglucinol)



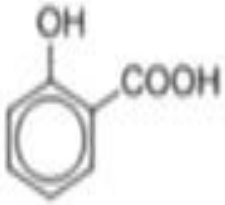
1,2,4-Trihydroxybenzene
or (Hydroxyquinol)



m-bromophenol

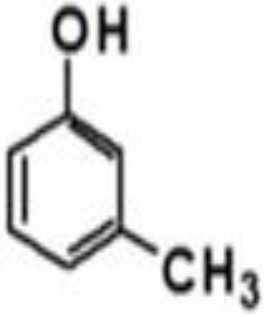


o-cresol

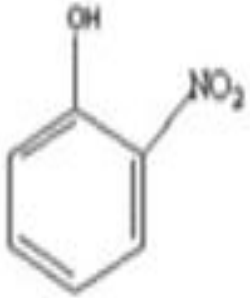


salicylic acid

p-hydroxybenzoic acid

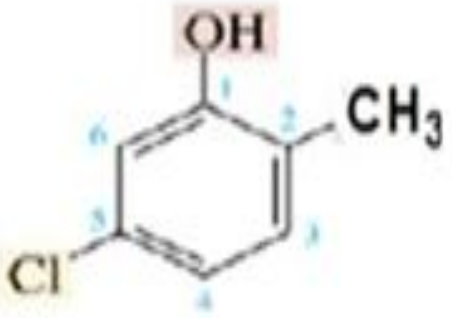


3-Methylphenol
(*m*-Cresol)



O-Nitrophenol

p-Aminopheno



5-Chloro-2-methyl phenol

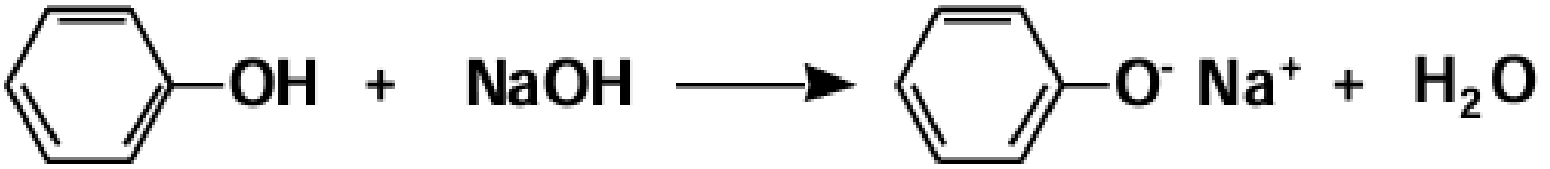
physical properties

1- phenols are polar and can hydrogen bond

2- phenols are water insoluble

3- phenols are stronger acids than water and

will dissolve in 5% NaOH



Phenol — pK_a 9.95 (stronger acid)

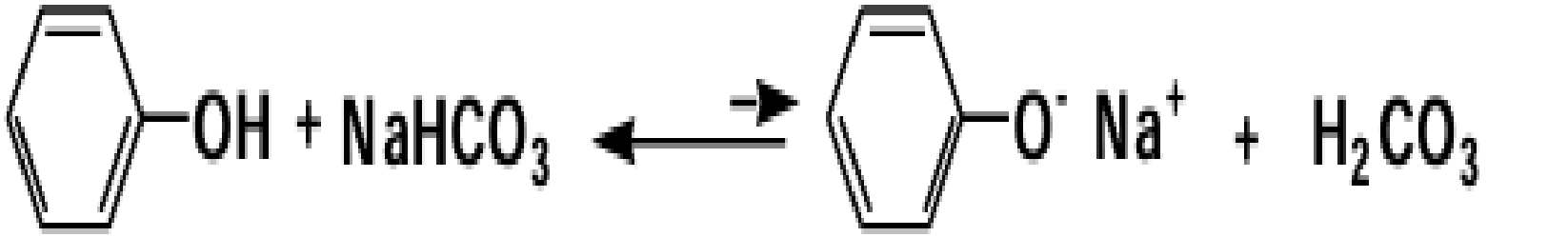
Sodium hydroxide

Sodium phenoxide

Water — pK_a 15.7 (weaker acid)

4- phenols are weaker acids than carbonic acid and

do not dissolve in 5% $NaHCO_3$



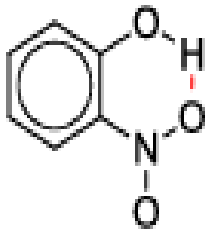
Phenol — pK_a 9.95 (weaker acid)

Sodium bicarbonate

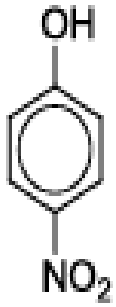
Sodium phenoxide

Carbonic acid — pK_a 6.36 (stronger acid)

* Intramolecular hydrogen bonding is possible in some ortho-substituted phenols. This intramolecular hydrogen bonding reduces water solubility and increases volatility. Thus, *o*-nitrophenol is steam distillable while the isomeric *p*-nitrophenol is not.



o-nitrophenol
bp 100°C at 100 mm
0.2 g / 100 mL water
volatile with steam



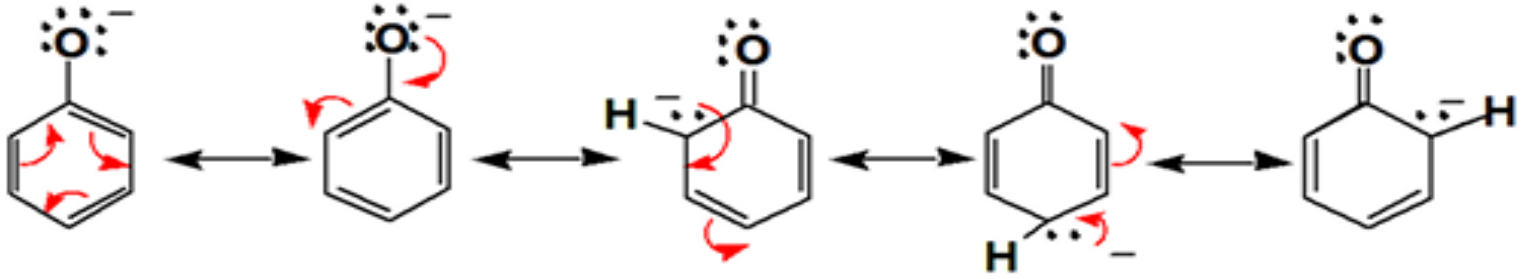
p-nitrophenol
bp *decomposes*
1.69 g / 100 mL water
non-volatile with steam

Acidity of Phenols

Phenols are significantly more acidic than alcohols. •

$CH_3CH_2OH + H_2O \rightleftharpoons CH_3CH_2O^- + H_3O^+ \qquad pK_a = 15.9$

The greater acidity of phenols compared with alcohols is due to the greater stability of the phenoxide ion relative to an alkoxide ion

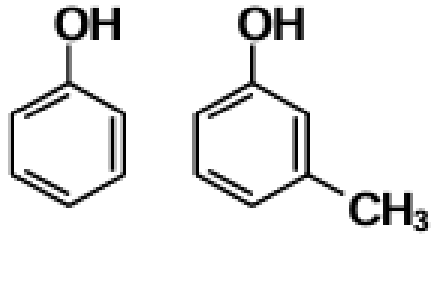


Substituent Effects on the Acidity of Phenols

Alkyl and halogen substituents effect acidities by inductive effects

Alkyl groups are electron-releasing.

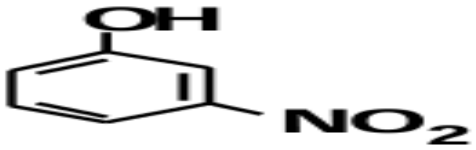
Halogens are electron-withdrawing.



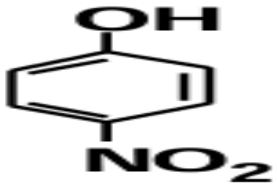
Phenol	*m*-Cresol	*p*-Cresol	*m*-Chlorophenol	*p*-Chororophenol
pK_a 9.95	pK_a 10.01	pK_a 10.17	pK_a 8.85	pK_a 9.18

Nitro groups increase the acidity of phenols by both an electron-withdrawing inductive effect and a resonance effect.

Phenol
pK_a 9.95



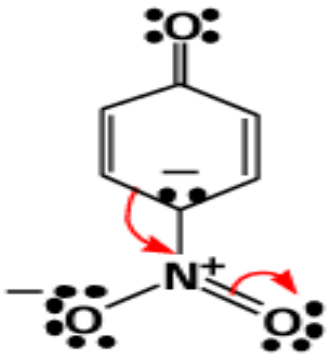
***m*-Nitrophenol**
pK_a 8.28

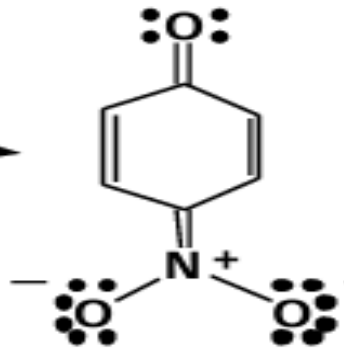


***p*-Nitrophenol**
pK_a 7.15

Part of the acid-strengthening effect of -NO_2 is due to its electron-withdrawing inductive effect.

In addition, -NO_2 substituents in the ortho and para positions help to delocalize the negative charge.

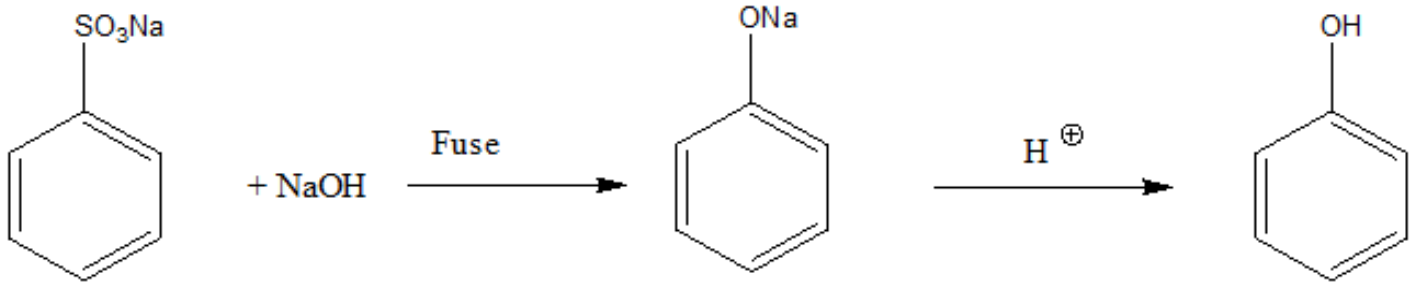




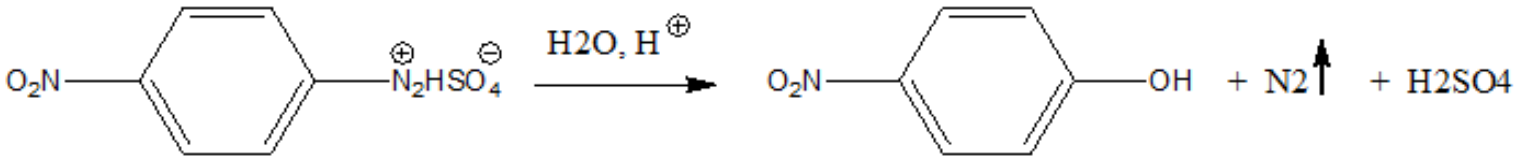
delocalization of negative charge onto oxygen further increases the resonance stabilization of phenoxide ion

PREPARATION

- From aryl sulphonic acids



- From diazonium salts



p-Nitrobenzendiazonium hydrogen sulphate

p-Nitrophenol

Reaction of Phenols

1. Reaction with reactive metals

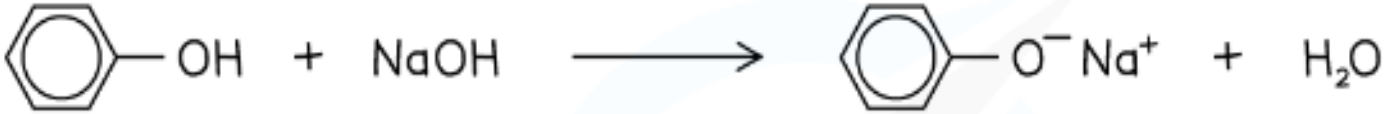
- **Molten phenols** react **vigorously** with reactive metals such as **sodium** (Na)
- This is also an **acid-base** reaction
- Now, a soluble salt is formed and **hydrogen gas** is given off
- **Phenol with metals reaction**

2. Reaction with diazonium ion

- **Diazonium ions are very reactive compounds containing an $-N_2^+$ group**
- **When phenols are dissolved in sodium hydroxide (NaOH), a solution of sodium phenoxide is obtained**
- **This solution is cooled in ice and cold diazonium ion is added to the sodium phenoxide**
- **After the reaction has occurred, a yellow-orange solution or precipitate of an azo compound is formed**
- **These are compounds in which two benzene rings are linked by a nitrogen bridge**

Phenol in diazonium ion reactions

STEP 1



PHENOL

SODIUM PHENOXIDE

STEP 2

BENZENE DIAZONIUM ION

PHENOXIDE ION

AZO COMPOUND (YELLOW–ORANGE PRECIPITATE)

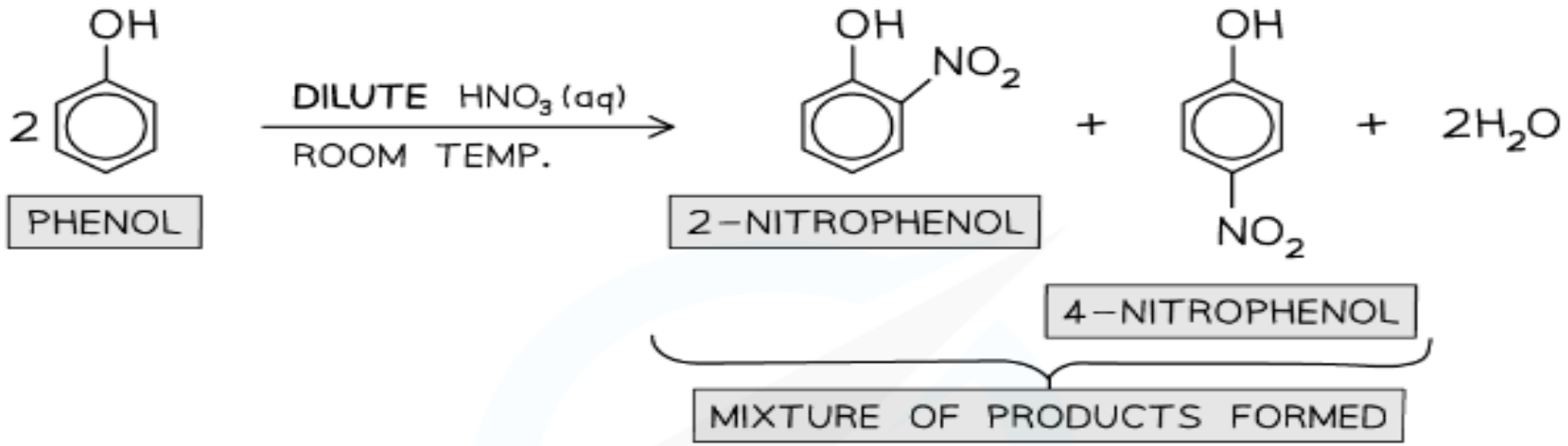
Azo compounds are formed from the reaction of phenols with diazonium ions

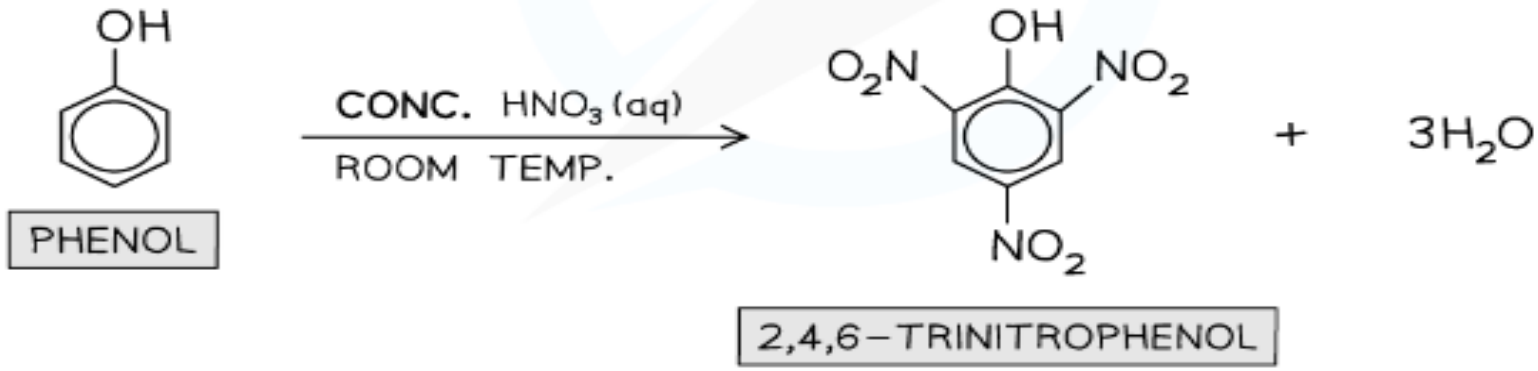
3. Reactions of the aromatic ring in phenols

- Phenols react
  more **readily** with **electrophiles** compared to benzene
- This is because one of the lone pairs of electrons on the oxygen atom in -OH overlaps with the π bonding system
- This increases the **electron density** of the benzene ring making it more **susceptible** to **electrophilic attack**
- The -OH group in phenols
  is **activating** and **directs** incoming electrophiles to the **2, 4, and 6 positions**

- **Nitration**
- Phenols can undergo **electrophilic substitution** reactions when reacted with **dilute nitric acid** (HNO_3) at **room temperature** to give a mixture of **2-nitrophenol** and **4-nitrophenol**
  - When **concentrated HNO_3** is used, the product will be 2,4,6-trinitrophenol instead
- A hydrogen atom in the benzene ring is **substituted** by a nitro ($-NO_2$) group
- This is also known as the **nitration** of phenol

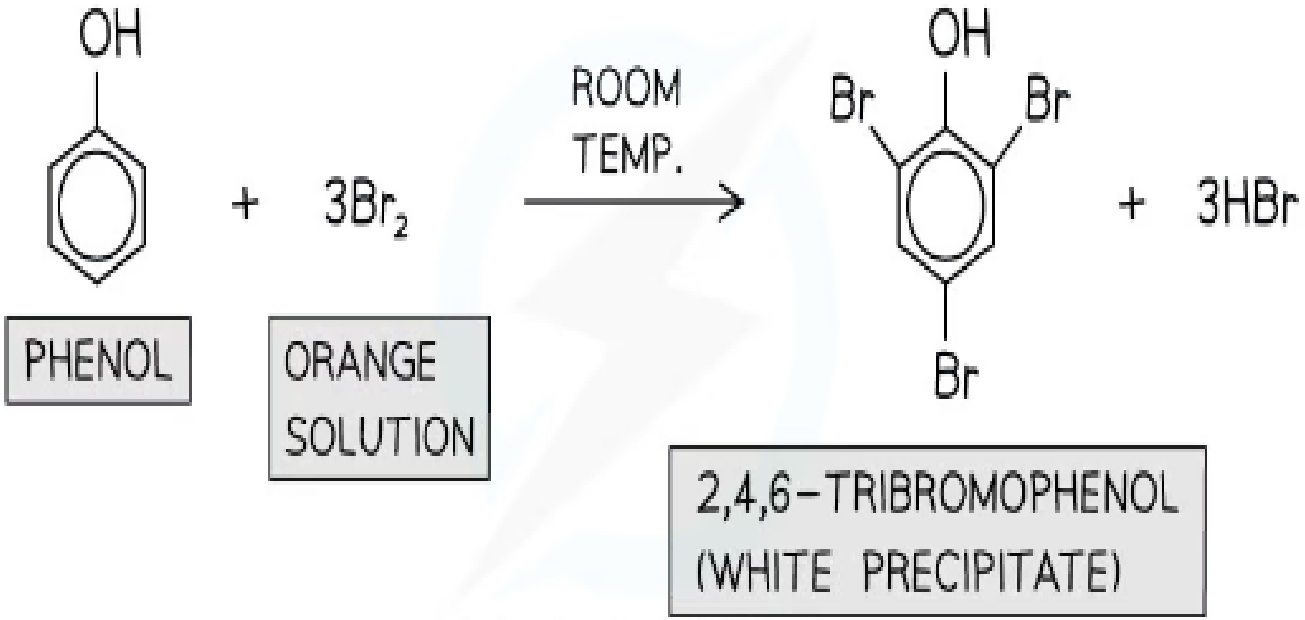
Phenol in nitration reactions





- **Bromination**
- Phenols also undergo **electrophilic substitution** reactions when reacted with **bromine water** at **room temperature**
- Phenol **decolourises** the **orange** bromine solution to form a **white precipitate** of 2,4,6-tribromophenol
- This is also known as the **bromination** of pheno

Phenol in bromination reactions



Phenols undergo bromination when reacted with bromine water at room temperature