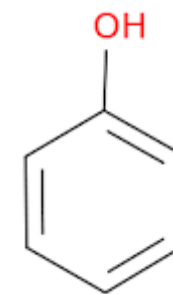


# School of Basic and Applied Sciences

Course Code : BSCC2004

Course Name: Organic Chemistry-II

*Phenol*



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## Phenol

### ❖ Nomenclature

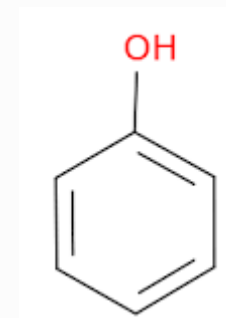
- Acidity
- substitution effect on the acidity of phenol
- synthesis of phenol
- Reaction of phenol

#### 1- Reactions of Phenolic Hydrogen

- Esterification of phenol
- Friedel – Crafts acylation: Fries Rearrangement
- Williamson ether synthesis
- Reactions with bases

#### 2- Reactions of Phenolic Benzene Rings

- Electrophilic aromatic substitution
- Carboxylation of phenol: Kolb-Schmitt reaction and aspirin



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## Nomenclature

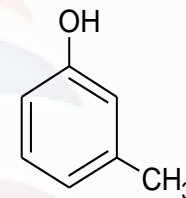
In Nomenclature of phenol

Functional group suffix = *-common - phenol*

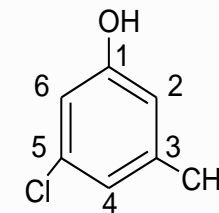
Functional group prefix = *hydroxy*

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.

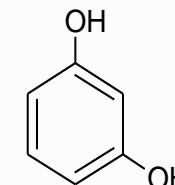
**Ortho, meta or para ?** Mono-substituted phenols are characterized using the prefix ortho (*o-*), meta (*m-*) or para (*p-*) depending on the placement of the substituent from the hydroxyl group or the hydroxyl group from a higher priority functional group.



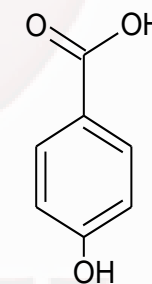
m-cresol



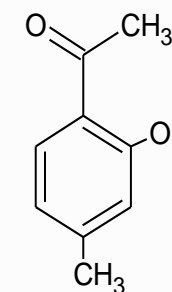
5-chloro-3-methyl phenol



resorcinol



p-hydroxy benzoic acid



2-hydroxy-4-methylacetophenone

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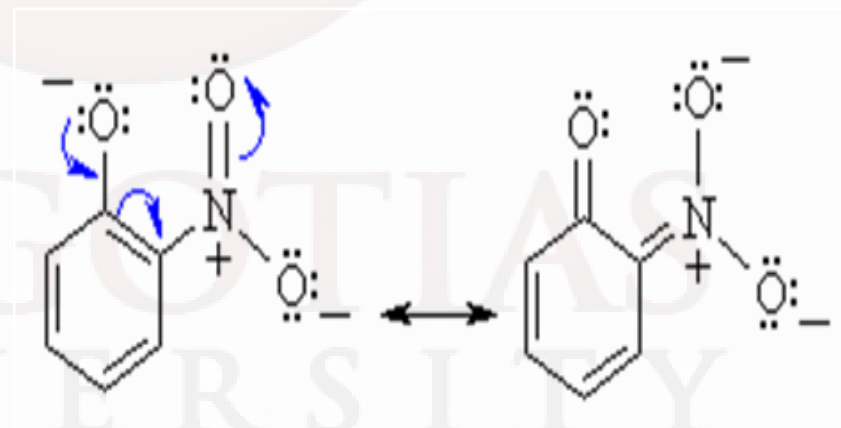
## Acidity

Phenols are more acidic ( $pK_a \approx 10$ ) than alcohols ( $pK_a \approx 16 - 20$ ), but less acidic than carboxylic acids ( $pK_a \approx 5$ ). The negative charge of the phenolate ion is stabilized by resonance due to electron delocalization onto the ring as shown (slide 3)

### Substituent effect on Acidity

Substituents, particularly those located *ortho* or *para* to the -OH group, can dramatically influence the acidity of the phenol due to resonance and / or inductive effects. Electron withdrawing groups enhance the acidity, electron donating substituents decrease the acidity. The resonance stabilization of *o*-nitrophenol is shown below:

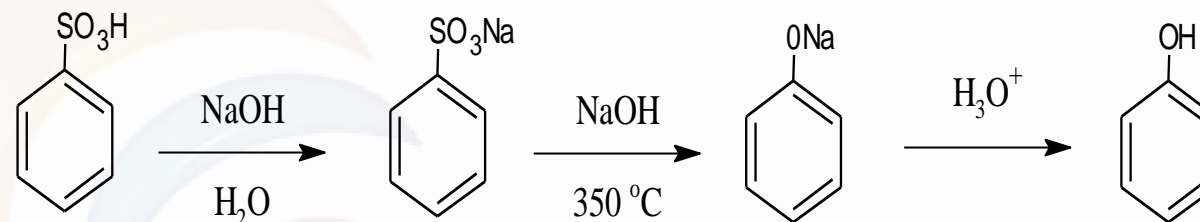
Compound	pKa
Phenol	10.0
<i>o</i> -Methoxyphenol	10.0
<i>p</i> -Methoxyphenol	10.2
<i>o</i> -Methylphenol	10.3
<i>p</i> -Methylphenol	10.3
<i>o</i> -Chlorophenol	8.6
<i>p</i> -Chlorophenol	9.4
<i>o</i> -Nitrophenol	7.2
<i>p</i> -Nitrophenol	7.2
<i>m</i> -Nitrophenol	8.4



## Synthesis of Phenols

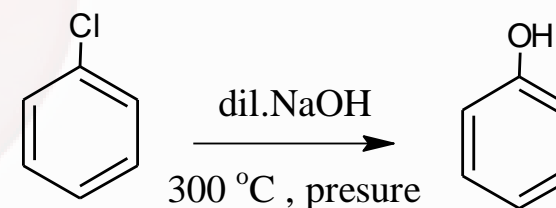
- 1- Alkali fusion of sulfonate**

phenols prepare in large quantities by the pyrolysis of the sodium salt of benzene sulfonic acid.



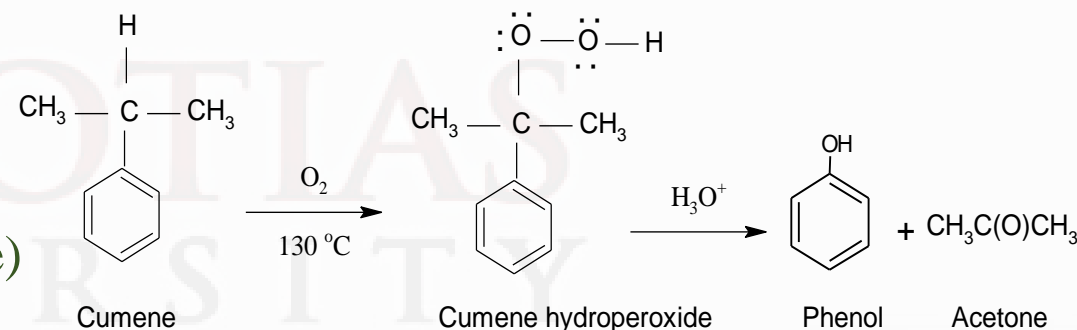
- 2- Dow process**

In the Dow process, chlorobenzene is reacted with dilute sodium hydroxide at 300°C and 3000 psi pressure.



- 3- Air oxidation of cumene**

The air oxidation of cumene (isopropyl benzene) leads to the production of both phenol and acetone.



## Reactions of Phenol

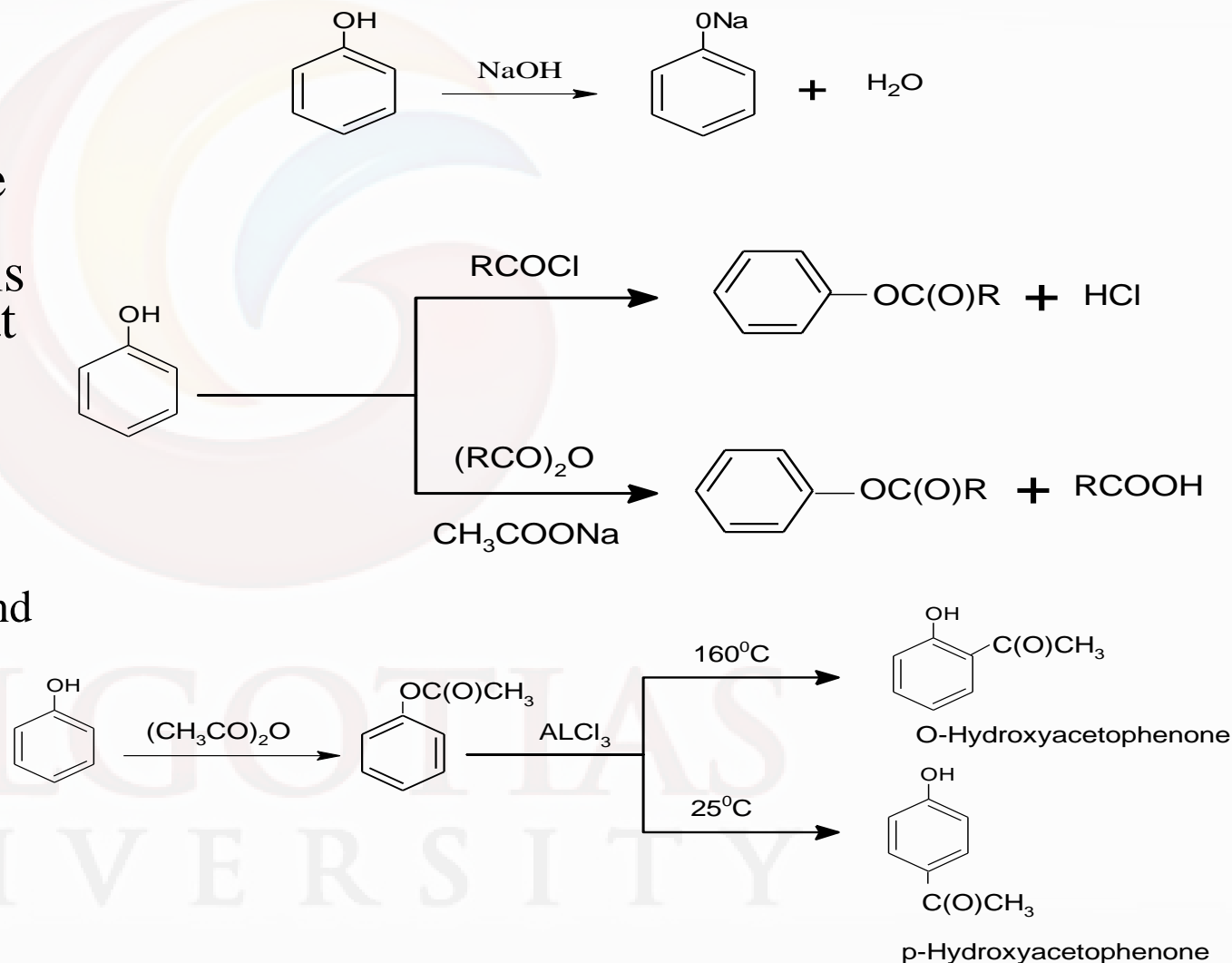
### 1- Reactions of Phenolic Hydrogen

- Phenols are acidic because of the ease with which the oxygen atom will release the hydrogen bonded to it. This section describes typical reactions that occur as a result of the acidity of phenols

- Esterification of phenol**

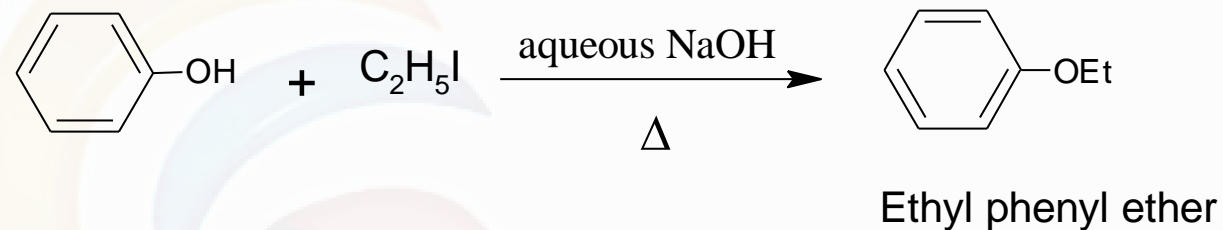
Phenols form esters with acid anhydrides and acid chlorides.

- Friedel – Crafts acylation:**  
**Fries Rearrangement**



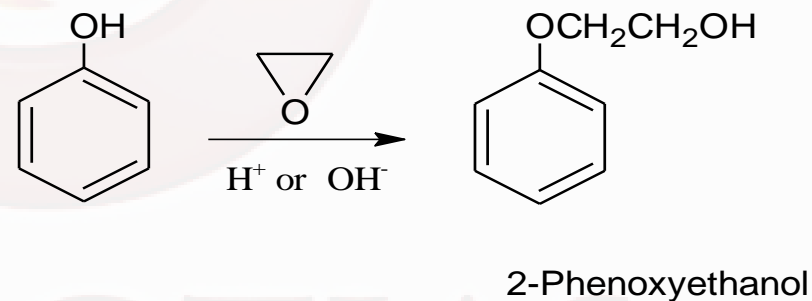
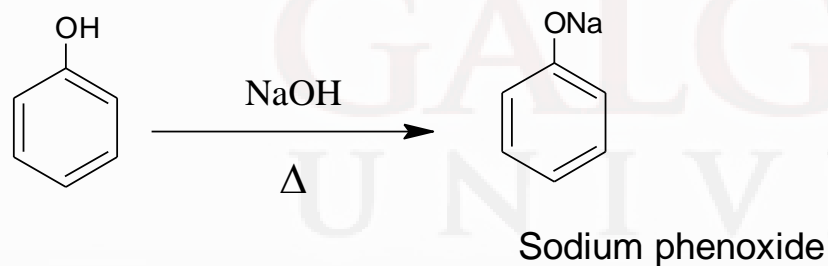
## 1- Reactions of Phenolic Hydrogen

**Williamson ether synthesis** Ethers are produced from phenol by the Williamson method via an  $S_N2$  mechanism.



### Reactions with bases

Because phenol is acidic, it reacts with bases to form salts.



## 2- Reactions of Phenolic Benzene Rings

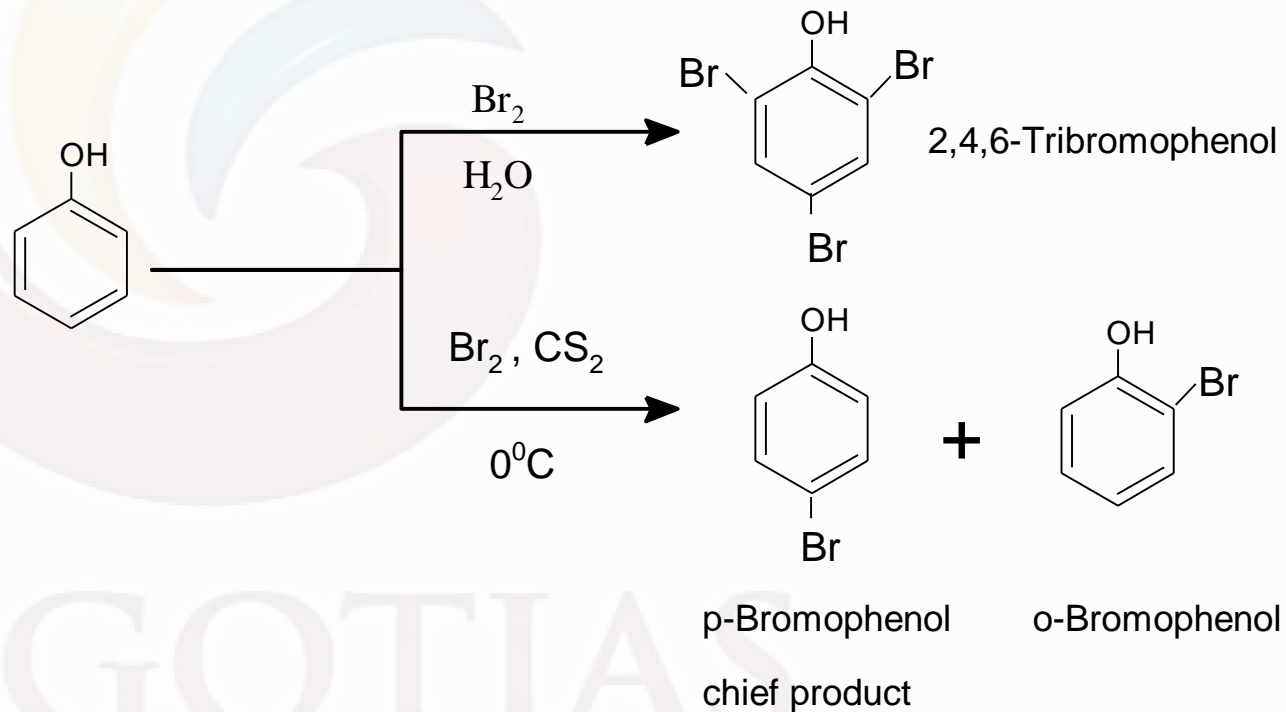
- Electrophilic aromatic substitution**

The hydroxy group in a phenol molecule exhibits a strong activating effect on the benzene ring because it provides a ready source of electron density for the ring. This directing influence is so strong that you can often accomplish substitutions on phenols without the use of a catalyst.

- Halogenation**

Phenols react with halogens to yield mono-, di-, or tri-substituted products, depending on reaction conditions. For example, an aqueous bromine solution brominates all ortho and para positions on the ring.

Likewise, you can accomplish monobromination by running the reaction at extremely low temperatures in carbon disulfide solvent.





## **Source & References:**

*The materials presented in this lecture has been taken from various books and internet websites. This instruction materials is for instructional purposes only.*

[https://uomustansiriyah.edu.iq/media/lectures/4/4\\_2017\\_09\\_29!08\\_11\\_50\\_PM.ppt](https://uomustansiriyah.edu.iq/media/lectures/4/4_2017_09_29!08_11_50_PM.ppt)

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<https://slideplayer.com/slide/7628468/>

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**Thank You.....**

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