241 Chem

CH-3

Phenols

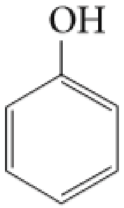
Learning Objectives

By the end of this chapter the student will Know:

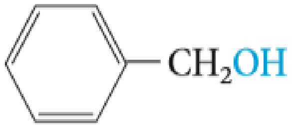
- The structure of phenols.
- The difference in structure between alcohols and phenols.
- The nomenclature of phenols.
- The Physical properties of phenols.
- The acidic properties of phenols vis acidic of alcohols.
- The different methods of preparation of phenols.
- The chemical reactions of phenols.

Structure of Phenols

- Phenols are compounds of the general formula ArOH, where Ar is an groups.
- Phenols differ from alcohols in having the OH group attached directly to an benzene ring.
- Phenols is the specific name for hydroxybenzene, and it is the general name for the family of compounds derived from hydroxybenzene.



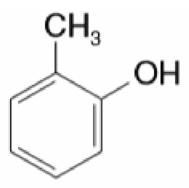
phenol



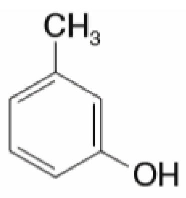
phenylmethanol
(benzyl alcohol)

Nomenclature of phenols

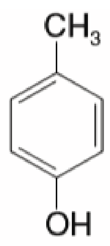
- The simplest member of this class of compounds is named phenol.
- Phenols are usually named as derivatives of the parent compounds.
- Numbering of the ring begins at the hydroxyl-substituted carbon and proceeds in the direction that gives the lower number to the next substituted carbon. Substituents are cited in alphabetical order.



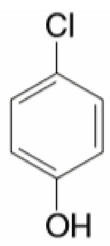
2-Methylphenol
(*o*-cresol)



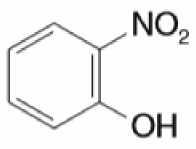
3-Methylphenol
(*m*-cresol)



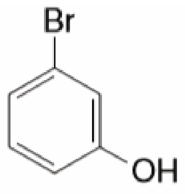
4-Methylphenol
(*p*-cresol)



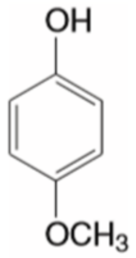
4-Chlorophenol
(*p*-chlorophenol)



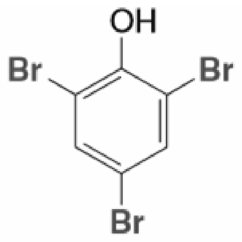
2-Nitrophenol
(*o*-nitrophenol)



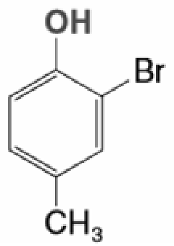
3-Bromophenol
(*m*-bromophenol)



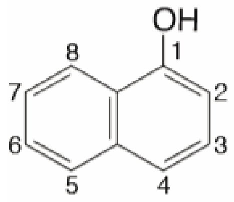
4-Methoxyphenol



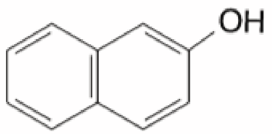
2,4,6-Tribromophenol



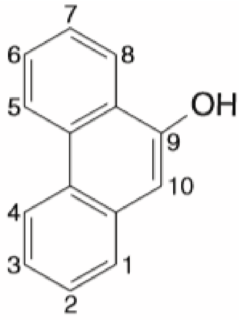
2-Bromo-4-methylphenol



1-Naphthol
(*α*-naphthol)



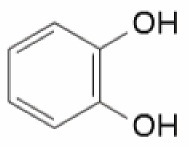
2-Naphthol
(*β*-naphthol)

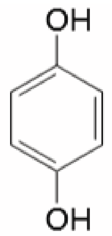


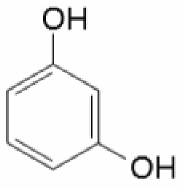
9-Phenanthrol

Nomenclature of phenols

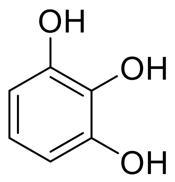
- Dihydroxypenols

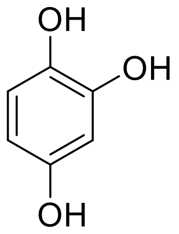

1,2-Benzenediol
(catechol)

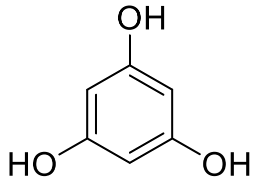

1,4-Benzenediol
(hydroquinone)


1,3-Benzenediol
(resorcinol)

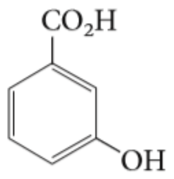
- Polyhydroxypenols

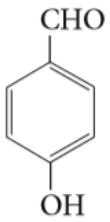

1,2,3-Trihydroxy benzene
Pyrogallol


1,2,4-Trihydroxy benzene
Hydroxy quinol

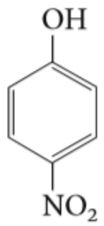

1,3,5-Trihydroxy benzene
(Phloroglucinol)

- The hydroxyl group is named as a substituent when it occurs in the same molecule with carboxylic acid, aldehyde, or ketone functionalities, which have priority in naming.


m-hydroxy benzoic acid

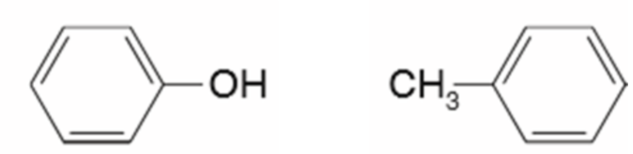

p-hydroxybenzaldehyde

but


p-nitrophenol
(*not p*-hydroxynitrobenzene)

Physical properties of phenols

- Phenol is a colourless, crystalline
- The presence of hydroxyl groups in phenols means that phenols are like alcohols. For example, they are able to form strong intermolecular hydrogen bonds, and therefore have higher boiling points than hydrocarbons of the same molecular weight.



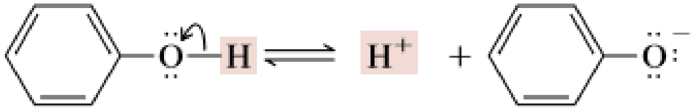
mol wet	94	92
bp	132°C	111°C

- Phenols are also modestly soluble in water because of their ability to form strong hydrogen bonds with water molecules.

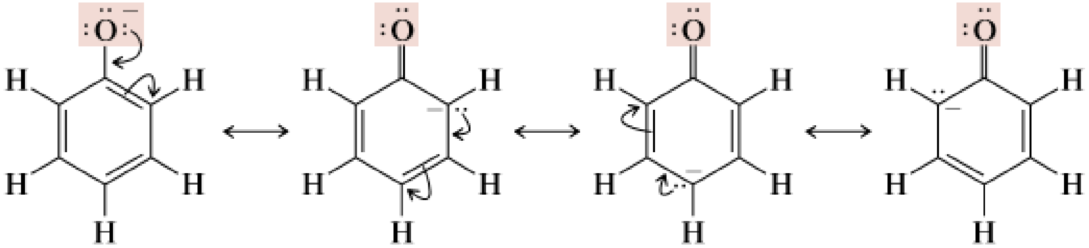
Physical properties of phenols

Acidity of phenols

- Like water, alcohols and phenols are weak acids. The hydroxyl group can act as a proton donor, and dissociation occurs in a manner similar to that for water



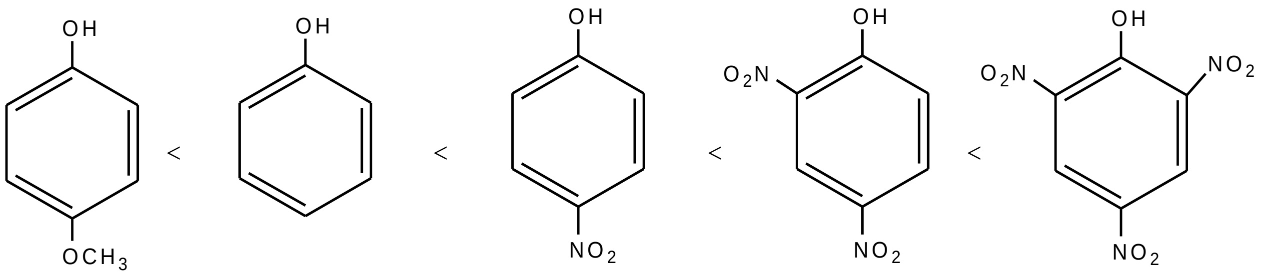
- Phenols are more acidic than alcohols, and weaker acids than carboxylic acids.
- Phenols are stronger acids than alcohols mainly because the corresponding phenoxide ions are stabilized by resonance.



- The negative charge of an alkoxide ion is concentrated on the oxygen atom, but the negative charge on a phenoxide ion can be delocalized to the ortho and para ring positions through resonance.

Substituents effects on the Acidity of Phenols

- Electron-withdrawing groups increase acidity by stabilizing the conjugate base.
- Electron-donating groups decrease acidity because they destabilize the conjugate base.



4-Methoxyphenol *p*-Cresol (Common)	Phenol	4-Nitrophenol	2,4-Dinitrophenol	Picric acid 2,4,6-Trinitrophenol
pH> 10	**pH = 10**	**pH = 7**	**pH = 4**	**pH = 0.25**

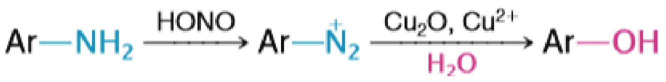
Preparation of Phenols

1. Hydrolysis of Diazonium salts
2. Alkali fusion of Benzenesulfonic acid or Sodium benzene-sulfonates
3. .Hydrolysis of Chlorobenzene (The Dow process)
4. From Cumene Hydroperoxide

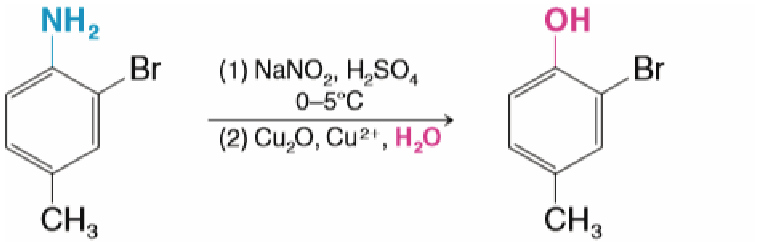
Preparation of Phenols

1. Hydrolysis of Diazonium salts

Diazonium salts react with water in the presence of mineral acids to yield phenols.

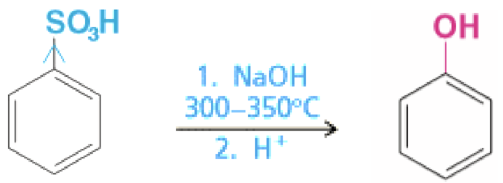


$$Ar{-}NH_2 \xrightarrow{HONO} Ar{-}\overset{+}{N}_2 \xrightarrow[H_2O]{Cu_2O,\ Cu^{2+}} Ar{-}OH$$

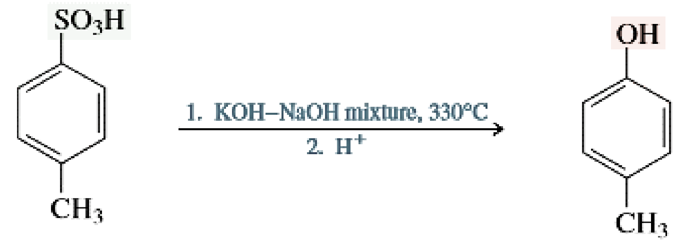


2-Bromo-4-methylphenol
(80–92%)

2. Alkali fusion of Benzenesulfonic acid or Sodium benzene-sulfonates



Addition-elimination of nucleophilic aromatic substation

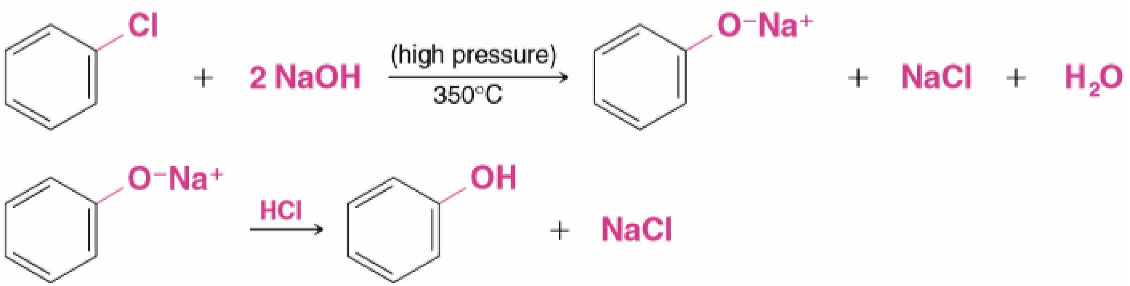


p-Toluenesulfonic acid

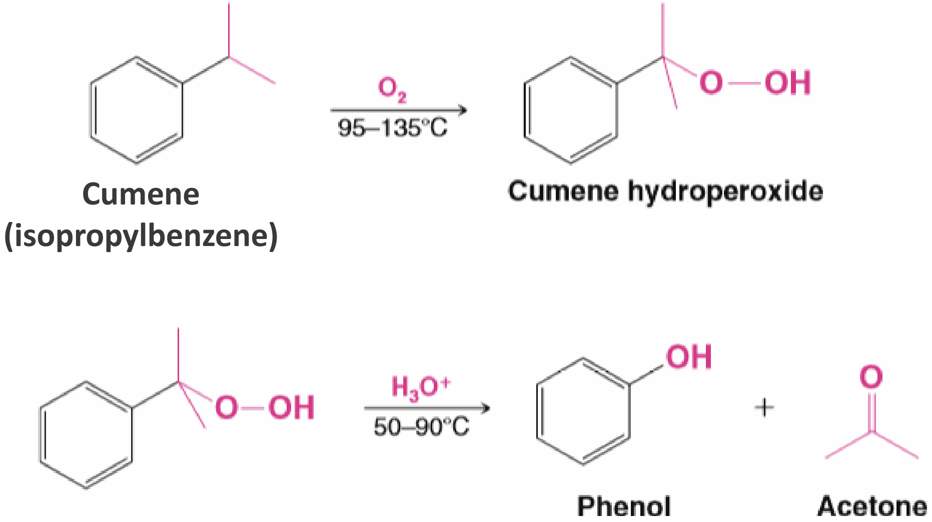
p-Cresol (63–72%)

Preparation of Phenols

3. Hydrolysis of Chlorobenzene (The Dow process)



4. From Cumene Hydroperoxide



Reactions of phenols

1. Salt formation via strong base or active metal
2. Ester formation
3. Reaction of aromatic nucleus of phenol:
    - Nitration
    - Friedel-Crafts acylation
    - Sulphonation
    - Halogenation
4. Oxidation of Phenols

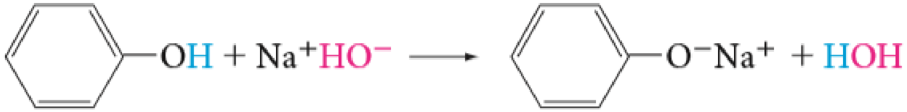
Reactions of phenols

1. Salt formation via strong base or active metal

- With active metals

phenol　　sodium phenoxide

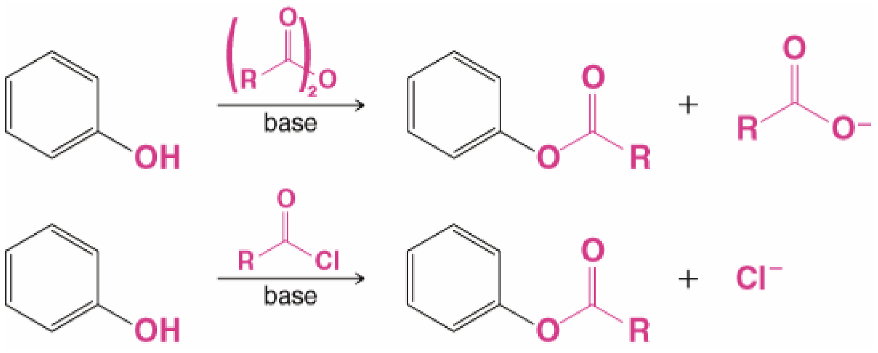
- With bases

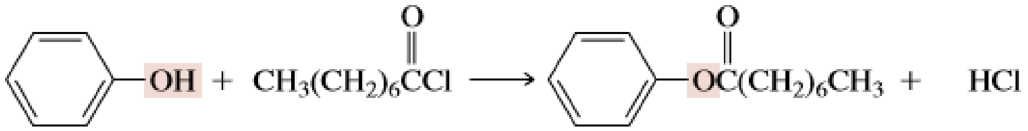


phenol　　sodium phenoxide

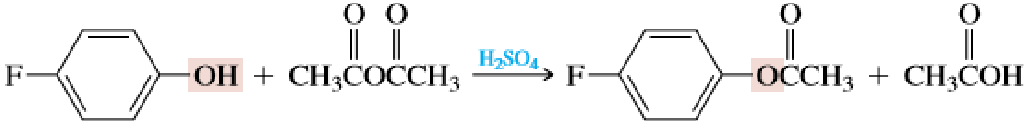
2. Formation of Esters From Phenols react with carboxylic acid anhydrides and acid chloride

O-Acylation





Phenol　　Octanoyl chloride　　Phenyl octanoate (95%)　　Hydrogen chloride



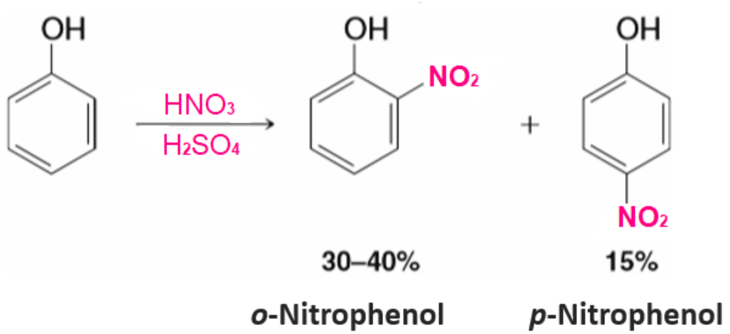
p-Fluorophenol　　Acetic anhydride　　*p*-Fluorophenyl acetate (81%)　　Acetic acid

Reactions of phenols

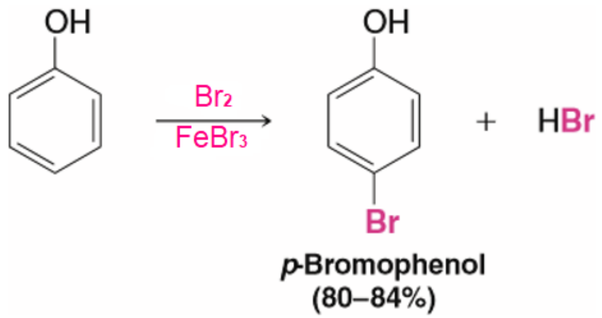
3. Reaction of aromatic nucleus of phenol

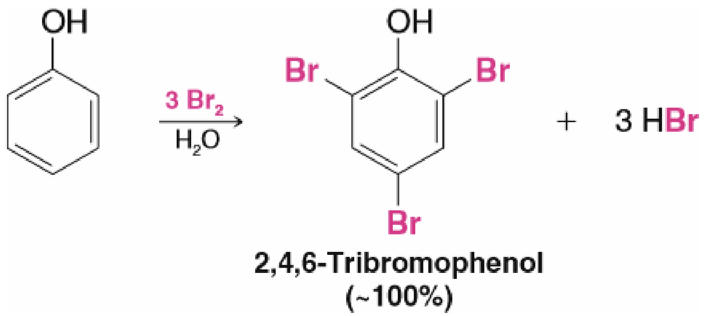
The hydroxyl group is a powerful activating group and an ortho - para director in Electrophilic Aromatic Substitutions

a. Nitration

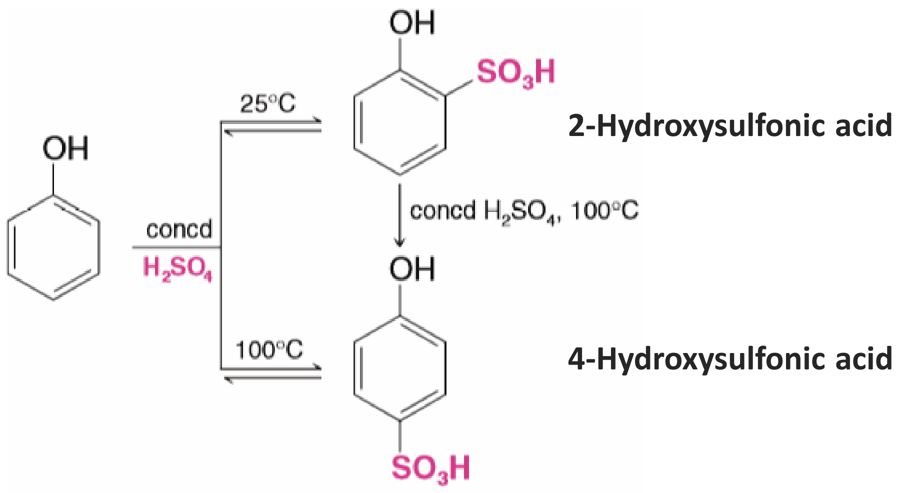


c. Halogenation



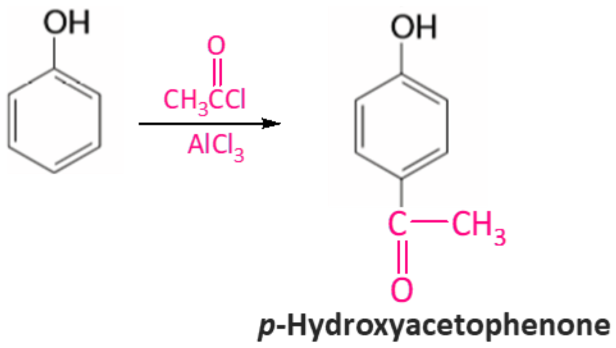


b. Sulfonation



d. Acylation

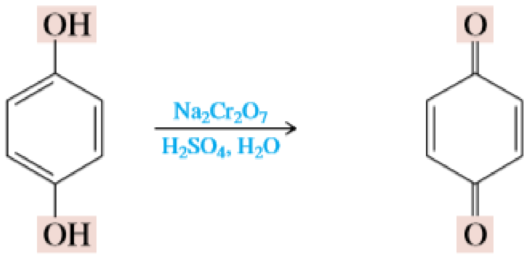
Friedel-Crafts Acylation (C-Acylation)



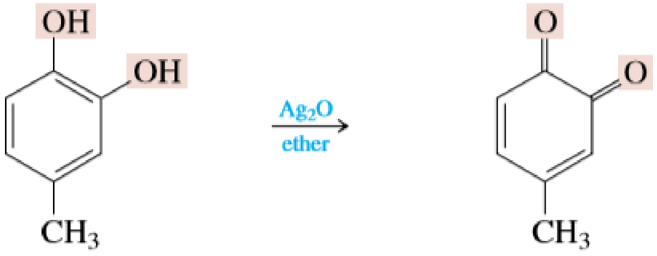
Reactions of phenols

4. Oxidation of Phenols: Quinones

Oxidation of derivatives of 1,2-benzenediol (pyrocatechol) 1,4-benzenediol (hydroquinone) by oxidizing agents (Silver oxide or Chromic acid)



Hydroquinone → *p*-Benzoquinone (76–81%)



4-Methylpyrocatechol (4-methyl-1,2-benzenediol) → 4-Methyl-1,2-benzoquinone (68%)