



JES'S College of Pharmacy Nandurbar

# Phenols, Aromatic amines, Aromatic acids

Assistant Professor

**Ms. Rina P. Patil**

M Pharm

**Department of Pharmaceutical Chemistry**

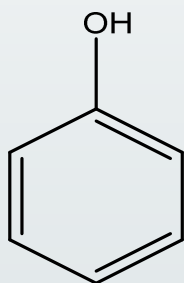
# INDEX

- ✍ Phenols\*
- ✍ Acidity of phenols
- ✍ Effect of substituents on acidity
- ✍ Qualitative tests
- ✍ Structure and uses of phenol
- ✍ Cresols, resorcinol, naphthols
- ✍ Aromatic Amines\*
- ✍ Basicity of amines
- ✍ Effect of substituents on basicity
- ✍ Synthetic uses of aryl diazonium salts
- ✍ Aromatic Acids\*
- ✍ Acidity
- ✍ Effect of substituents on acidity
- ✍ Important reactions of benzoic acid.

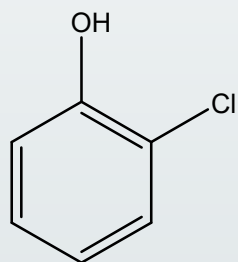
# Phenols

## Introduction

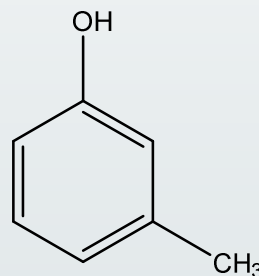
- ❖ Phenols are aromatic hydroxy compounds in which the hydroxyl group is directly attached to an aromatic ring. Phenols are having general formula  $\text{ArOH}$ , Where Ar is phenyl, substituted phenyl, or other aryl group. Phenols differ from alcohols in having the  $-\text{OH}$  group attached directly to an aromatic ring.
- ❖ Phenols are generally named as derivatives of the simplest number of the family, phenol.
- ❖ The methylphenols are given as the special name of cresols. sometimes phenols are named as hydroxy- compounds.



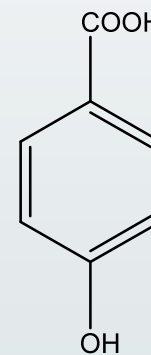
Phenol



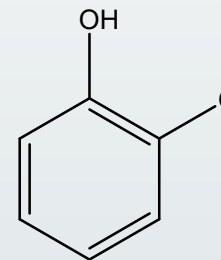
2-chlorophenol  
*o*-chlorophenol



*m*-cresol



4-hydroxybenzoic acid  
*p*-hydroxybenzoic acid



Catechol  
*o*-Dihydroxybenzene  
1,2-Dihydroxybenzene

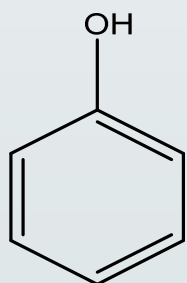
# Phenols

- ❖ Both phenols and alcohols contain the -OH group, and as a result the two families resemble each other to a limited extent. One more important thing i.e. both phenols and alcohols can be converted into ethers and esters.
- ❖ In most of their properties however, and in their preparations, the two kinds of compounds differ so greatly that they well deserve to be classified as different families.

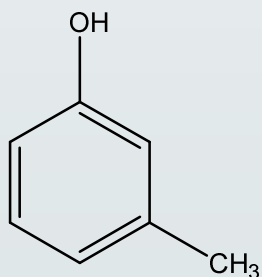
## Classification and Nomenclature

- ❖ Phenols are classified as mono, di, tri-hydric phenols depending upon whether one, two, or three hydroxy groups are attached to the aromatic ring. The position of the substituent in phenol derivatives is indicated by prefixes ortho (o-), meta (m-), and para (p-) or by number.

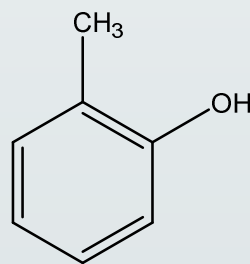
### 1. Monohydric Phenols



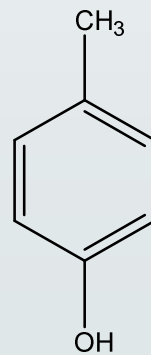
Phenol



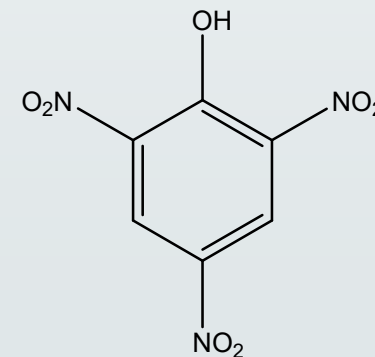
*m*-cresol



*o*-cresol



*p*-cresol



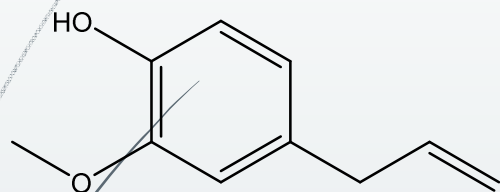
Picric  
2,4,6-Trinitrophenol

## Industrial source

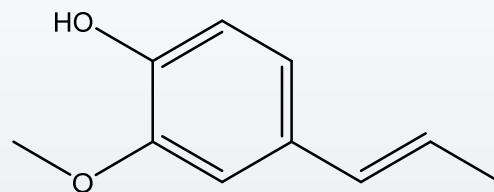
5

Most phenols are made industrially by the same methods that are used in the laboratory. There are, however, special ways of obtaining certain of these compounds on a commercial scale, including the most important one, phenol.

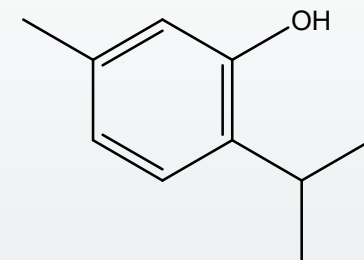
In quantity produced, phenol ranks near top of the synthetic aromatic compounds. Its principal uses in the manufacturing of the formaldehyde polymers.



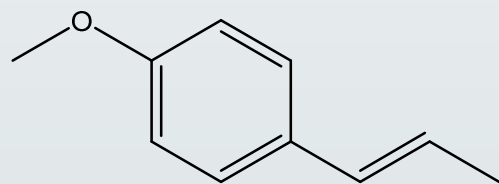
4-allyl-2-methoxyphenol  
Eugenol



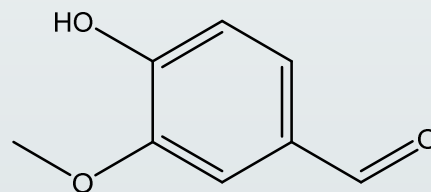
(E)-2-methoxy-4-(prop-1-en-1-yl)phenol  
Isoeugenol



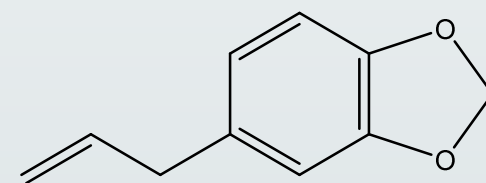
2-isopropyl-5-methylphenol  
Anethol



(E)-1-methoxy-4-(prop-1-en-1-yl)benzene  
Vanillin



4-hydroxy-3-methoxybenzaldehyde  
Thymol



5-allylbenzo[d][1,3]dioxole  
Safrole

# Method of preparation of Phenol

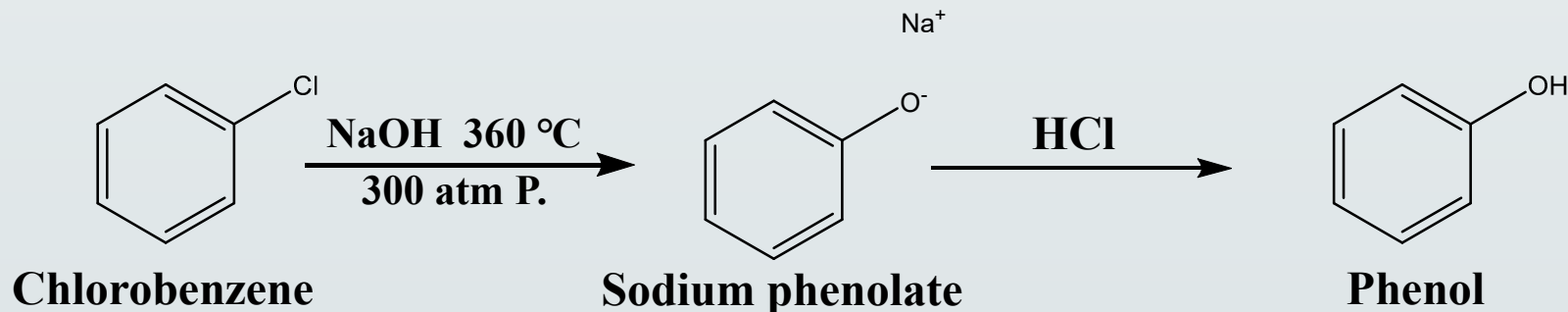
6

Phenol, also known as carboic acid was first isolated from coal tar. Now a days, phenol is commercially produced synthetically. The common methods employed for preparation of phenols are as follows.

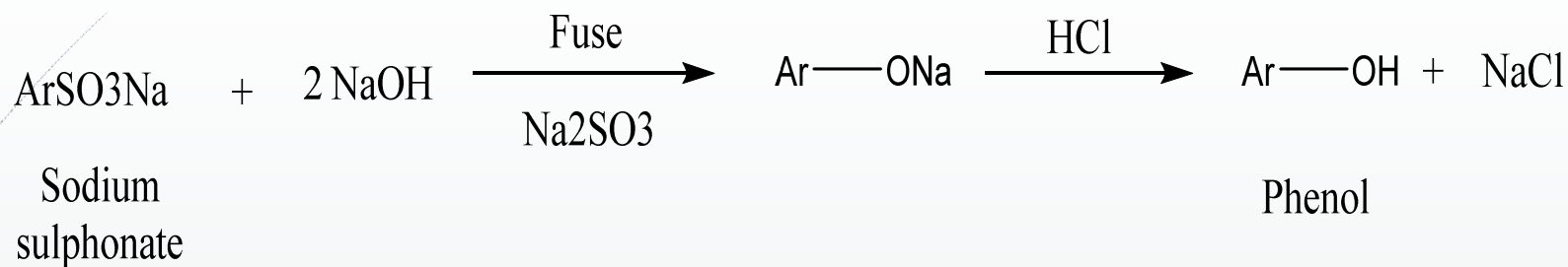
1. From haloarenes (DOW'S Process)
2. From Diazonium salts
3. From alkali fusion of sulphonates
4. From cumene (Isopropyl benzene)
5. From Grignard reagents
6. From phenolic acids
7. Rasching's process

## 1. From haloarenes (DOW'S Process)

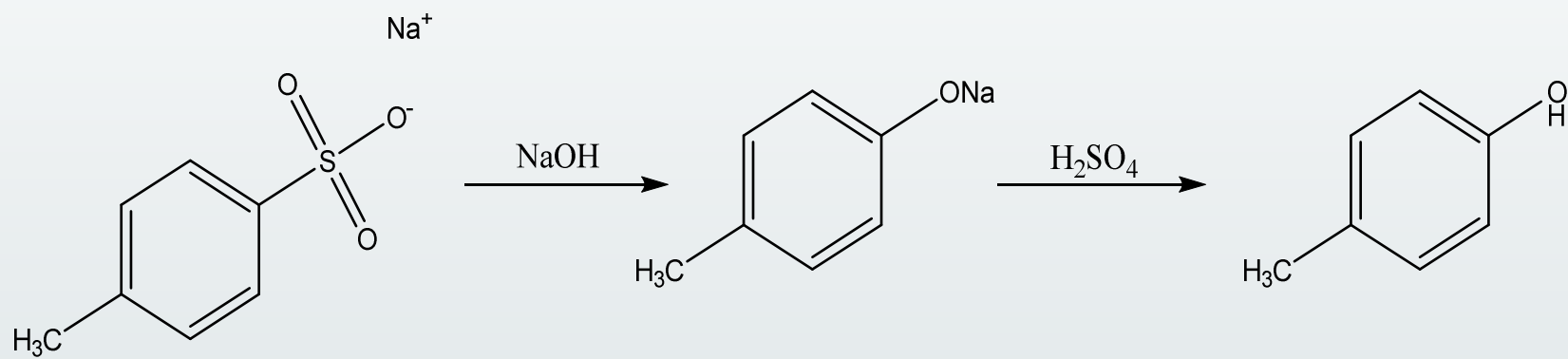
Chlorobenzene is fused with NaOH at 623K and 320 atmospheric pressure. Phenol is obtained *acidification* of sodium phenoxide so produced phenol as product.



### 3. From alkali fusion of sulphonates



e.g.



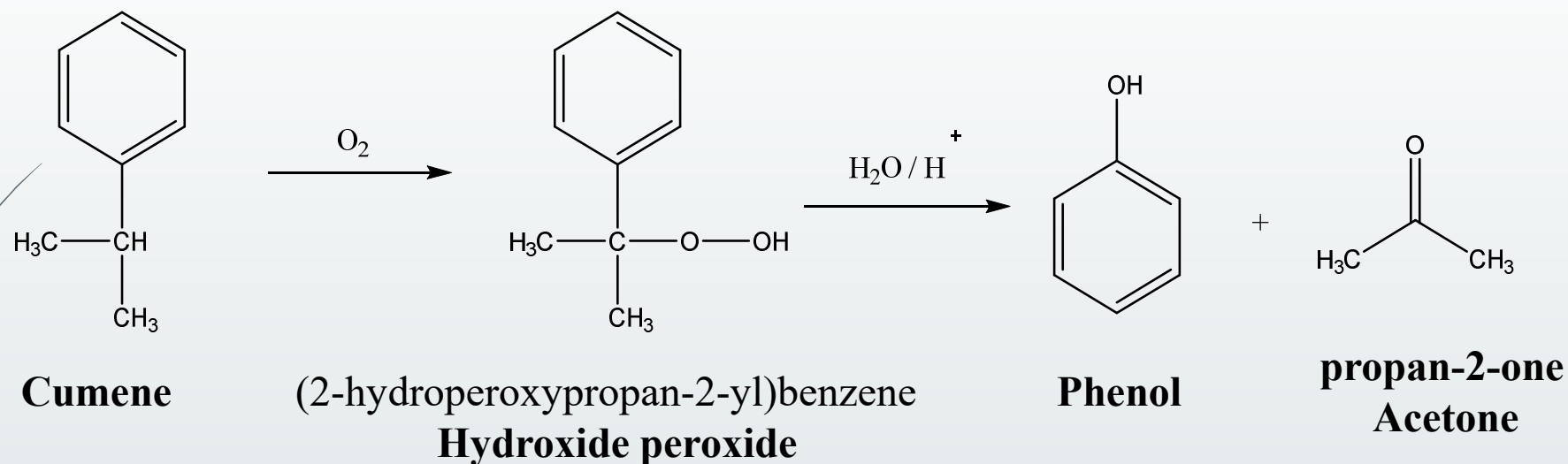
sodium 4-methylbenzenesulfonate  
**Sodium *p*-toluene sulphonate**

***p*-cresol**

When sodium salt of aromatic sulphonic acid is mixed with an excess of caustic soda, and heated to 573-623 K get sodium phenoxide which on acidification yields phenols.

#### 4. From cumene (Isopropyl benzene)

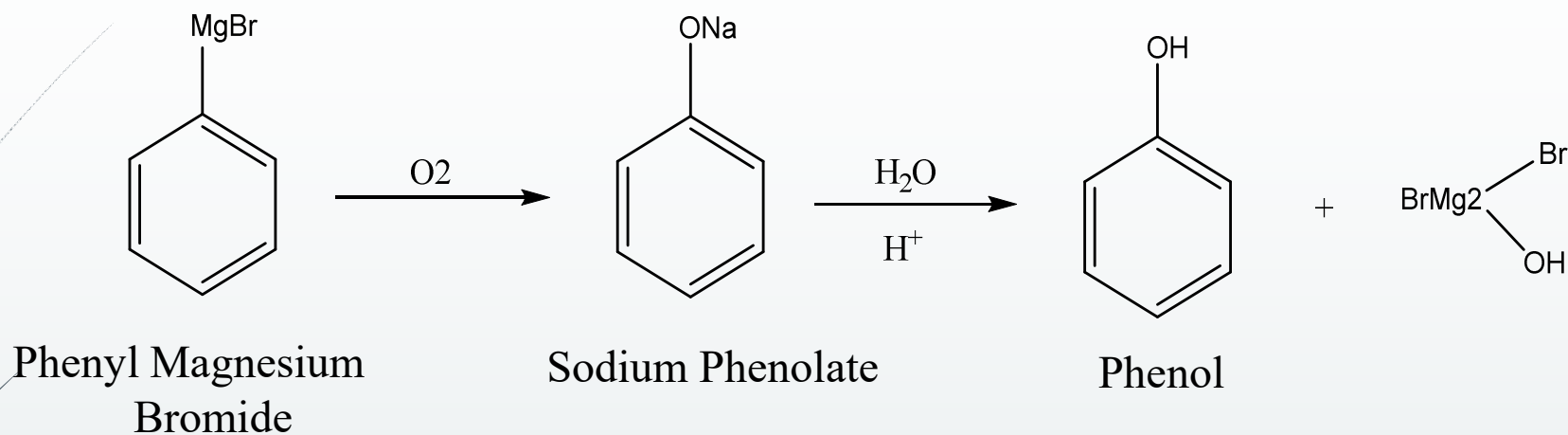
Phenol is manufactured from the hydrocarbon, cumene. Cumene (isopropylbenzene) is oxidised in the presence of air to cumene hydroperoxide. It is converted to phenol and acetone by treating it with dilute acid. Acetone, a by-product of this reaction, is also obtained in large quantities by this method.



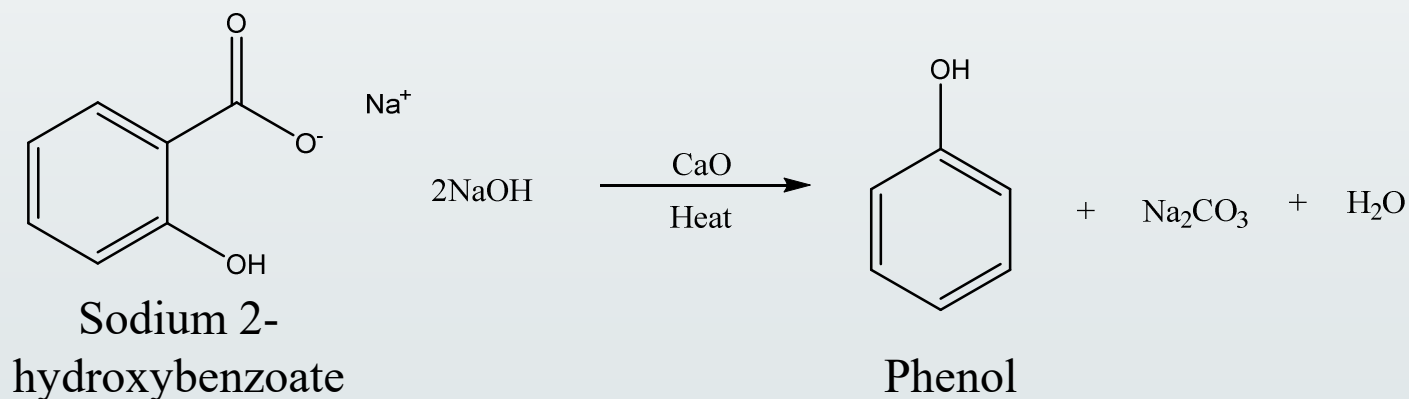


## 5. From Grignard reagent

Phenols may be prepared by treating aryl magnesium bromides with oxygen followed by hydrolysis of the product.

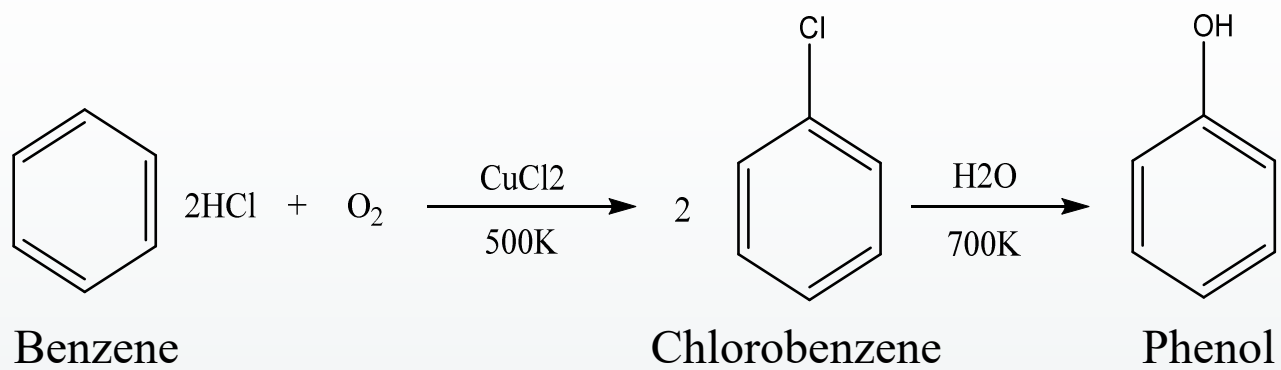


## 5. From Phenolic acids



Phenol can be obtained by distillation of sodium salts of phenolic acids with soda lime (NaOH + CaO) followed by acidification with dilute HCl.

## 5. Rasching's process



# Properties of Phenol

## 1. Physical properties of phenol

- A. Physical state
- B. Boiling point
- C. Solubility

### A. Physical state

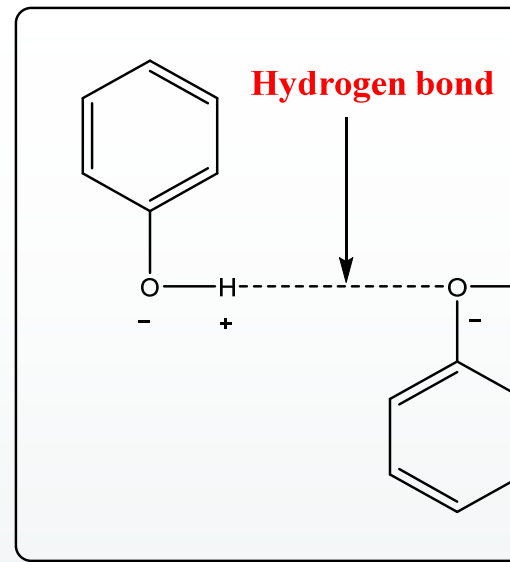
The simplest phenols are liquids or low melting point solids; because of hydrogen bonding they have high boiling points.

Phenol itself is somewhat soluble in water (9 gm per 100 gm of water), because of sometimes phenol is capable of hydrogen bonding with water; most other phenols are essentially insoluble in water. Except some phenols capable of producing colour is present, phenols themselves are colourless, However, like aromatic amines they are easily oxidized; unless carefully purified, many phenols are coloured by oxidation products.

### B. Boiling point

Due to stronger association of molecules by intermolecular hydrogen bonding, phenols have high boiling points than those of corresponding hydrocarbon and aryl halides for e.g. Phenol (**94 gm/mol**) & boils at 455K While toluene molecular wt. (**92gm/mol**) & boils at 284 K.

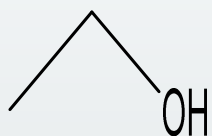
The boiling points of alcohols and phenols increase with increase in the number of carbon atoms (**increase in van der Waals forces**). In alcohols, the boiling points decrease with increase of branching in carbon chain (because of decrease in van der Waals forces with decrease in surface area).



It is interesting to note that boiling points of **alcohols** and **phenols** are **higher** in comparison to other classes of compounds, namely hydrocarbons, ethers, haloalkanes and haloarenes of comparable molecular masses.

**For example**, ethanol and propane have comparable molecular masses but their boiling points differ widely. The boiling point of methoxymethane is intermediate of the two boiling points.

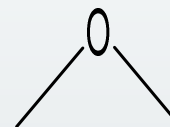
The high boiling points of alcohols are mainly due to the presence of intermolecular hydrogen bonding in them which is lacking in ethers and hydrocarbons.



**ethanol**  
**MW- 46.07**  
**BP- 351 K**



**propane**  
**MW- 44.10**  
**BP-248 K**

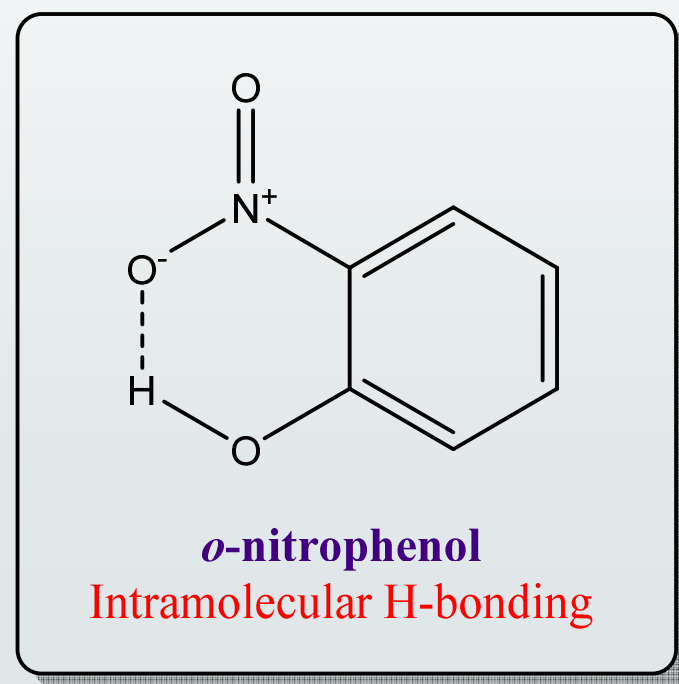
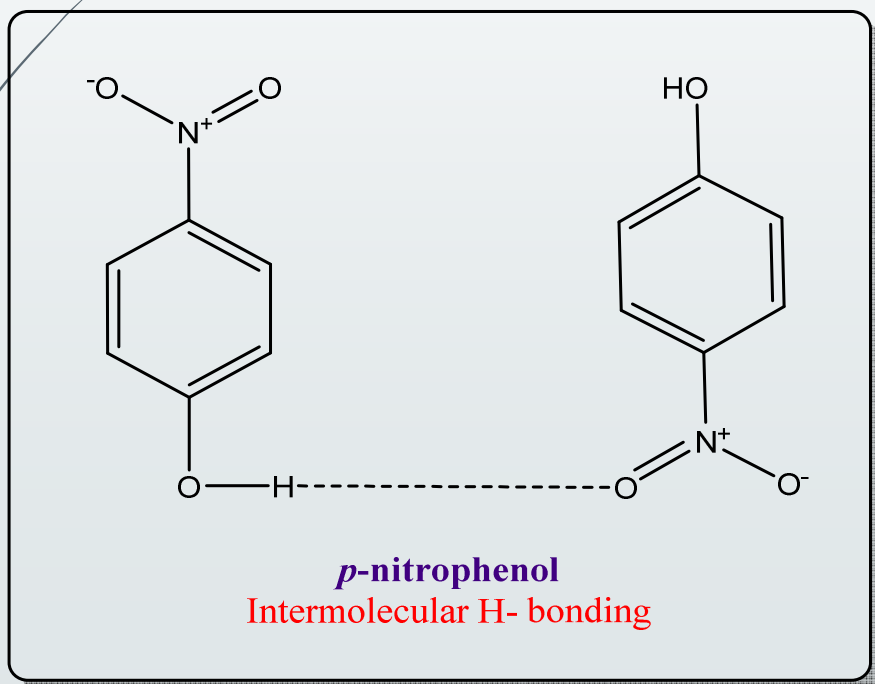


**methoxymethane**  
**MW- 46.07**  
**BP- 231 K**

### C. Solubility

Phenol itself is somewhat soluble in water (9 gm per 100 gm of water), because of sometimes ph forms hydrogen bonding with water; most other phenol are essentially insoluble in water. Except s group capable of producing colour is present, phenols themselves are colourless, However, aromatic amines, they are easily oxidized; unless carefully purified, may phenols are coloured oxidation products.

Phenol itself and some di & trihydric phenols are some what soluble in water since its molecule form hydrogen bond with water.



**THANK YOU...**

---