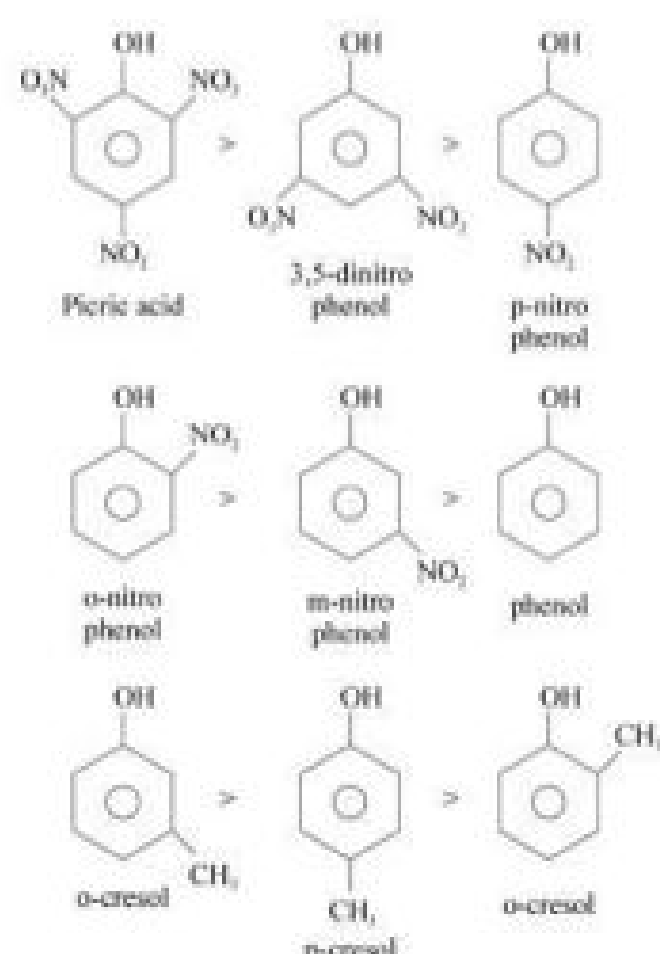


# Which is also called carboic acid?

## PHENOLS

Continued from January 10<sup>th</sup>..

- The hydroxyl group in phenol is directly attached to  $sp^2$  carbon of benzene ring. The  $sp^2$  carbon attached to 'O' being more electronegative than  $sp^3$  carbon of alcohols, it decreases the electron density on oxygen. Because of this oxygen develops still more electron seeking character and releases proton by taking the shared pair of electrons with it.
- The acidic nature of phenol can also be explained on the basis of resonance stabilization of phenoxide ion.
- Electron withdrawing groups present at **ortho and para positions (but not at meta)** increases the acidic nature of phenol. Greater the number of such groups at ortho and para positions higher is the acidic nature of phenol.
- Electron releasing group present at **ortho and para positions (but not at meta)** decreases the acidity of phenols. Greater the number of such groups at ortho and para positions lesser is the acidic nature of that phenol.
- Acidic strength increases with the decrease of the  $pK_a$  values.
- Order of acidic strength of phenols is as follows



- The greater the  $pK_a$  value, the weaker the acid.

Compound	Formula	$pK_a$
<i>o</i> -Nitrophenol	$o-O_2N-C_6H_4-OH$	7.2
<i>m</i> -Nitrophenol	$m-O_2N-C_6H_4-OH$	8.3
<i>p</i> -Nitrophenol	$p-O_2N-C_6H_4-OH$	7.1
Phenol	$C_6H_5-OH$	10.0
<i>o</i> -Cresol	$o-CH_3-C_6H_4-OH$	10.2
<i>m</i> -Cresol	$m-CH_3-C_6H_4-OH$	10.1
<i>p</i> -Cresol	$p-CH_3-C_6H_4-OH$	10.2
Ethanol	$C_2H_5OH$	15.9

**Esterification of Phenol:** Phenols react with carboxylic acids and their derivatives like acid chlorides and anhydrides to form esters. This reaction is called Schotten-Baumann reaction.



- During esterification H comes from phenol and 'OH' comes from carboxylic acid.

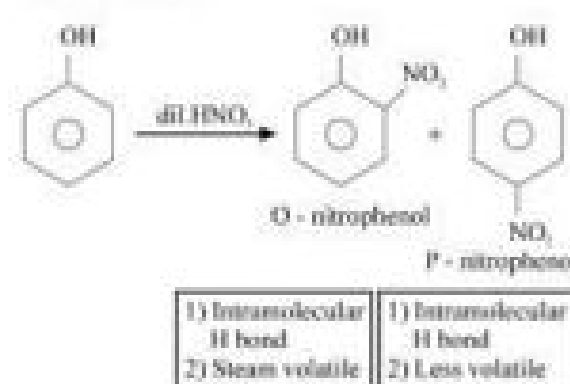


- Salicylic acid on acetylation gives acetyl salicylic acid known as Aspirin.



**Electrophilic aromatic substitution reactions of phenol:** In phenol, -OH group is ring activating and ortho and para directing as these positions get more electron density through resonance.

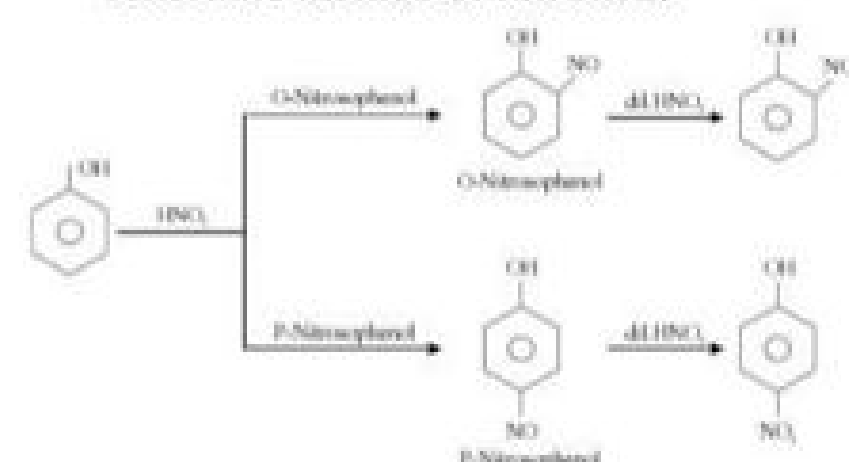
### Nitration



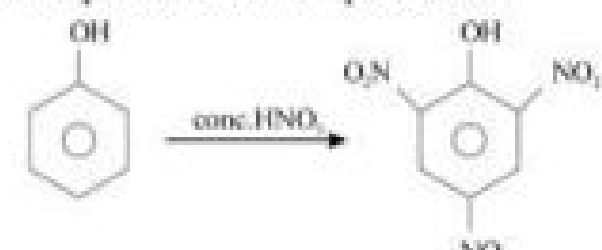
JEE  
MAIN  
Special

- Nitration of phenol gives a poor yield because nitric acid also causes oxidation of phenol.

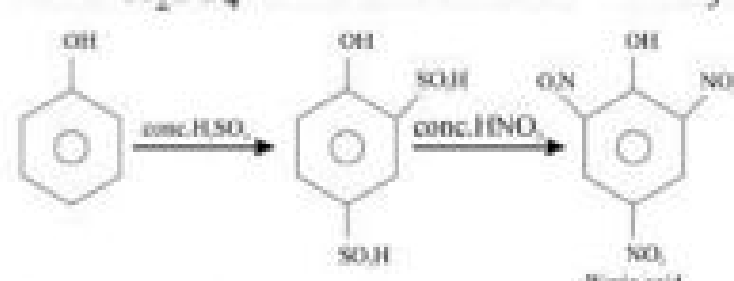
**Alternate method of nitration:-**



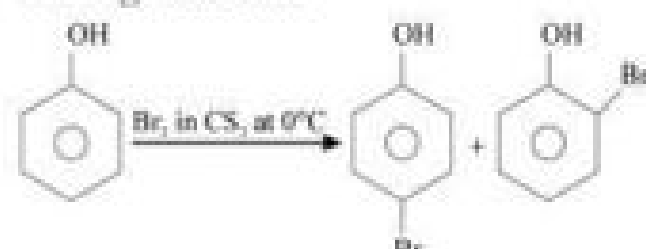
- Phenol when treated with conc.  $HNO_3$  gives 2,4,6-trinitrophenol known as picric acid



- The yield in the reaction is poor. Now a days picric acid is prepared by treating phenol with conc.  $H_2SO_4$  and then with conc.  $HNO_3$ .



### Halogenation:-

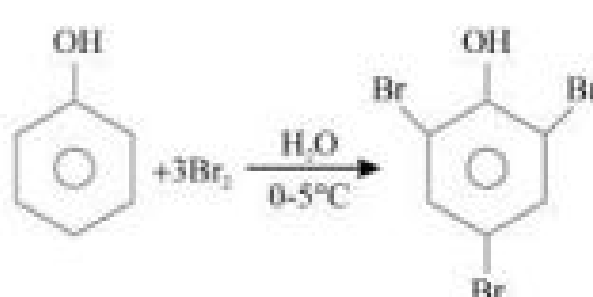


- When the reaction is carried out in solvents of low polarity such as  $CHCl_3$  or  $CS_2$  and at low temperature, monobromophenols are formed.

- Here no Lewis acids like  $FeBr_3$  are required because highly activating effect of -OH group polarises bromine quickly.

- Phenol reacts with bromine water and gives 2,4,6-tribromo phenol (white precipitate)

- In water phenol forms phenoxide ion which activates the benzene ring.

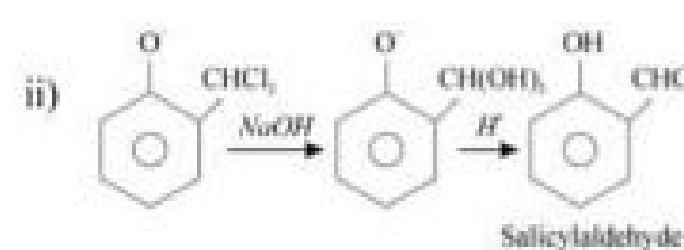
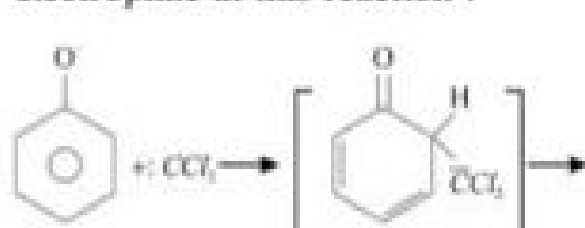


**Reimer-Tiemann reaction:** Phenol when treated with chloroform in the presence of NaOH gives salicylaldehyde.

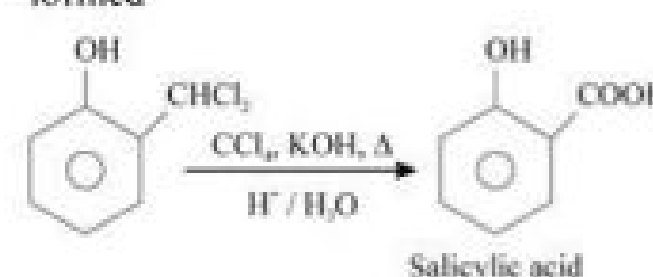
### Mechanism:



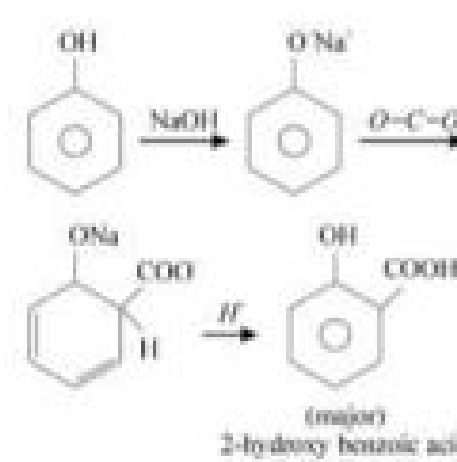
Dichloro carbene ( $:CCl_2$ ) is the attacking electrophile in this reaction :



- If  $CCl_4/KOH$  is used salicylic acid will be formed



**Kolbe's reaction:** Phenoxide ion generated by treating phenol with sodium hydroxide is even more reactive than phenol towards electrophilic aromatic substitution.

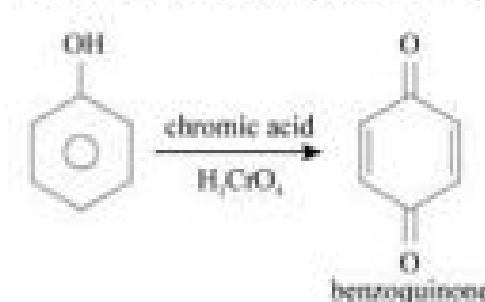


- If KOH is used parahydroxy benzoic acid will be formed as major product.

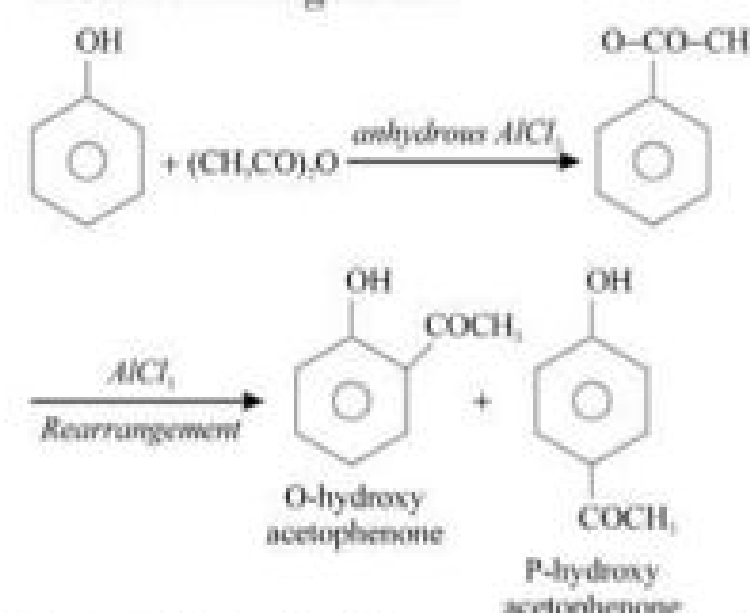
**Action of Zinc dust:** Phenol on heating with zinc dust produces benzene.



**Oxidation:** Phenol on oxidation with chromic acid ( $Na_2Cr_2O_7 + H_2SO_4$ ) produces benzoquinone, which is a conjugate diketone. In the presence of air, phenols are slowly oxidised to dark coloured mixtures containing quinones.



### Fries rearrangement:



**Uses of Phenol:** It is a raw material for the manufacture of important dyes, drugs and pharmaceuticals.

- 2,4-dichloro-3,5 dimethyl phenol is used as powerful antiseptic under the name Dettol.
- It is used in the manufacture of drugs like Aspirin, Salol etc.
- 0.2% aqueous Phenol is used as an antiseptic.
- Phenol on reaction with urea and formaldehyde gives condensation resin (PVF) used as wood adhesives.

### Tests of Phenol:

- Phenol in water gives violet colour with a drop of  $FeCl_3$ .
- Phenol in water gives white precipitate with bromine water.
- Phenol gives blue colour indophenol with ammonia and sodium hypochlorite.

### LEVEL I A

#### METHODS OF PREPARATION

- Phenol is also called**
  - salicylic acid
  - benzyl alcohol
  - carboic acid
  - salol
- Benzene diazonium chloride on hydrolysis gives**

# విజేత

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Urbane junior colleges  
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- Benzene
- Benzyl alcohol
- Phenol
- Chlorobenzene

### NOMENCLATURE

- Which does not have a carboxyl group?

- Picric acid
- Ethanoic acid
- Aspirin
- Benzoic acid

### PROPERTIES

- When phenol is treated with excess of bromine water, it gives

- m-bromophenol
- o- and p-bromophenol
- 2,4-dibromophenol
- 2,4,6-tribromophenol

- Phenols does not react with

- sodium bicarbonate
- sodium hydroxide
- potassium hydroxide
- ferrie chloride

- Phenol  $\xrightarrow{(i)CHCl_3/NaOH}$  Salicylaldehyde. This reaction is known as

- Gattermann aldehyde synthesis
- Sandmeyer's reaction
- Perkin's reaction
- Reimer-Tiemann reaction

- Phenol is

- a base weaker than ammonia
- an acid stronger than carbonic acid
- an acid weaker than carbonic acid
- a neutral compound

- Phenol reacts with bromine in carbon disulphide at low temperature to give

- m-bromophenol
- o- and p-bromophenol
- p-bromophenol
- 2,4,6-tribromophenol

- Phenol is less acidic than

- p-nitrophenol
- ethanol
- cresol
- benzyl alcohol

- Phenol on treatment with conc.  $HNO_3$  gives

- picric acid
- o- and m-nitrophenols
- cresol
- resorcinol

### LEVEL I A KEY

- 3
- 2
- 3
- 1
- 4
- 4
- 5
- 1
- 6
- 4
- 7
- 3
- 8
- 2
- 9
- 1
- 10
- 1

### LEVEL I B

#### METHODS OF PREPARATION

- Cumene  $\xrightarrow{(i)O, (ii)H_2O/H^+}$  (X) and (Y)

(X) and (Y) respectively are

- toluene, propene
- toluene, propylchloride
- phenol, acetone
- phenol, acetaldehyde

- In the reaction  $C_6H_5NH_2 \xrightarrow{NaNO_2/HCl, 0^\circ C} X$

$\xrightarrow{H_2O, \text{warm}}$  Y, 'Y' is

- $C_6H_5Cl$
- $C_6H_6$
- $C_6H_5OH$
- $C_6H_5CHO$

### NOMENCLATURE

- Picric acid is a yellow coloured compound. Its chemical name is

- m-nitrobenzoic acid
- 2,4,6-trinitrophenol
- trinitrotoluene
- trinitroaniline

### PROPERTIES

- $C_6H_5OH + CHCl_3 + NaOH \rightarrow$  salicylaldehyde  
The electrophile involved in the above reaction is.

- dichloromethyl cation ( $^{\oplus}CHCl_2$ )
- dichlorocarbene ( $:CCl_2$ )
- trichloromethyl anion ( $^{\ominus}CCl_3$ )

- formyl cation ( $^{\oplus}CHO$ )

### LEVEL I B KEY

- 3
- 2
- 3
- 2
- 4
- 2