

PHENOL

Preface

When -OH group is directly attached with benzene ring, than the compounds are called phenols. This topic is a part of the syllabus of aromatic hydroxy compounds.

This topic deals with the study of its salient features of phenol, its resonating structures, its o-& p- directing property, its chemical properties, its how to solve all the problems based on it.

This book consists of theoretical & practical explanations of all the concepts involved in the chapter. Each article followed by a ladder of illustration. At the end of the theory part, there are miscellaneous solved examples which involve the application of multiple concepts of this chapter.

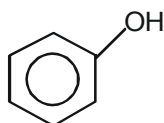
Students are advised to go through all these solved examples in order to develop better understanding of the chapter and to have better grasping level in the class.

Total No.of questions in **Phenol** are -

In chapter Examples	07
Solved Examples	21
Total No. of questions	28

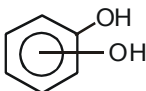
1. INTRODUCTION ::

- (a) It is also called as **carbolic acid**.
 (b) The compounds in which —OH group is directly attached with benzene ring are called as '**Phenol**'.
 (c) It is discovered by the scientist '**Runge**'.
 (d) The scientist '**Hofmann**', prepared it first from 'coaltar'.
 (e) Aromatic hydroxy compounds in which a single —OH group is attached with benzene ring are called phenols.
 eg.

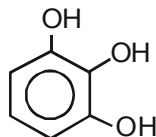


phenol (monohydroxy)

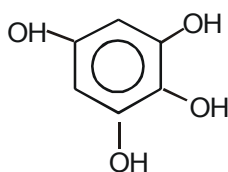
- (f) If two or three OH groups are attached at benzene ring then they are called dihydroxy or trihydroxy phenols respectively.
 eg.



o, m - or - p - dihydroxy benzene (dihydroxy)



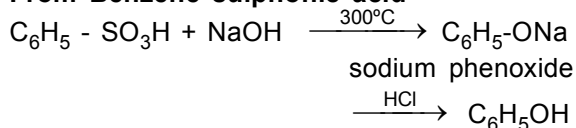
pyrogallol (trihydroxy)



fluoroglucinol (trihydroxy)

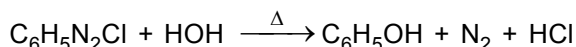
2. METHODS OF PREPARATION ::

2.1 From Benzene sulphonic acid -



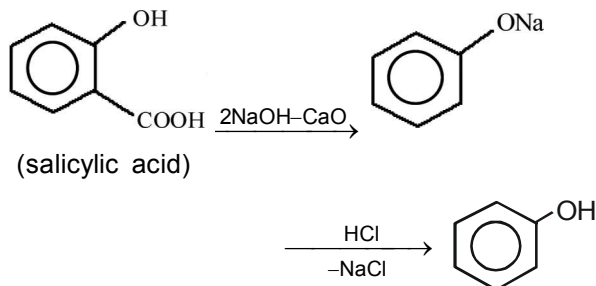
2.2 From Benzene diazonium chloride -

On heating with water, it gives phenol.



2.3 From Salicylic acid -

Salicylic acid, on heating with sodalime, initially forms sodium phenoxide which gives phenol on acidic hydrolysis.



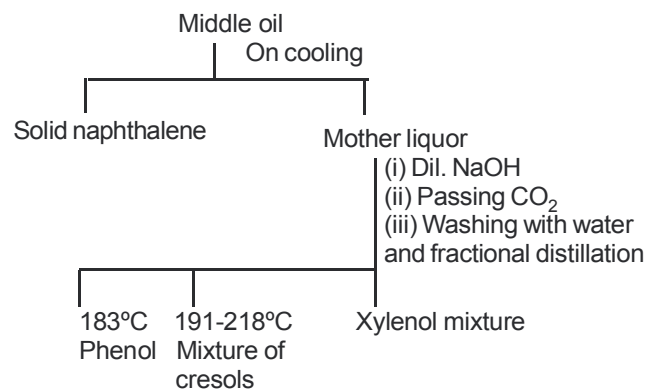
2.4 From Grignard reagent -



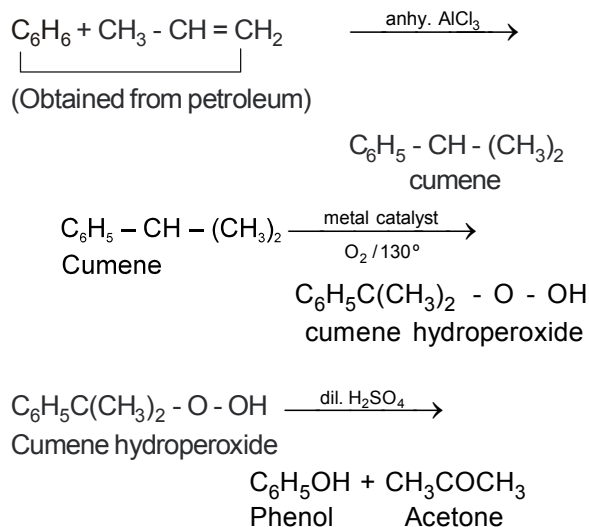
2.5 Industrial Methods -

2.5.1 From middle oil fraction of coaltar -

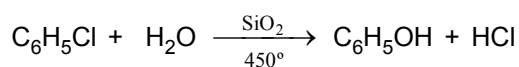
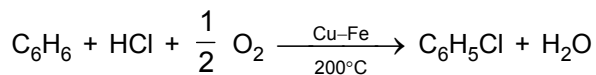
Phenol is obtained from the middle oil fraction of coaltar after removing other homologous of phenol, Cresol and naphthalene.



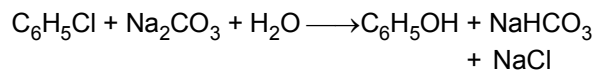
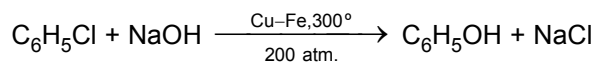
2.5.2 From Cumene -



2.5.3 From Rasching process -



2.5.4 From Dow's process -



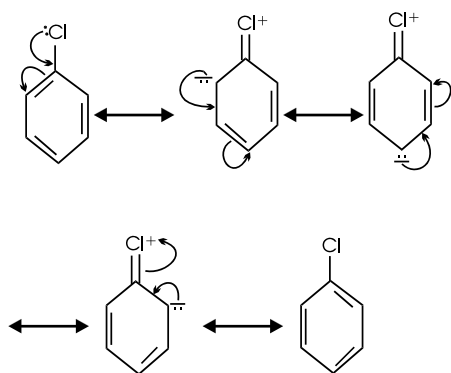
Examples based on methods of preparation

Ex.1 In chlorobenzene, the — Cl group -

- (A) Activates the benzene ring more, via resonance effect than deactivating it via inductive effect.
- (B) Deactivates the benzene ring more, via inductive effect than activating it via resonance effect.
- (C) Activates the benzene ring via resonance effect and deactivates it via inductive effect. Both these effect are evenly matched.
- (D) It is a net deactivating group with director characteristics.

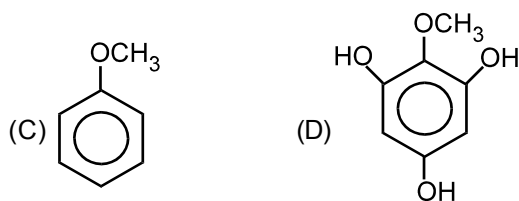
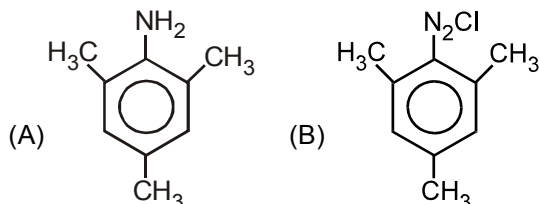
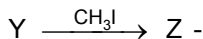
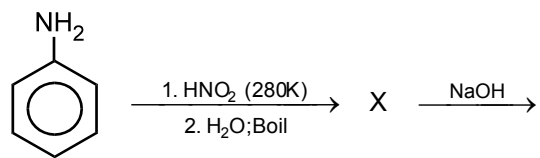
(Ans. B)

Sol.

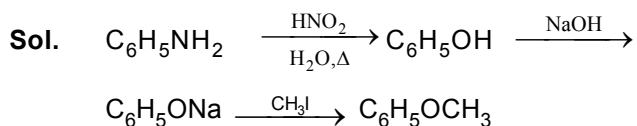


(Resonance activating o-and p-position)
Also electron withdrawing nature or — I.E. decreases this activation.

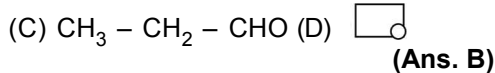
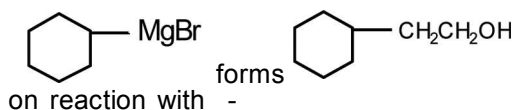
Ex.2 Identify 'Z' in the reaction given below -



(Ans. C)

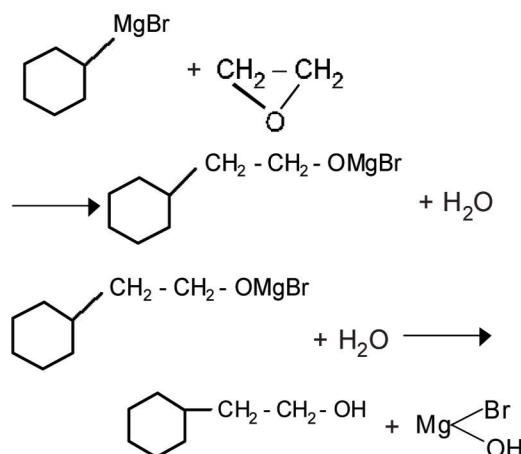


Ex.3



(Ans. B)

Sol.

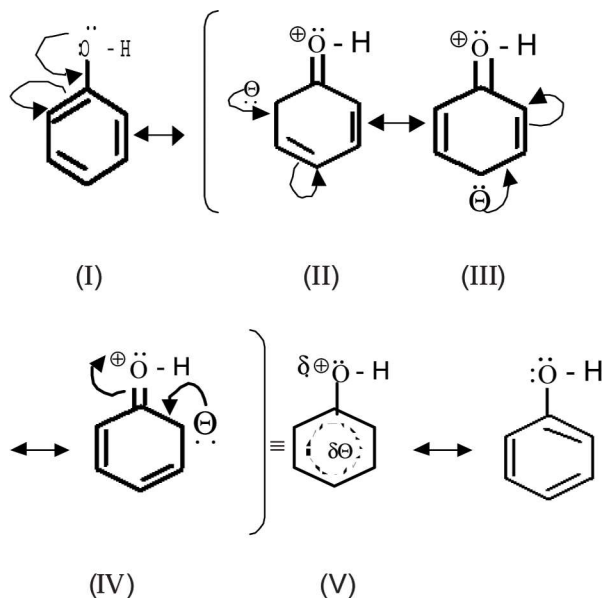


3. PHYSICAL PROPERTIES ::

- (i) It is colourless crystalline solid with specific smell.
- (ii) It is partially soluble in water.
- (iii) Due to oxidation, it becomes pink in open air.
- (iv) It is poisonous.
- (v) It is soluble in organic solvents.
- (vi) Melting point is 40°C & boiling point is 182°C

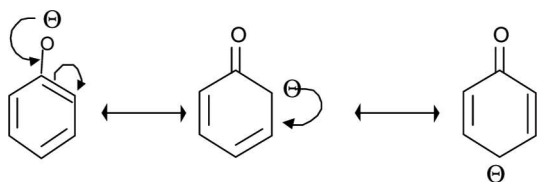
4. RESONATING STRUCTURES OF PHENOL ::

(a) Resonance in phenol molecule -



- OH group of phenol is o & p-directing as there are electron richer places so electrophile attack at these places.

(b) Resonance in phenate ion -



etc.

[equivalent configurations more stable]

Phenate ion is resonance stabilised that is why phenol shows acidic character. The next point to remember is —OH group in phenol is attached with enolic carbon. This is also a reason for showing its acidic character.

5. CHEMICAL PROPERTIES ::

Chemical properties of phenol are classified in the following four categories.

5.1 Reactions of —H atom of —OH group.

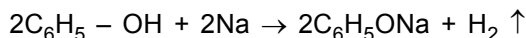
5.2 Reactions of —OH group of phenol.

5.3 Reactions of Benzene ring.

5.4 Other Reactions.

5.1 Reactions of —H atom of —OH group

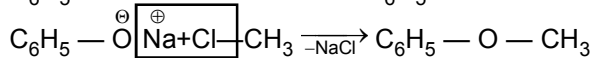
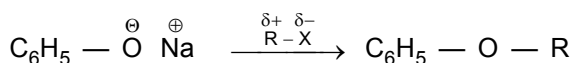
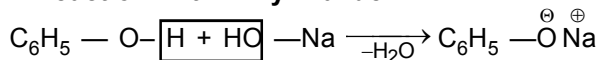
5.1.1 Reaction with Na Metal -



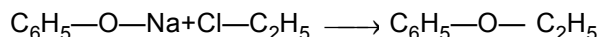
NOTE :

Phenol reacts with strong bases like NaOH but does not react with weak bases like Na_2CO_3 . The reaction is used for the difference between carboxylic acid and phenol.

5.1.2 Reaction with Alkyl halide -

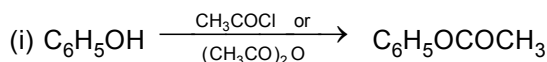


anisole
(methyl phenyl ether)

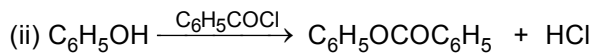


phenetole
(ethyl phenyl ether)

5.1.3 Esterification -



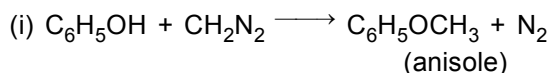
(phenyl acetate)



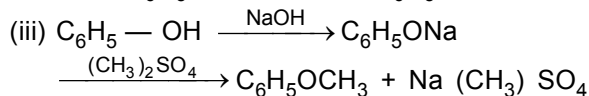
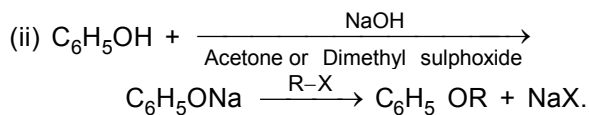
(phenyl benzoate)

NOTE : The above reaction is called ' **Schotten - Baumann**' reaction.

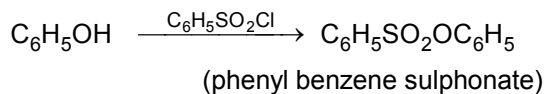
5.1.4 Etherification -



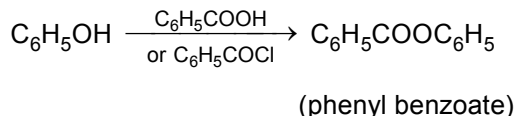
(anisole)



5.1.5 Reaction with Benzene sulphonyl chloride-

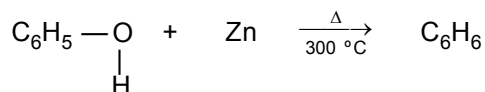


5.1.6 Reaction with Benzoic acid or benzoyl chloride -

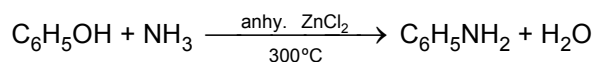


5.2 Reactions — OH group of phenol

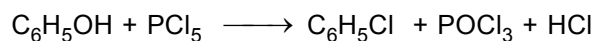
5.2.1 Reaction with Zn dust (Deoxygenation)-



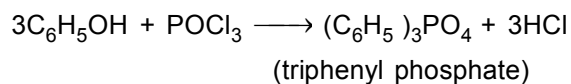
5.2.2 Reaction with Ammonia-



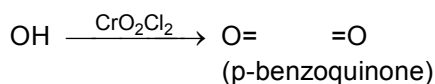
5.2.3 Reaction with PCl_5 -



5.2.4 Reaction with POCl_3 -

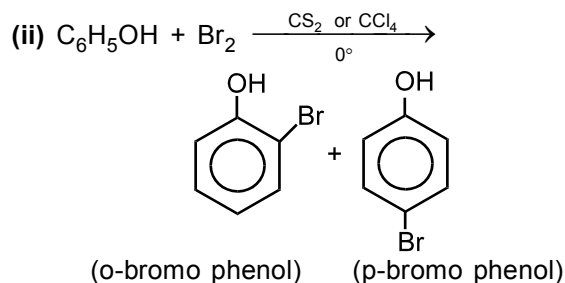
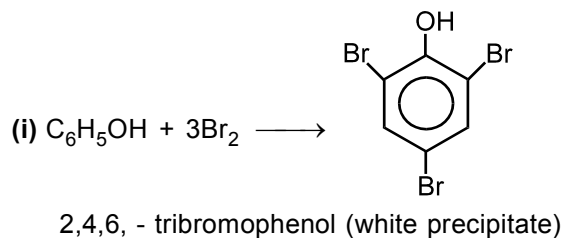


5.2.5 Oxidation -

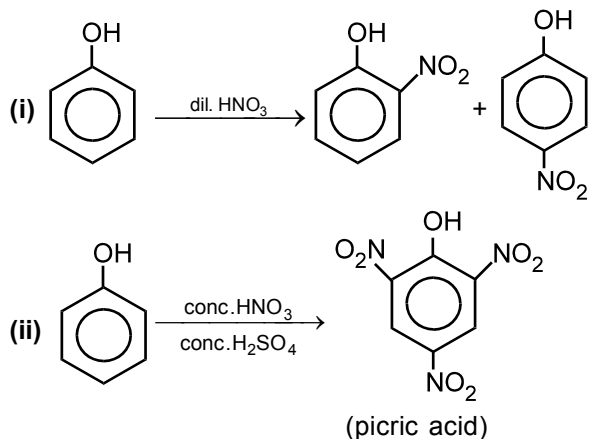


5.3 Reactions of benzene ring -

5.3.1 Bromination

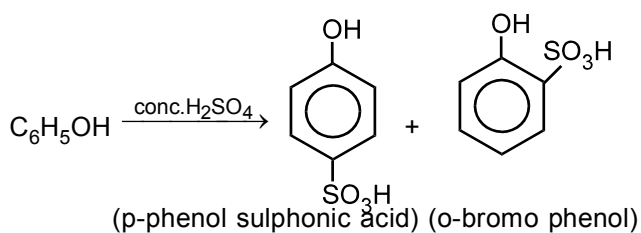


5.3.2 Nitration -

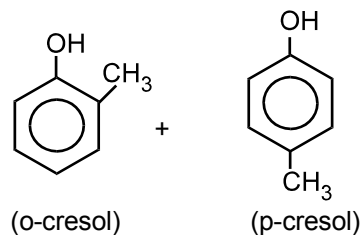
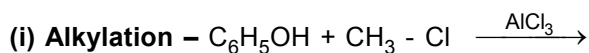


NOTE : Picric acid is yellowish crystalline solid. It is used in dynamite.

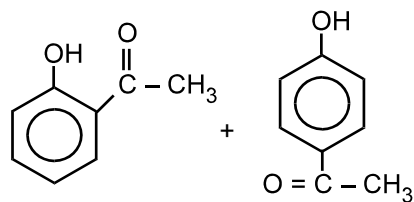
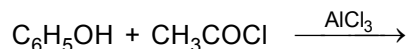
5.3.3 Sulphonation -



5.3.4 Friedel-Craft's reaction -



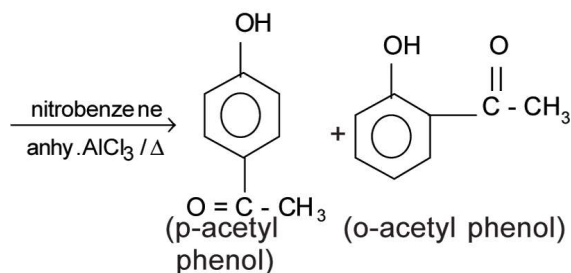
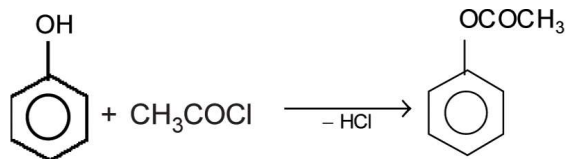
(ii) Acetylation -



(o - hydroxy acetophenone) (p-hydroxy acetophenone)

5.3.5 Fries rearrangement reaction -

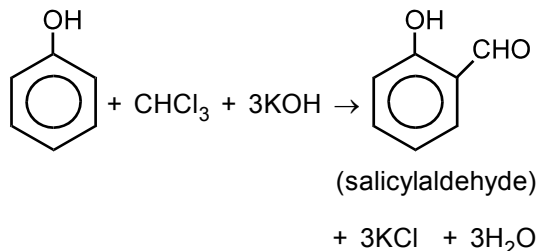
When phenyl ester is heated in nitrobenzene solution, in the presence of anhy. AlCl_3 then rearrangement takes place in which acyl group is transferred at o - & p-positions of phenolic group. Up to 60°C , para product is obtained mainly and above 160°C ortho products are obtained as major product.



5.3.6 Formylation -

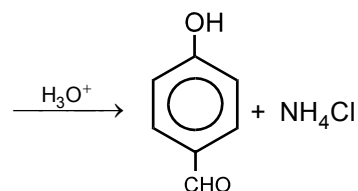
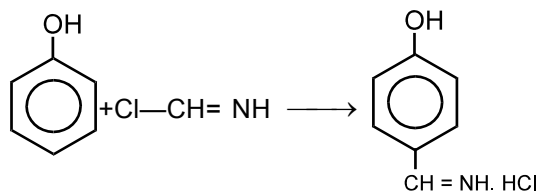
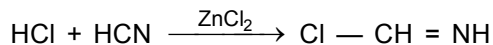
(i) Reimer - Tiemann reaction -

The basic solution of phenol, on reaction with chloroform forms salicylaldehyde as major product.



(ii) Gattermann reaction -

When phenol reacts with $(\text{HCl} + \text{HCN})$ mixture in the presence of ZnCl_2 catalyst and the obtained intermediate aldimine is hydrolysed then p-hydroxy benzaldehyde is formed as major product.

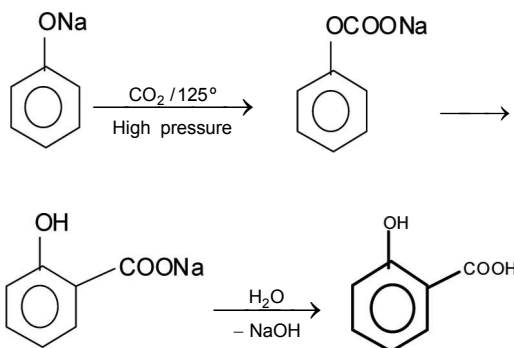


(p-hydroxy benzaldehyde)

NOTE : The reacting species in the above reaction is aldimine.

5.3.7 Carboxylation -

(i) Kolbe or Kolbe Schmidt reaction -

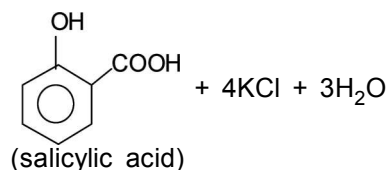


IMPORTANT NOTE :

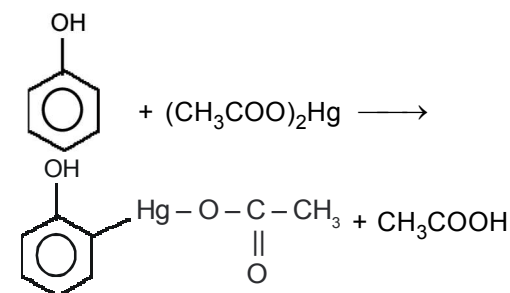
- If it reacts with CO_2 at 25°C , unstable $\text{C}_6\text{H}_5\text{OCOONa}$ is formed.
- If $\text{C}_6\text{H}_5\text{ONa}$ reacts with CO_2 at $250 - 300^\circ\text{C}$

the product is $\text{HO}-\text{C}_6\text{H}_4-\text{COOH}$

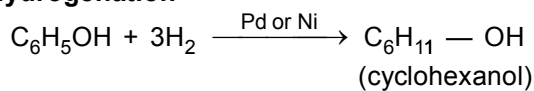
(ii) Reimer - Tiemann reaction -



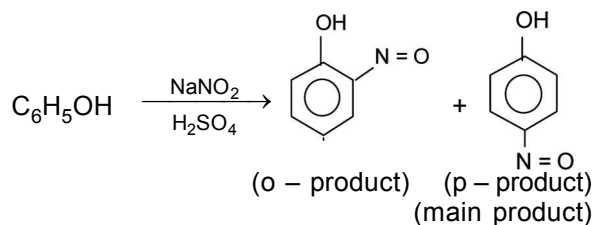
5.3.8 Mercuration -



5.3.9 Hydrogenation -

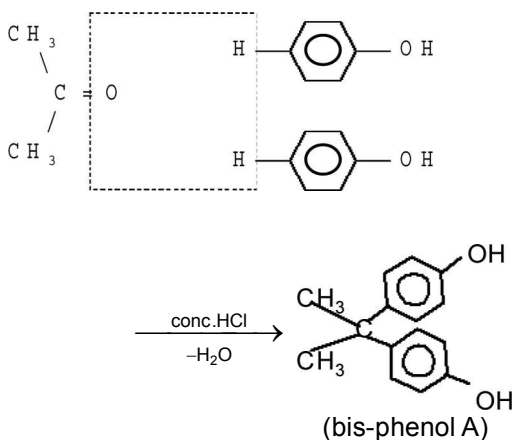


5.3.10 Nitrosation -

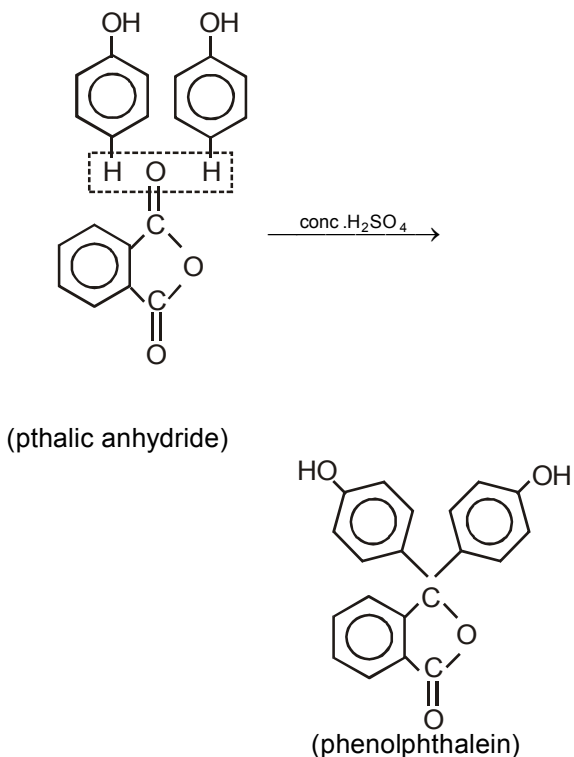


5.4 Other Reactions -

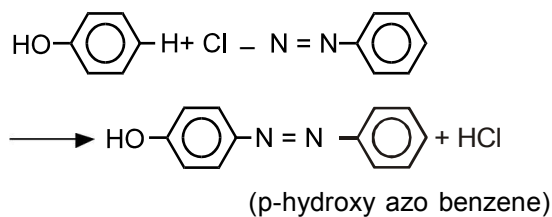
5.4.1 Reaction with Acetone -



5.4.2 Reaction with Phthalic anhydride -

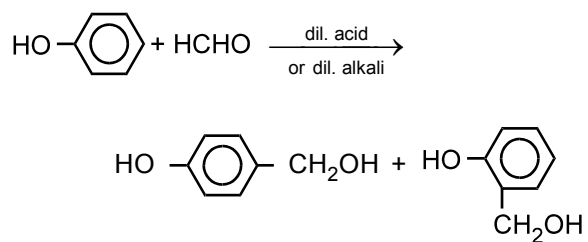


5.4.3 Reaction with Benzene diazonium chloride-



5.4.4 Lederer - Manasse reaction -

Phenol gives condensation reactions with aliphatic and aromatic aldehydes at o- & p-positions. At low temperature, formaldehyde condenses with phenol in the presence of dil. acid or base and p-hydroxy benzyl alcohol is formed as major product.



Examples based on

chemical reaction

Ex. 4 The correct order of reactivity towards electrophilic substitution is -

- (A) Phenol > Benzene > Chlorobenzene > Benzoic acid
(B) Benzoic acid > Chlorobenzene > Benzene > Phenol
(C) Phenol > Chlorobenzene > Benzene > Benzoic acid
(D) Benzoic acid > Phenol > Benzene > Chlorobenzene

(Ans.A)

Sol. Presence of o-, p- directing groups in benzene nucleus activates ring for SE reaction. Presence of m-directing group deactivates ring for SE reactions. Also halogens are deactivating gp. due to -IE. inspite of o-and p-directing nature.

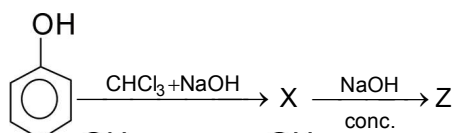
Ex.5 Which among the following is the strongest o-, p-directing group in benzene is -

- (A) -OH (B) -Cl (C) -OCH₃ (D) -CH₃

(Ans.A)

Sol. -OH gp. posses the maximum tendency to throw electron pair towards benzene nucleus.

Ex.6 Identify 'Z' in the reaction -



- (A)
- (B)
- (C)
- (D)

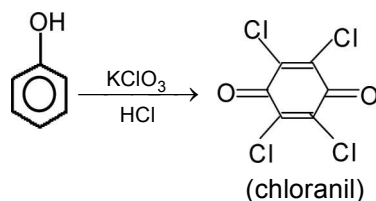
(Ans.B)

Sol. X is which undergoes Cannizzaro's reaction to give Z.

Ex.7 Phenol on oxidation gives chloranil. The oxidant used is -

- (A) $\text{K}_2\text{S}_2\text{O}_8$ (B) KMnO_4
 (C) $\text{KClO}_3 + \text{HCl}$ (D) None **(Ans.C)**

Sol. $\text{K}_2\text{S}_2\text{O}_8$ gives quinol ; KMnO_4 gives mesotartaric acid



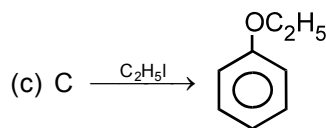
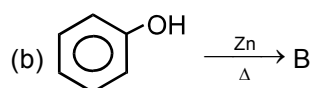
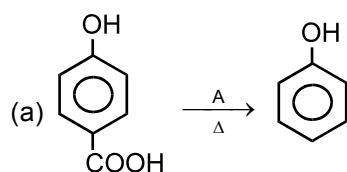
SOLVED EXAMPLE

- Ex.1** The compound represented by the molecular formula C_7H_8O are -
 (A) Only alcohol
 (B) Only ether
 (C) Only phenolic compound
 (D) All the three types of compounds

(Ans.D)

Sol. Benzyl alcohol, anisole and o-, m-, p-cresols can be written by the molecular formula C_7H_8O .

- Ex.2** Identify A, B, and C in the following reactions—



- (A) Sodalime, benzene, potassium phenoxide
 (B) Zn, benzene, sodium ethoxide
 (C) Zn, cyclohexanone, sodium ethoxide
 (D) None of the above **(Ans.A)**

Sol. Sodalime, benzene, potassium phenoxide are the A, B and C compounds respectively.

- Ex.3** Water insoluble aromatic compound dissolves in sodium hydroxide but remain insoluble in sodium bicarbonate. Hence the expected compound should be - [where $\phi = C_6H_5$]
 (A) $\phi-COOH$ (B) $\phi-OH$
 (C) $\phi-CO-CH_3$ (D) $\phi-NH_2$

(Ans.B)

Sol. Phenol is a weak acid. It does not decompose sodium bicarbonate.

- Ex.4** Salicylaldehyde and o-nitrophenol are less soluble in water because -
 (A) Their molecular weights are high
 (B) They exhibit intra molecular H-bonding
 (C) They are aromatic compounds
 (D) $-CHO$ and $-NO_2$ groups are not polar

(Ans.B)

Sol. They exhibit intramolecular H-Bonding. Therefore, they are unable to form H-bonding with water.

- Ex.5** Rate of substitution reaction in phenol is -
 (A) Slower than the rate of benzene
 (B) Faster than the rate of benzene
 (C) Equal to the rate of benzene
 (D) None **(Ans.B)**

Sol. $-OH$ group is activating group towards electrophilic substitution reactions.

- Ex.6** Which is least soluble in water -
 (A) Phenol (B) Ethanol
 (C) Benzoic acid (D) Benzene

(Ans.D)

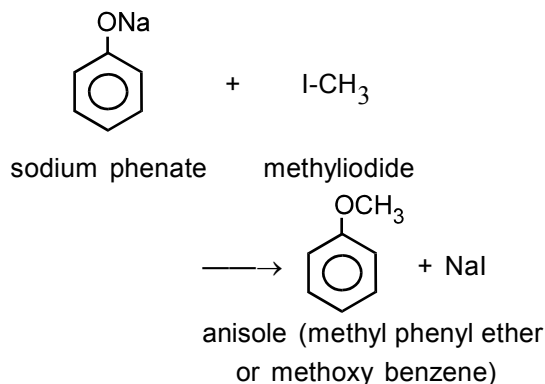
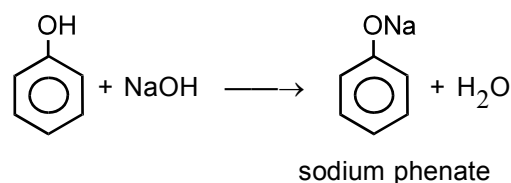
Sol. Benzene can not form H-bonding thus, it is least soluble.

- Ex.7** Anisole is obtained by the reaction of phenol with -

- (A) $NaOH + CHCl_3$ (B) $NaOH + CH_3I$
 (C) $NaOH + C_2H_5I$ (D) $NaOH + CO_2$

(Ans.B)

Sol. Anisole is obtained by the reaction of phenol with $NaOH$ and CH_3I . It is phenyl methyl ether



Ex.14 Which of the following reagent(s) cannot be used to distinguish between phenol and benzyl alcohol -

- (A) NaOH (B) NaHCO₃
(C) Br₂/CCl₄ (D) FeCl₃

(Ans.C)

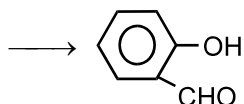
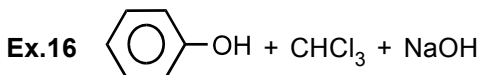
Sol. Only phenol reacts with NaOH, NaHCO₃ and FeCl₃ none of the two compounds react with Br₂/CCl₄.

Ex.15 Phenol condenses with formaldehyde to form-

- (A) Bakelite (B) Asbestos
(C) Polyacrylaldehyde (D) Polyester

(Ans.A)

Sol. When phenol and formaldehyde react in presence of dilute alkali, p-hydroxybenzyl alcohol is obtained as a major product on further heating for some time, a cross-linked polymer, called phenol- formaldehyde resin or bakelite is formed.

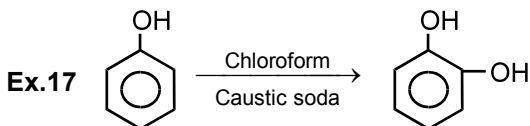


The above reaction is called -

- (A) Gattermann Kosch aldehyde synthesis
(B) Gattermann aldehyde synthesis
(C) Reimer Tiemann reaction
(D) Ledrer Mannase reaction

(Ans.C)

Sol. The above reaction is Reimer Tiemann reaction.



The above reaction is -

- (A) Electrophilic substitution
(B) Nucleophilic substitution
(C) Free radical addition
(D) Electrophilic addition

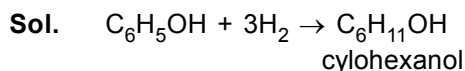
(Ans.A)

Sol. Attacking species in the above reaction is dichlorocarbene which is an electrophile.

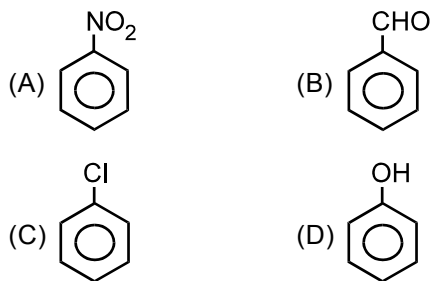
Ex.18 Hydrogenation of phenol gives -

- (A) p-Benzoquinone (B) Cyclohexanol
(C) Salicylic acid (D) None of these

(Ans.B)

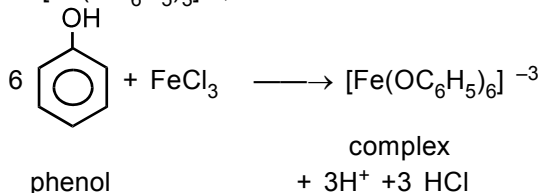


Ex.19 The compound which gives violet colouration with FeCl₃ soln. is :



(Ans.D)

Phenol gives violet colouration with FeCl₃ solution. It is due to the complex formation of [Fe(OC₆H₅)₃]⁻³, as follows:

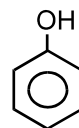


Ex.20 Which of the following tests is not given by carbolic acid -

- (A) It turns blue litmus red
(B) It liberates H₂ on reaction with Na
(C) It forms ester with other acids
(D) It liberates CO₂ from NaHCO₃ soln.

(Ans.D)

Sol Carbolic acid is also known as phenol. It is acidic in nature but does not contain a carboxylic group, hence it does not exhibit the test of carboxylic acid to liberate CO₂ from NaHCO₃ solution. However phenol turns blue litmus red.



phenol (carbolic acid)

Ex.21 A characteristic group-test for phenolic -OH -

- (A) Libermann's nitroso reaction
(B) Coupling reaction with diazonium salt
(C) Aq. FeCl₃ solution
(D) All

(Ans.D)

Sol. All tests are characteristic of phenol.

