CHAPTER / 16

Phenols

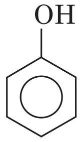
Topics Covered

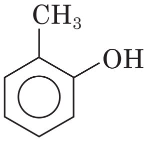
- Nomenclature of Phenols
- Method of Preparations
- Physical Properties
- Chemical Properties
- Uses of Phenols

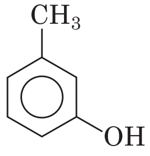
Phenols are the hydroxy derivatives of arenes in which one or more —OH groups are directly attached to the carbon atoms of an aromatic ring.

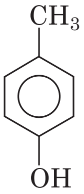
Nomenclature of Phenols

The simplest hydroxy derivative of benzene is phenol. It is its common name and also an accepted IUPAC name. As the structure of phenol involves a benzene ring in its substituted compounds the terms *ortho* (1, 2-disubstituted), *meta* (1,3-disubstituted) and *para* (1,4-disubstituted) are often used in the common names.



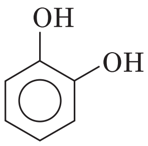


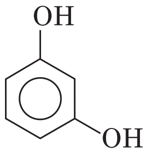


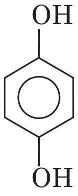


Common name	Phenol	*o*-cresol	*m*-cresol	*p*-cresol
IUPAC name	Phenol	2-methyl phenol	3-methyl phenol	4-methyl phenol

Dihydroxy derivatives of benzene are known as 1,2, 1,3- and 1,4-benzene diol.







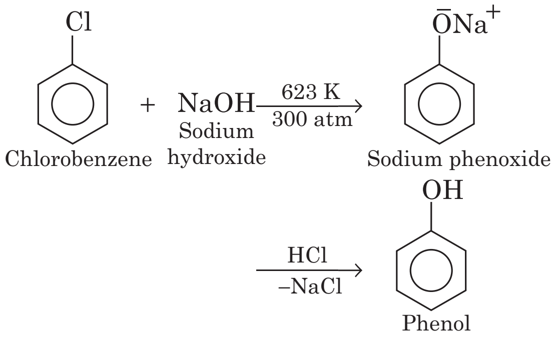
Common name	Catechol	Resorcinol	Quinol or hydroquinone
IUPAC name	Benzene-1, 2-diol	Benzene-1, 3-diol	Benzene-1,4-diol

Method of Preparations

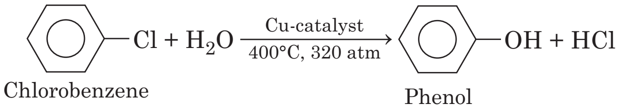
Some general methods for the preparation of phenols are as follows:

1. Hydrolysis of Aryl Halides (Dow's process)

Chlorobenzene on fusion with NaOH at 623 K and 320 atm pressure gives sodium phenoxide which on acidification yields phenol. This reaction is known as Dow's process.



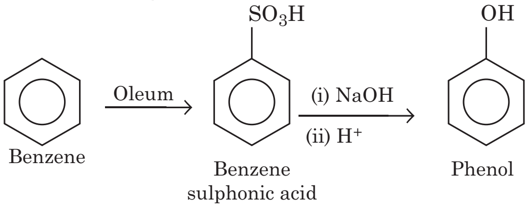
The above process can also be carried out by water in presence of Cu as catalyst at 400°C and 320 atm.



2. From Benzene Sulphonic Acid

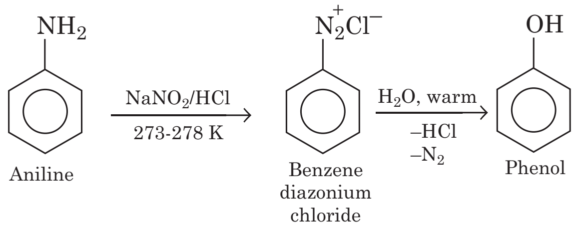
(Alkali Fusion of Sodium Arene Sulphonates)

Benzene is sulphonated with oleum ($H_2S_2O_7$ = conc. $H_2SO_4 + SO_3$) and benzene sulphonic acid, so formed is converted to sodium phenoxide on heating with molten sodium hydroxide. Acidification of sodium phenoxide gives phenol.



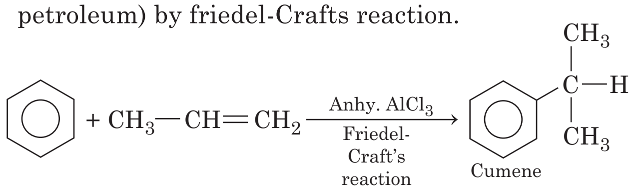
3. From Diazonium Salts

A diazonium salt of aromatic amine (aniline) is formed by treating aromatic amine with nitrous acid ($NaNO_2$ + HCl) at 273-278K . Diazonium salts on hydrolysis with warm water or dilute acids give phenols.

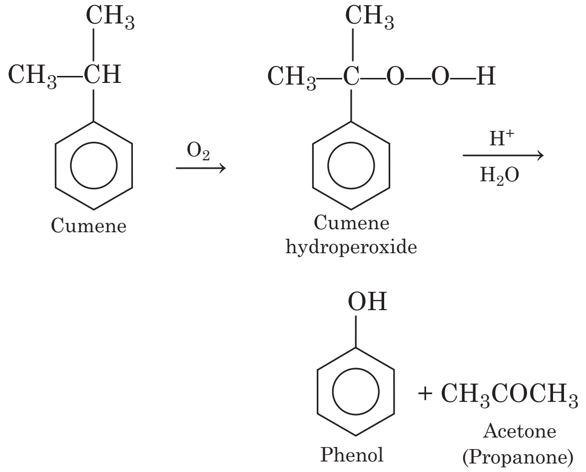


4. From Cumene (isopropylbenzene)

(i) **Preparation of Cumene** It is synthesis from benzene and propylene, (both derived from petroleum) by friedel-Crafts reaction.



(ii) Cumene (isopropyl benzene) on aerial oxidation form cumene hydroperoxide which upon subsequent hydrolysis with dilute acid gives phenol and propanone.



Physical Properties

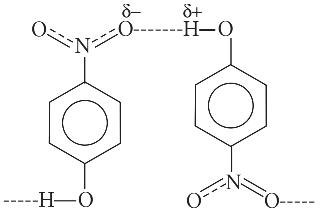
The various physical properties of phenols are discussed below:

(i) It is a colourless, crystalline, deliquescent solid. It attains pink colour on exposure to air and light.

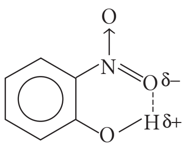
(ii) It has a characteristic carbolic odour and a strong corrosive action on skin.

(iii) It is sparingly soluble in water, but readily soluble in organic solvents such as alcohol, benzene and ether.

(iv) They are capable of forming intermolecular H-bonding. Thus, they have high boiling point.



Intermolecular hydrogen bonding in *p*-nitrophenol molecules

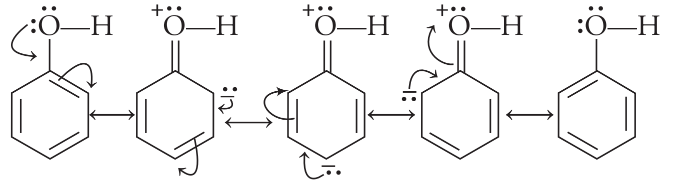


Intramolecular hydrogen bonding in *o*-nitrophenol (chelation)

Chemical Properties

Acidity of Phenols

The reactions of phenol with metals such as Na, Al and sodium hydroxide indicate its acidic nature. In phenol, —OH group is directly attached to sp^2-hybridised carbon of benzene ring which acts as electron withdrawing group.

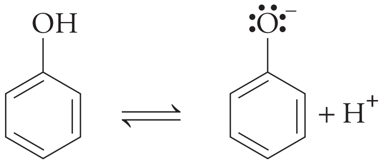


As a result of resonance, the oxygen atom acquires a partial positive charge. This weakens the O—H bond and thus facilitates the release of a proton. The reaction of phenol with aqueous NaOH indicates that phenols are stronger acids than alcohols. It is because the phenoxide ion left after the release of a proton is stabilised by resonance but not the alkoxide ion.

$$R-\ddot{\underset{\cdot\cdot}{O}}-H \rightleftharpoons R-\ddot{\underset{\cdot\cdot}{O}}{:}^{-} + H^{+}$$

Alcohol

Alkoxide ion (not stabilised by resonance)

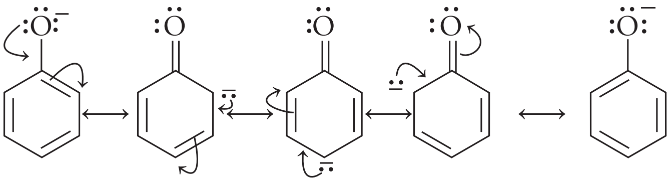


Phenol

Phenoxide ion

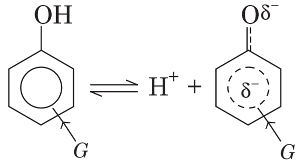
In alkoxide ion, the negative charge is localised on oxygen, while in phenoxide ion, the charge is delocalised.

The delocalisation of negative charge makes phenoxide ion more stable and favours the ionisation of phenol. Phenol is less stable than phenoxide ion because its resonance structures have charge separation. Phenoxide ion also exists as a resonance hybrid (without positve center at O-atom) of the following structures:



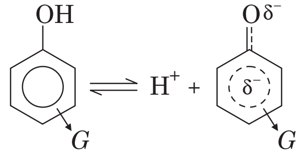
Effect of Substituents on Acidity of Phenols

Acidity of phenols is attributed to the resonance stabilisation of phenoxide ion relative to phenol. Therefore, if a substituent stabilises the phenoxide ion by dispersal of negative charge, it increases the acidity of phenols, e.g. Electron Withdrawing groups (EWG) such as NO_2, —CN, —CHO, —*X* (halogens) increases the acidity of phenols, whereas electron donating groups (EDG) such as —NH_2, —O*R* (alkoxy), —*R* (alkyl) decreases the acidity of phenols.



G releases electrons, intensifies the negative charge, destabilises ion, decreases acidity.

$G = -CH_3, -C_2H_5, -NH_2, -OR$



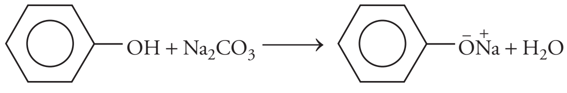
G withdraws electrons, disperses negative charge, stabilises ion, increases acidity.

$G = -NO_2, -CN, X, -\overset{\oplus}{N}R_3, -CHO, -COX, -COOR$

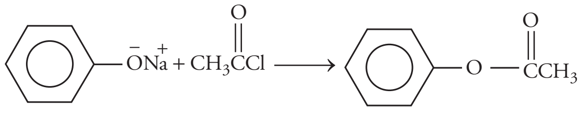
Some of the chemical reactions of phenol are given below:

1. Esterification Reaction

Phenol reacts with acid chlorides or acid anhydrides in presence of aqueous alkali solution to give phenyl esters. In this method, alkali first forms the phenoxide ion which then reacts with the acid chloride to form ester.

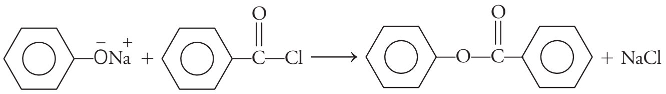


Sodium phenoxide



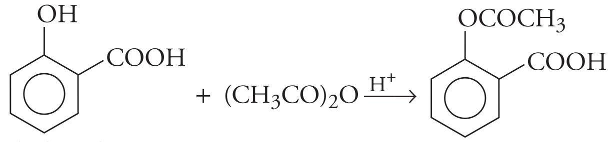
Phenyl acetate

+ NaCl



Phenyl benzoate

The introduction of acetyl (CH_3CO—) group in alcohols or phenols forming an ester is known as acetylation. Acetylation of salicylic acid produces aspirin.



Salicylic acid

Acetyl salicylic acid (Aspirin)

+ CH_3COOH

When a mixture of phenol and benzoyl chloride is shaken with excess of aqueous NaOH, the ester phenyl benzoate is formed and this is called **benzoylation**. This reaction is known as **Schotten-Baumann reaction**.

2. Electrophilic Substitution Reactions

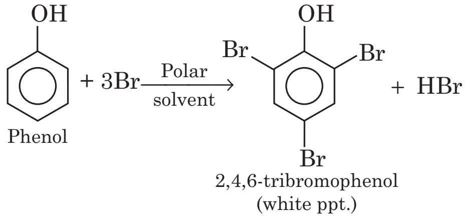
Phenols undergo electrophilic substitution reaction readily because —OH group attached to the benzene ring activates it towards electrophilic substitution. Further, it directs the incoming group to *ortho* and *para* -positions in the ring as these positions become electron rich due to the resonance effect.

Common electrophilic aromatic substitution reactions taking place in phenol are

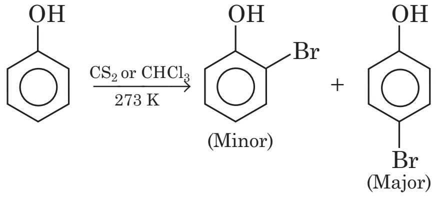
(i) Halogenation

When phenol is treated with bromine water, 2,4,6-tribromophenol is formed as white precipitate. In the reaction, Br^+ acts as an electrophilic.

$$\{Br_2 + Br_2 \rightleftharpoons Br^+ + Br_3^-\}$$



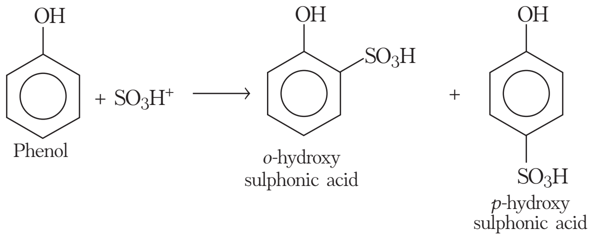
In polar solvent, phenol is in equilibrium with phenoxide ion which is the actual substrate. However, in the presence of CS_2 or $CHCl_3$, *ortho* and *para* halophenols are the main products.



(ii) Sulphonation

The replacement of a hydrogen atom by a sulphonic acid group in a ring is called sulphonation. Phenol reacts with concentrated H_2SO_4 or oleum to form a mixture of *o*-and *p*-hydroxy benzene sulphonic acids. In the reaction SO_3H^+ acts as an electrophile.

$$2H_2SO_4 \rightleftharpoons SO_3H^+ + HSO_4^- + H_2O$$

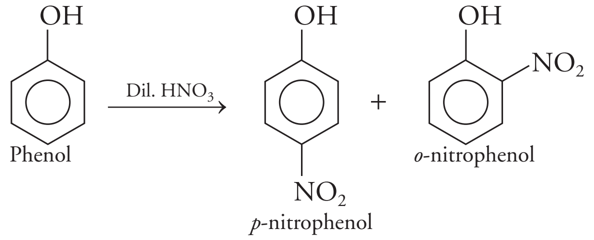


At low temperature, *ortho*-isomer is the major product and at high temperature (373 K), *para*-isomer is favoured.

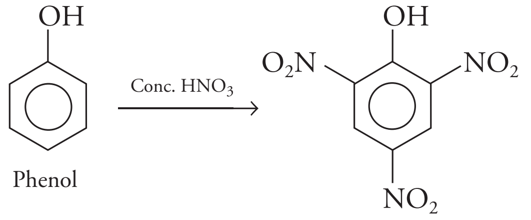
(iii) Nitration

With dilute HNO_3 at low temperature, i.e. 298K, phenol yields a mixture of *ortho* and *para* nitrophenols. In this reaction, NO_2^+ acts as an electrophile.

$$\{2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O\}$$



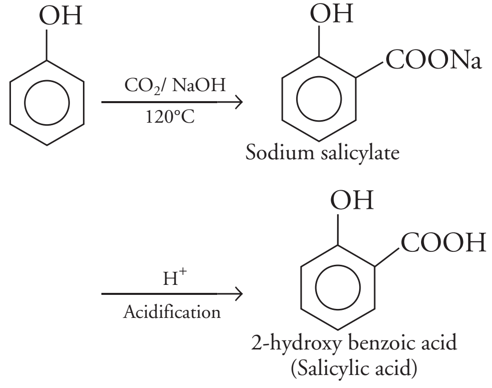
With conc. HNO_3, phenol gives 2,4,6-trinitrophenol which is commonly known as picric acid. The yield of the reaction product is poor.



2,4,6-trinitrophenol (Picric acid)

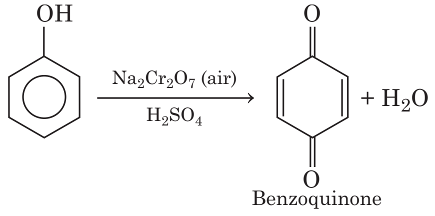
(iv) Kolbe's Reaction

Phenoxide ion produced by treating phenol with NaOH is more reactive than phenol towards electrophilic substitution. Hence, it undergoes electrophilic substitution with weak electrophile, CO_2.



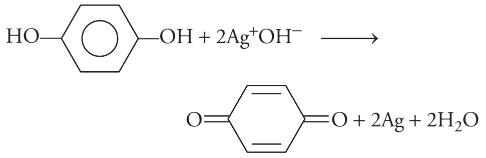
(v) Oxidation

Oxidation of phenol with chromic acid produces a conjugated diketone known as benzoquinone.



Benzoquinone

Similarly, hydroquinone on oxidation with silver salt yields *p*-benzoquinone.

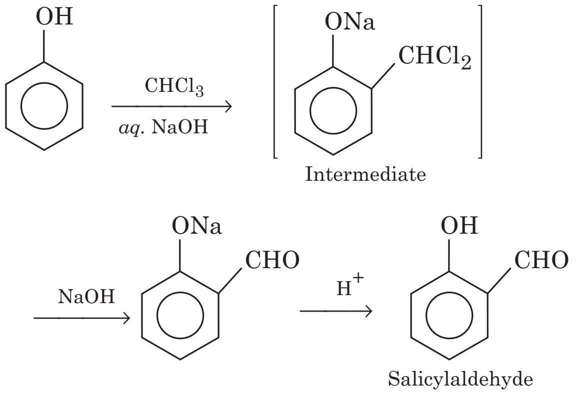


p-benzoquinone

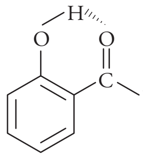
In the presence of air, phenol undergoes oxidation and gives dark-coloured mixtures containing quinones.

(vi) Reimer-Tiemann Reaction

On treating phenol with $CHCl_3$ (chloroform) in the presence of sodium hydroxide, a —CHO group introduced at *ortho*-position of benzene ring. This reaction is called Reimer-Tiemann reaction.



In the above reaction, *ortho* isomer is a major product because of its greater stability resulting from intramolecular hydrogen bonding which is shown below.



Intramolecular hydrogen bonding in salicylaldehyde

Uses of Phenols

(i) It is a versatile precursor to large number of drugs such as aspirin, salol, phenacetin etc.

(ii) It is an active ingredient in some oral analgesics such as chloroseptic sprays.

(iii) Phenol is an important component of industrial paint strippers used in aviation industry for removal of epoxy, polyurethane and other chemical resistant coating.

(iv) Phenol derivatives are used in preparation of cosmetics such as sunscreens, hair colourings and skin lightening preparations.

(v) Concentrated phenol liquids are used for permanent treatment of ingrown toe and finger nails.

(vi) It is used as an antiseptic in soaps, lotions and ointments. "Dettol" is a phenol derivative (2, 4,-dichloro –3, 5-dimethylphenol).

(vii) It is used in manufacture of azodyes, phenolphthalein etc.

(ix) It is used in preparation of picric acid (used as an explosive) and for dying silk and wool.

PRACTICE QUESTIONS

Exams', Textbook's Other Imp. Questions

1 MARK *Questions*

Exams' Questions

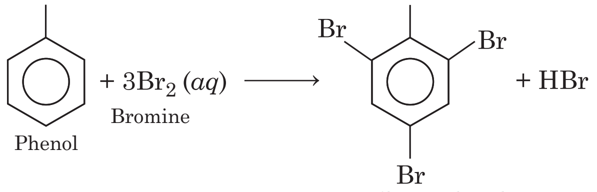
Q.1 Phenol on oxidation with air gives ……… . **[2017]**

Sol. mixtures of quinones. **(1)**

Q.2 Treatment of phenol with Br_2/H_2O yields **[2015, 2011 Instant]**

(a) *o*-bromophenol (b) *p*-bromophenol
(c) 2, 4, 6-tribromophenol (d) *m*-bromophenol

Sol (*c*) Phenol reacts with aqueous bromine or bromine water to give white precipitate of 2, 4, 6-tribromophenol.



(1)

Q.3 Electrophilic substitution reaction in phenol takes place at …… position. **[2014, 2009]**

Sol *ortho* and *para*-position **(1)**

Q.4 Phenol is acidic because ....is more stable than .... **[2013, Textbook]**

Sol phenoxide ion, phenol **(1)**

Important Questions

Q.5 Phenol reacts with .... to give *o*- and *p* -nitrophenols. **[Textbook]**

Sol dil.HNO_3 **(1)**

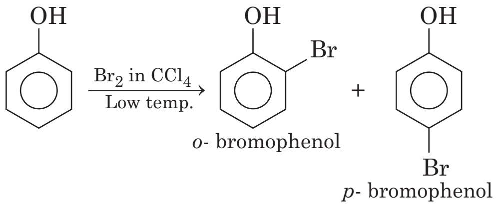
Q.6 Phenol gives .... with CrO_2Cl_2. **[Textbook]**

Sol *p*-benzoquinone **(1)**

Q.7 Phenol reacts with Br_2 in CCl_4 at low temperature to give **[Textbook]**

(a) *m*-bromophenol (b) *o* and *p*-bromophenol
(c) *p*-bromophenol (d) 2,4,6-tribromophenol

Sol (*b*) When bromination is carried out in CCl_4 at low temperature, monobromophenols are obtained.

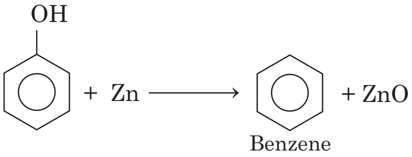


(1)

Q.8 When phenol is distilled with zinc dust, the product is **[Textbook]**

(a) toluene (b) benzene
(c) xylene (d) None of these

Sol (*b*) When phenol is distilled with zinc dust, then benzene is obtained.

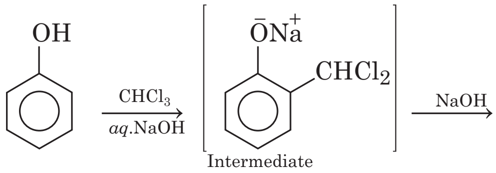


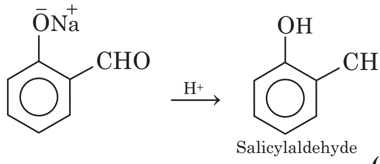
(1)

Q.9 Phenol gives salicylaldehyde on heating with $CHCl_3$ and NaOH. The reaction is called

(a) Cannizzaro's reaction
(b) Claisen condensation
(c) Reimer-Tiemann reaction
(d) Perkin reaction

Sol (*c*) On treating phenol with $CHCl_3$ (chloroform) in presence of sodium hydroxide, a —CHO group is introduced at *ortho* position of benzene ring. This reaction is called Reimer-Tiemann reaction.



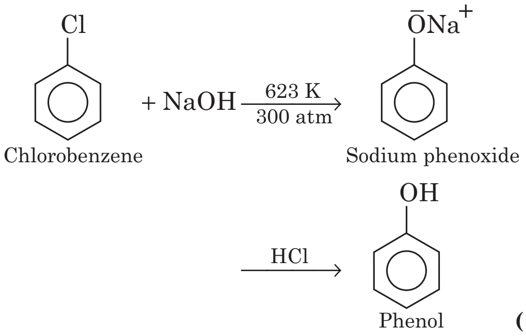


(1)

Q.10 Chlorobenzene on heating with NaOH at high temperature and pressure gives

(a) phenol (b) benzaldehyde
(c) benzene (d) chlorophenol

Sol (*a*) Chlorobenzene on fusion with NaOH at 623 K and 320 atm pressure gives sodium phenoxide which on acidification yield phenol.



(1)

Q.11 Electrophilic substitution in phenol takes place at

(a) *o*-position only (b) *p*-position only
(c) *o* and *p*-position (d) *m*-position only

Sol (c) Phenols undergo electrophilic substitution reaction readily because — OH group attached to the benzene ring activates it towards electrophilic substitution.

Further, it directs the incoming group to *ortho* and *para*-positions in the ring as these positions become electron rich due to resonance. **(1)**

Q.12 Sodium salt of benzene sulphonic acid on fusion with caustic soda gives

(a) C_6H_5OH (b) C_6H_6
(c) C_6H_5COOH (d) None of these

Sol (*a*) Sodium salt of benzene sulphonic acid on fusion with caustic soda gives phenol (C_6H_5OH). **(1)**

2 MARK *Questions*

Exams' Questions

Q.13 Discuss Reimer-Tiemann reaction. **[2019]**

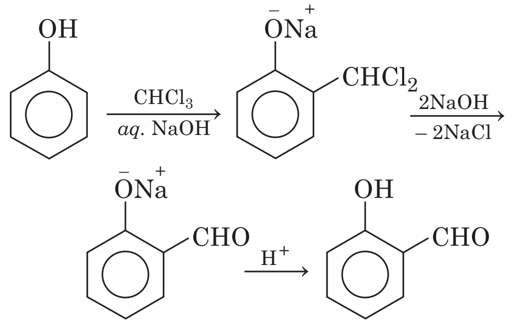
Or

What happens, when phenol is treated with chloroform and dilute alkali solution? **[2012]**

Or

What is Reimer-Tiemann reaction? Give equation. **[2012, 2006, 2004]**

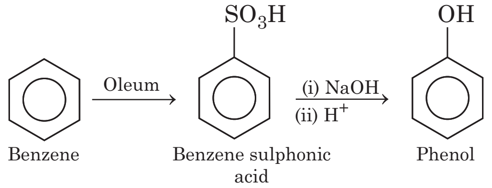
Sol. On treating phenol with $CHCl_3$ in the presence of NaOH, salicylaldehyde is formed. This reaction is called Reimer-Tiemann reaction.



Salicylaldehyde **(2)**

Q.14 How can you convert benzene to phenol? **[2012, 2003]**

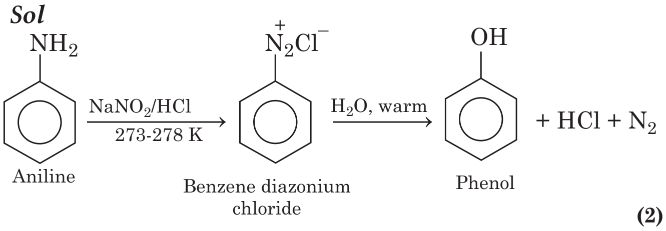
Sol



(2)

Q.15 How is phenol prepared? Give equation. **[2012]**

Sol

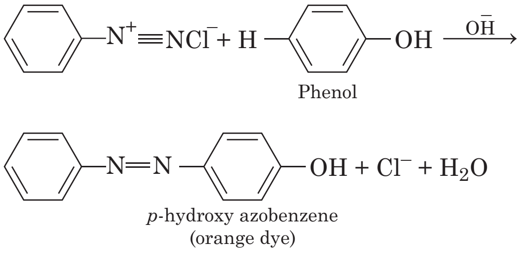


(2)

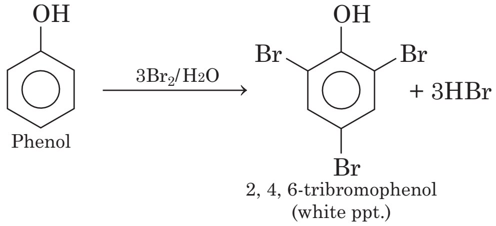
Q.16 Suggest two tests to distinguish between ethanol and phenol. **[2011]**

Sol Ethanol can be distinguished from phenol by the following tests:

(i) **Coupling reaction** Phenols react with diazonium salts in weakly basic solution to form orange coloured azo dyes but ethanol does not react with diazonium salts. **(1)**

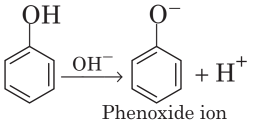


(ii) **Bromine water test** Phenol on reaction with bromine water gives a white ppt. of 2, 4, 6-tribromophenol but ethanol does not react with bromine water. **(1)**

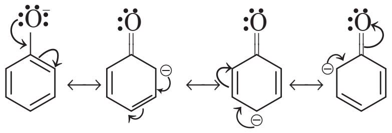


Q.17 Explain, why phenol is acidic while C_2H_5OH is neutral? **[2006, 2004]**

Sol. The phenoxide ion, produced by the loss of a proton by phenol, is stabilised by resonance due to delocalisation of the negative charge on the benzene ring. In contrast, methoxide ion, however is not stabilised by resonance. On the other hand, it is further destabilised by positive inductive effect of alkyl group. **(1)**



Resonance of phenoxide ion



$$CH_3OH \xrightarrow{OH^-} CH_3O^- + H^+$$

Methoxide ion

$$CH_3 \rightarrow O^- \quad + I\text{-effect}$$ **(1)**

Important Questions

Q.18 Give the resonating structures for phenol. **[Textbook]**

Sol Refer to text on page 240. **(2)**

Q.19 Phenol is an acid but it does not react with sodium bicarbonate solution. Why? **[Textbook]**

Sol Phenol is a weaker acid than carbonic acid (H_2CO_3) therefore it cannot liberate carbon dioxide from sodium bicarbonate solution. **(2)**

Q.20 How will you distinguish between ethyl alcohol and phenol? **[Textbook]**

Sol **Distinguish between ethyl alcohol and phenol**

Ethanol when warmed with NaOH and I_2 gives yellow ppt. of iodoform, while phenol does not give this test.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + 4NaOI \longrightarrow \underset{\text{Iodoform (yellow ppt).}}{CHI_3} + HCOONa + NaI + H_2O + 2NaOH$$

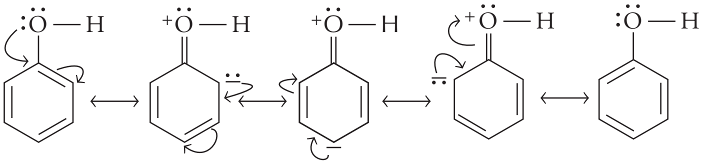
$$\underset{\text{Phenol}}{C_6H_5OH} + NaOH \longrightarrow \text{No yellow ppt.}$$ **(2)**

3 MARK *Questions*

Exams' Questions

Q.21 Why phenol is acidic in nature? **[2018]**

Sol Phenol is acidic in nature because after losing a proton (H^+), it forms phenoxide ion which is more stabilised by resonance. Due to this, the lone pairs of electrons of — OH group are involved in resonance with C-atom of benzene ring. This delocalisation of electrons (or resonance) can be represented as :



As a result of resonance, the oxygen atom acquires a partial positive charge. This weakens the O—H bond and thus facilitates the release of a proton. **(3)**

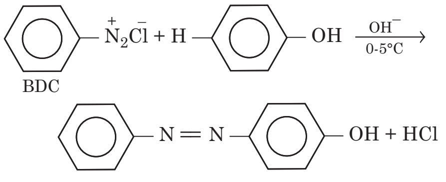
Q.22 (i) How can you prepare phenol from chlorobenzene?

(ii) Write the coupling reaction of BDC with phenol. **[2014]**

Sol. (i) Refer to text on page 239.

(ii) When benzene diazonium chloride (BDC) is treated with alkaline solution of phenol, then *para*-hydroxyazobenzene is formed. This reaction takes place at 0-5°C and known as coupling reaction.

The products are used as dyes and indicators.



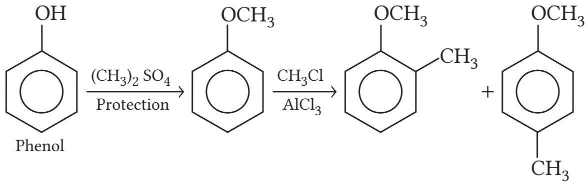
p-hydroxyazobenzene **(3)**

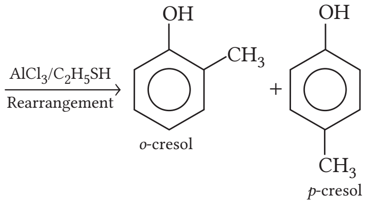
Important Questions

Q.23 How will you obtain the following from phenol?

(i) Salicylaldehyde (ii) Benzene **[Textbook]**
(iii) Picric acid (iv) Nitrophenol
(v) Salicylic acid (vi) *p*-cresol

Sol (i) **Phenol to salicylaldehyde** See page 5 **(1/2)**
(ii) **Phenol to benzene** Refer page 6 **(1/2)**
(iii) **Phenol to picric acid** Refer page 5 **(1/2)**
(iv) **Phenol to nitrophenol** Refer page 5 **(1/2)**
(v) **Phenol to salicylic acid** Refer page 5 **(1/2)**
(vi) **Phenol to *p*-cresol** **(1/2)**





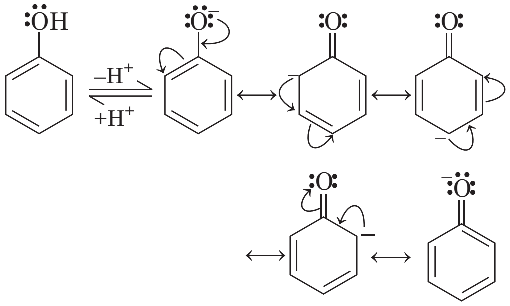
The above reaction is known as Friedel-Craft's alkylation.

Q.24 How can you carry nitration in phenol? Explain. **[Textbook]**

Sol Refer to page on 241. **(3)**

Q.25 What is the directive influence of phenolic group? Explain with reasons. **[Textbook]**

Sol The phenolic group (— OH) tends to be electron-donating because the extra electrons around the oxygen atom can be shared with the aromatic benzene ring. Thus, it contributes resonance structures, which are as follows:



In the resonance structure of the phenol molecule, the 2, 4 and 6 (or *ortho*/*para* positions) positions have a partial negative charge. This leads to possible attack at these positions by an electrophile, through the process known as electrophilic aromatic substitution. **(3)**

7 MARK *Questions*

Exams' Questions

Q.26 (i) How is phenol prepared from diazonium salt? Explain its acidic character.

(ii) What is Reimer-Tiemann reaction? Give equation. **[2015]**

Sol. (i) Refer to text on pages 239 and 240.

(ii) Refer to text on page 242. **(7)**

Q.27 (i) How phenol is prepared from benzene ?

(ii) Explain the acidity of phenol.

(iii) How phenol can be converted into Salicylaldehyde? **[2011, 2001]**

Sol. (i) Refer to text on page 239.

(ii) Refer to text on page 240.

(iii) Refer to text on page 242 **(2 + 2 + 3 = 7)**

Important Questions

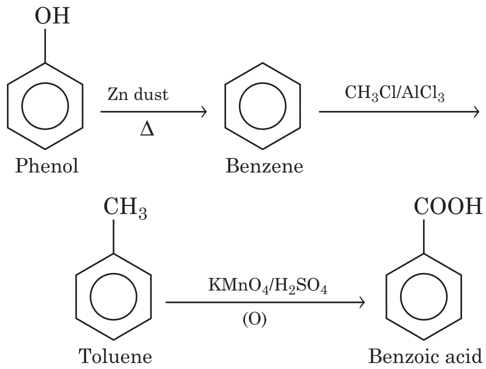
Q.28 (i) How will you convert phenol to benzoic acid?

(ii) An organic compound *A* having molecular formula C_6H_6O gives a characteristic colour with aqueous $FeCl_3$ solution. *A*, on treatment with CO_2 and NaOH at 400 K under pressure gives *B* which on acidification gives a compound *C*.

The compound *C* reacts with acetyl chloride to give *D* which is a popular pain killer. Deduce structure of *A*, *B*, *C* and *D*.

Sol

(i)

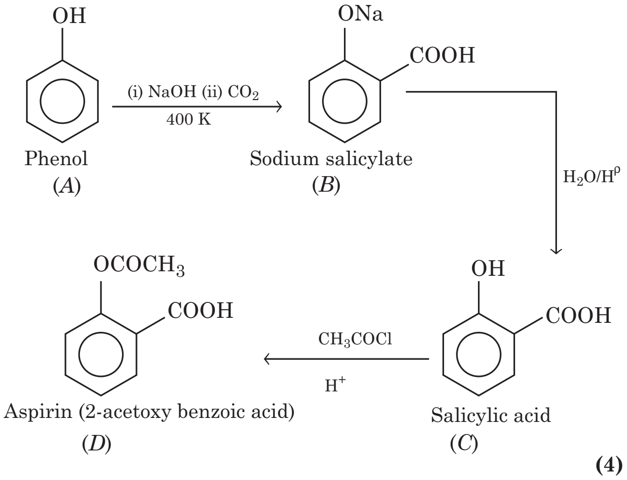


(3)

(ii) Phenol (*A*) reacts with $FeCl_3$ to give violet coloured complex.

$$C_6H_5OH + FeCl_3 \longrightarrow C_6H_5OFeCl_2 + HCl$$

Phenol (*A*) reacts with alkali and CO_2 to give sodium salicylate (*B*). Sodium salicylate (*B*) on acidification gives salicylic acid (*C*). Salicyclic acid (*C*) reacts with acetyl chloride to give aspirin which is a popular pain killer.



(4)

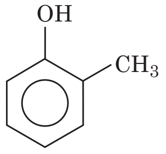
Q.29 (i) Give the structures and IUPAC names of monohydric phenols of molecular formula C_7H_8O.

(ii) How will you synthesise?

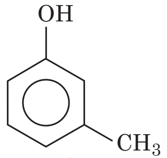
(a) 1-phenyl ethanol from a suitable alkene.

(b) Cyclohexyl methanol using an alkyl halide by an S_N2 mechanism.

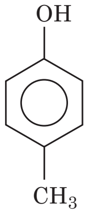
Sol (i) The three isomers are as follows:



o-cresol or
2-methyl phenol



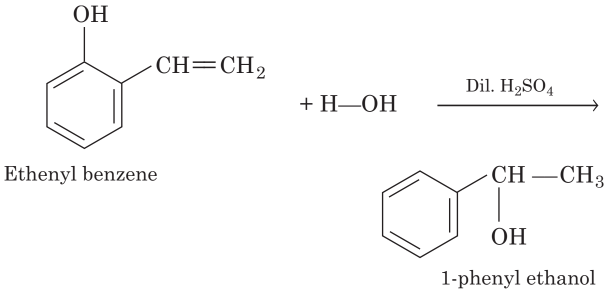
m-cresol or
3-methyl phenol



p-cresol or 4-methyl phenol

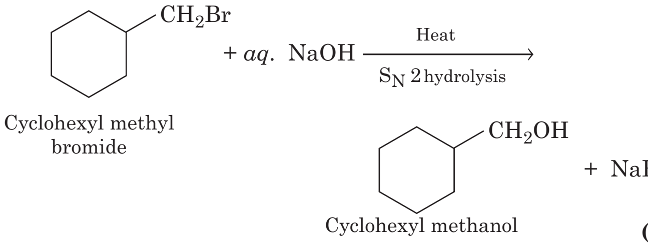
(3)

(ii) (a) On adding H_2O to ethenyl benzene in the presence of dilute H_2SO_4, we get 1-phenyl ethanol.



(2)

(b) Hydrolysis of cyclohexyl methyl bromide by aqueous NaOH gives cyclohexyl methanol.



(2)

Chapter Test

1 MARK *Questions*

1 Intramolecular hydrogen bonding is found in **[Textbook]**
- (a) phenol
- (b) *o*-nitrophenol
- (c) *p*-nitrophenol
- (d) *m*-nitrophenol

2 *p*-nitrophenol is stronger acid than phenol because nitro group is **[Textbook]**
- (a) electron donating
- (b) electron withdrawing
- (c) acidic
- (d) basic

3 The most convenient method of removing a phenolic group from a compound is by **[Textbook]**
- (a) reduction with Sn + HCl
- (b) heating strongly
- (c) heating strongly with copper
- (d) distilling with zinc dust

4 Which of the following reactions yield salicylic acid as the final product.
- (a) Kolbe's reaction
- (b) Reimer-Tiemann reaction
- (c) Reaction of phenol with Zn dust
- (d) Reaction of phenol with dilute HNO_3

5 Phenol is less acidic than **[Textbook]**
- (a) acetic acid
- (b) *p*-methoxy phenol
- (c) *o*-nitrophenol
- (d) ethanol

[***Ans.*** **1.** (b), **2.** (b), **3.** (d), **4.** (a), **5.** (a, c)]

6 Formylation of phenol is ……… reaction.

[***Ans.*** Reimer-Tiemann]

7 Benzene can be obtained by heating phenol with ……… .

[***Ans.*** Zn dust]

2 MARK *Questions*

8 Give the reaction of phenol with benzene diazonium chloride. **[Textbook]**

9 How will you convert phenol to salicyclic acid?

10 Give reason, why phenol is more easily nitrated than benzene?

11 Give balanced equation and explain what happens when phenol is treated with bromine water?

12 How will you convert phenol to benzoic acid?

3 MARK *Questions*

13 (i) Give reason, why phenol does not get protonated easily.

(ii) Complete the following reaction:

$$\underset{(A)}{\text{Benzene}} \xrightarrow[+AlCl_3]{Ac_2O} B \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) MeMgBr}} C \xrightarrow[H_2SO_4]{\text{Conc.}}$$

$$D \xrightarrow[\text{(ii) } H_2O_2/OH^-]{\text{(i) } BH_3/THF} E$$

14 (i) Phenol is more acidic than methanol. Give reason.

(ii) Convert the following:
- (a) Phenol to *p*-benzoquinone
- (b) Aniline to phenol

7 MARK *Questions*

15 (i) Explain with reason:
- (a) Presence of electron withdrawing group increases the acidic character of phenol.
- (b) Solubility of alcohols in water decreases with increase in molecular mass.
- (c) Phenol is more acidic than ethanol.

(ii) How would you obtain
- (a) picric acid from phenol?
- (b) 2-methyl propanol from 2-methyl propene?

16 How can phenol be prepared from cumene? Convert phenol to aspirin and *p*-benzoquinone. **[Textbook]**

17 Starting from benzene diazonium chloride, how can phenol be prepared ? How can phenol be sulphonated ? What is the electrophile for this reaction? **[Textbook]**