# PHENOL (HYDROXY BENZENE)

This is a class of organic compounds in which one or more hydrogen atoms of the benzene nucleus is replaced by the –OH group. E.g. OH

Aromatic alcohols are compounds in which the –OH group is attached to a side chain of the Benzene ring. CH2-OH

Methods of preparation of phenol

1. From Chlorobenzene

Cl OH

+ NaOH

1. From Sulphonic acid

In this method benzene sulphonic acid is first treated with sodium hydroxide to form benzene sodium sulphonate.

SO3H SO3Na

The sodiumbenzenesulphonate is then heated to a temperature of about 3000C with sodium hydroxide to form phenol

SO3Na + NaOH ONa + Na2SO3

Sodium phenoxide

Then the sodium phenoxide is treated with hydrochloric acid to form phenol

ONa OH

Note: SO3H

1. From Cumene process

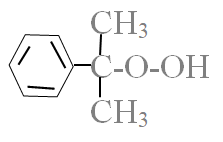
In the cumene process benzene is first treated with propene in the presence of phosphoric acid to give ethylmethylbenzene

CH(CH3)-CH3

A current of air is then passed through the methylethylbenzene to form hydroperoxide

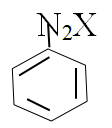
CH-CH3 CH3

CH3 C-O-OH  
 CH3

The hydroperoxide is then finally warmed with sulphuric acid

OH + CH3COCH3

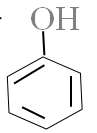
Show how benzene is converted to phenol using cumene process.

1. From Diazonium salts

(Where X = Cl-, HSO4­-, NO3-)

Benzene diazonium salts can be obtained from benzene as follows

NO2  NH2 N2Cl



1. From Grignard reagent

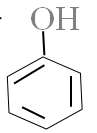
Grignard reagents are prepared from bromo or iodo and not iodo compounds.

Br MgBr OMgBr OH + Mg(OH)Br

## Physical Properties of phenol

1. Pure phenol is a colourless crystalline solid that turns pink or red on exposure to air and is highly deliquescent
2. It has a characteristic odour and is sparingly soluble in water
3. It is weakly acidic and therefore its aqueous solution turns blue litmus paper red
4. Phenol has relatively higher boiling point & this is attributed to formation of intermolecular hydrogen bonds between its molecules.
5. Phenol like aromatic compounds burns with a sooty flame.

### Chemical properties

Phenol exhibits both properties of the OH group & the aromatic group.

Aromatic group

### Reactions of the OH group

Note: Phenol differs from both aromatic alcohols and aliphatic alcohols { (R-OH) e.g CH3CH2OH,

CH2OH} in the following ways

1. It does not react with halogen acids (HX i.e. HBr, HCl, HI)
2. It does not react with phosphorous trihalides (PBr3, PI3)
3. Unlike alcohols phenol is not oxidized by for instance acidified potassium dichromate
4. Phenol unlike alcohols does not undergo elimination reactions
5. Phenol is a much stronger acid than alcohols e.g.CH3OH (1.0 x 10-16 ) C6H5OH(1.0 x 10-10)

#### Reactions in which phenol resembles alcohols

1. Like alcohols Phenol reacts with carboxylic acids to form esters

H+

OH

+ CH3COOH ⇌ O-COCH3 + H2O

1. Like alcohols phenol reacts with acid halides (RCOCl) to form esters

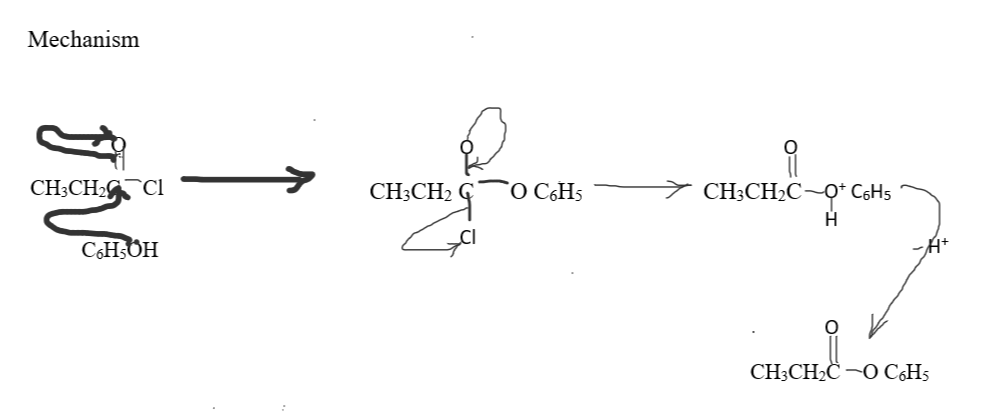
OH

+ RCOX O-COR + HX

E.g

C6H5OH + CH3CH­2COCl CH3CH­2COO C6H5 + HCl

Propanoyl chloride



1. Phenol like alcohols reacts with PCl5 (Phosphorous pentachloride)\

OH

+ PCl5 Cl + POCl + HCl

#### Reactions in which phenol differs from alcohols

1. **Acidic Properties**

Unlike alcohols phenol is acidic enough to react with both sodium metal and sodium hydroxide

OH

+ Na ONa + ½H2 (g)

OH

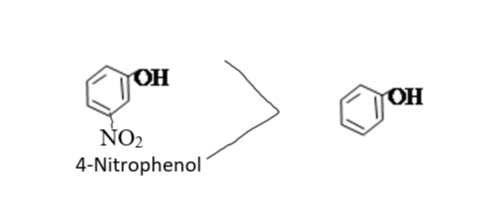
+ NaOH (aq) ONa + H2O (l)

Explanation

Phenol is more acidic than alcohols because the oxygen atom of the OH group tends to share its lone pair of electrons with carbon atom of the benzene ring and in so doing the oxygen – hydrogen is weekend while the carbon – oxygen bond becomes stronger and because the oxygen – hydrogen bond is weakened it can easily be overcome in the aqueous solution setting free hydrogen ions which makes the solution acidic.

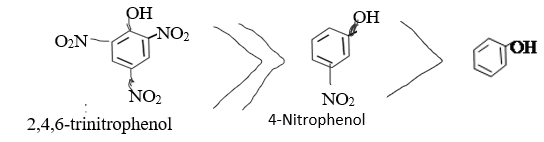
Explain why the carbon – oxygen bond in phenol is stronger and shorter than in an alcohol.

The partial creation of the double bond on the carbon – oxygen bond of phenol makes it shorter & stronger.

Note: The acidity strength of phenol will depend on the nature of groups which are attached to the benzene ring. Electron withdrawing groups like –CN, - NO2, X (-Cl) or - COOH, present at the ortho or para positions will increase the acidity of phenol.

That is to say

Hence 4 – nitrophenol is more acidic than phenol



These groups being electron withdrawing or having negative inductive effect decrease electron density in the ring and even further weaken the OH bond. The greater the number, the greater is the effect. This explains why 2, 4, 6-trinitrophenol is a very strong acid.

Note: This difference in the acidic strength between phenol & alcohols is used in qualitative analysis – litmus paper/solution, to distinguish between phenol & alcohols; also its used to distinguish between phenol and carboxylic acids using NaHCO3/Na2CO3.

Although phenol is acidic, it’s not acidic enough like carboxylic acids to react with sodium carbonate or sodium hydrogen carbonate.

All carboxylic acids react with either NaHCO3 or Na2CO3 to give effervescence of a colourless gas which is carbon dioxide or bubbles of a colourless gas.

*Name the reagent that can be used to distinguish each of the following pairs of compounds and in each case state what would be observed.*

OH

1. and CH3COOH

OH

1. and COOH

When each member of the pair above is treated with either sodium carbonate or sodium hydrogen carbonate solution, only the carboxylic acid in each pair will give bubbles or effervescence of a colourless gas.

Phenol in both of the pairs will give no observable change.

**(ii) *Reaction with neutral iron (III) chloride solution***

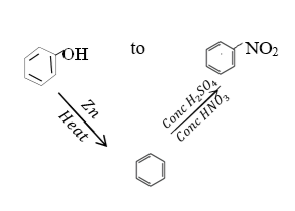
Addition of neutral iron (III) chloride solution to phenol gives a violet coloured product.

1. ***Unlike alcohols phenol reacts with zinc when heated to give benzene***



OH

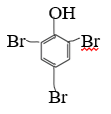
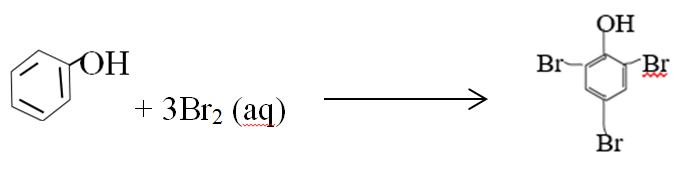
**+** Zn + ZnO

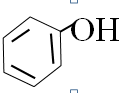
*Write equations to show how you can affect the following conversion*

### Reactions of the aromatic ring

The OH group in phenol greatly activates the benzene ring towards electrophilic substitution reaction. As a result phenol tends to undergo poly-substitution reaction.

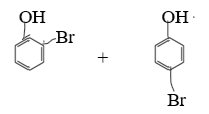
#### Halogenation

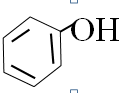
Phenol reacts with bromine water to give a white precipitate of 2, 4, 6 – tribromophenol



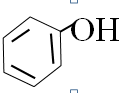
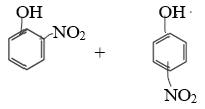
**Note:** The reaction of phenol with bromine water is used in qualitative analysis as a test for phenol.

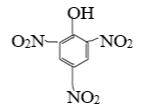
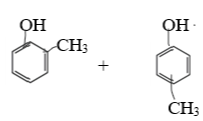
***Observation:***Initially the brown colour of bromine solution is discarded and a white precipitate is formed.

A mono derivative in the above reaction is usually obtained by carrying out the reaction at low temperatures in the presence of non – polar solvent like the carbon tetrachloride.

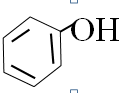
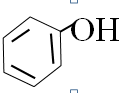


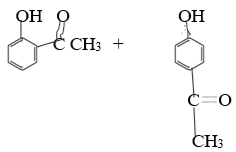
#### Nitration

A mono substituent product (Nitrophenol) is obtained by carrying out reactions with a dilute nitric acid and at a low temperature (200C)

However: Reaction with concentrated nitric acid leads to formation of poly substituted product called 2, 4, 6 – trinitrophenol

#### Other reactions of Phenol summarized





#### Coupling reactions of phenol

Phenol undergoes coupling reactions with diazonium salts to give brightly coloured products (yellow) called azo – compounds.

N2X + H OH N=N OH

Azo - compound