

B.Sc. Applied Physical Sciences (Chemistry) I Year (Industrial Chemistry)

Chemistry- Thermodynamics, Equilibria and Functional Group Organic Chemistry

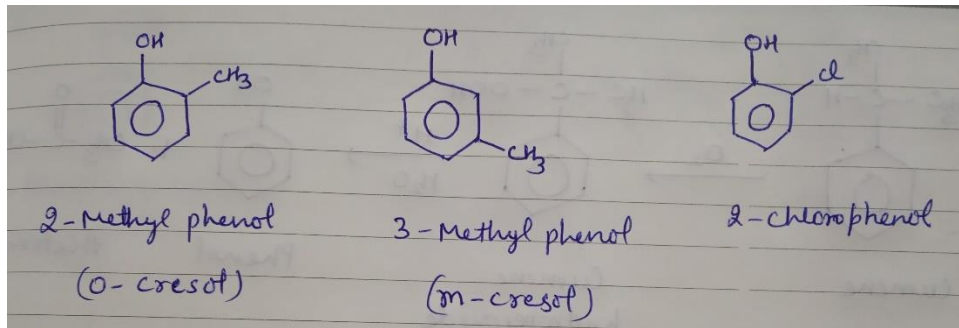
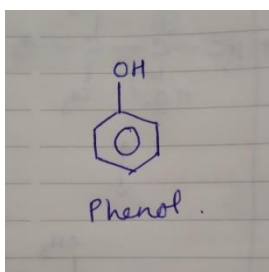
Section B Organic Chemistry-2

Unit 6

Alcohols, Phenols, Ether, aldehydes and Ketones

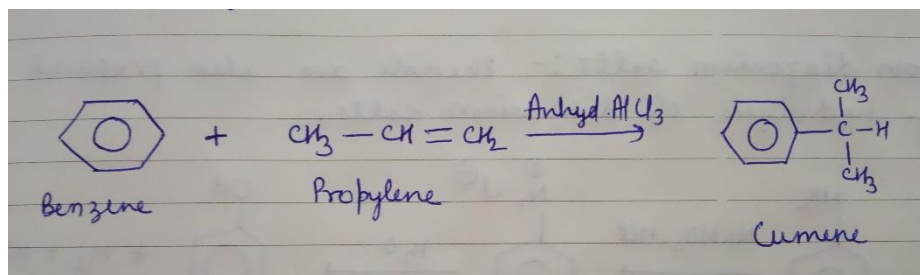
(C) Phenols

The compounds in which the hydroxyl group is attached directly with the aromatic ring are called phenols. They have general formula Ar – OH where, Ar is for Aryl group. The simplest one is phenol. For examples:



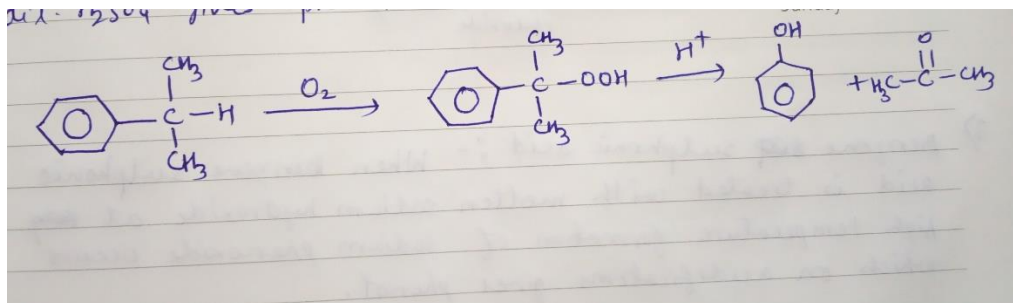
Methods of preparation of Phenols:

(1) From Cumene: Cumene is prepared from propylene and benzene by Friedel Crafts reaction.

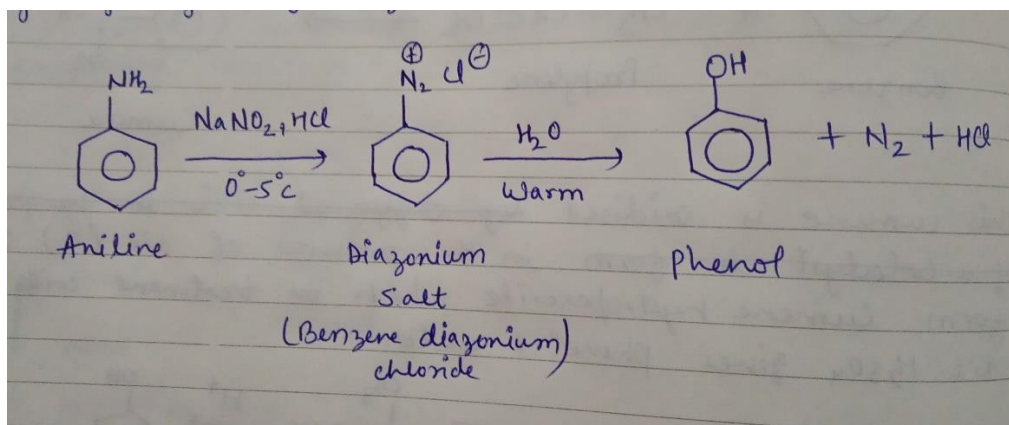


References: Organic Chemistry, R.T. Morrison, R.N. Boyd and S.K. Bhattacharjee, Pearson, 7th Edition and advance Organic Chemistry, Bahl and Bahl, S.Chand & Company Ltd.

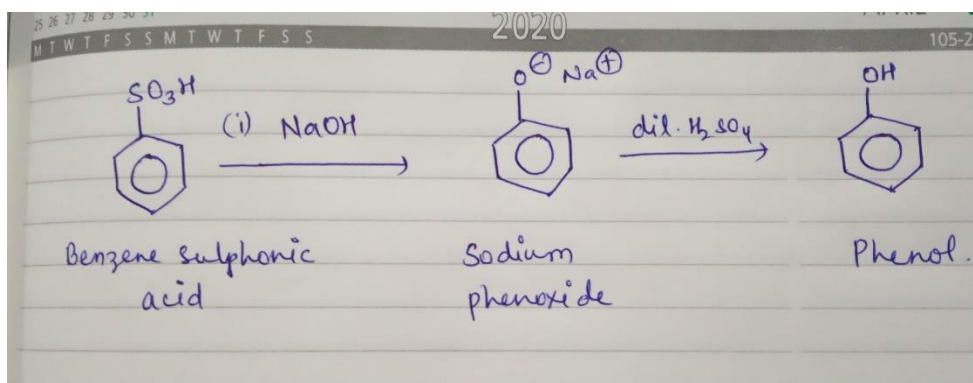
This cumene is oxidised in air (O_2) to give Cumene hydroperoxide which on treating with dilute sulphuric acid forms phenol and acetone. This method is very useful on commercial scale.



(2) From diazonium salts: Phenols are also prepared by the hydrolysis of diazonium salts.

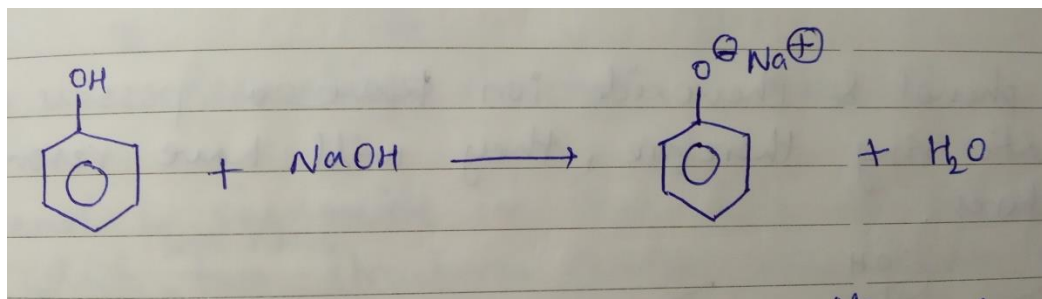


(3) From Benzene sulphonic acid: When Benzene sulphonic acid is treated with sodium hydroxide at high temperature it forms sodium phenoxide which on acidification with dilute sulphuric acid gives phenol.



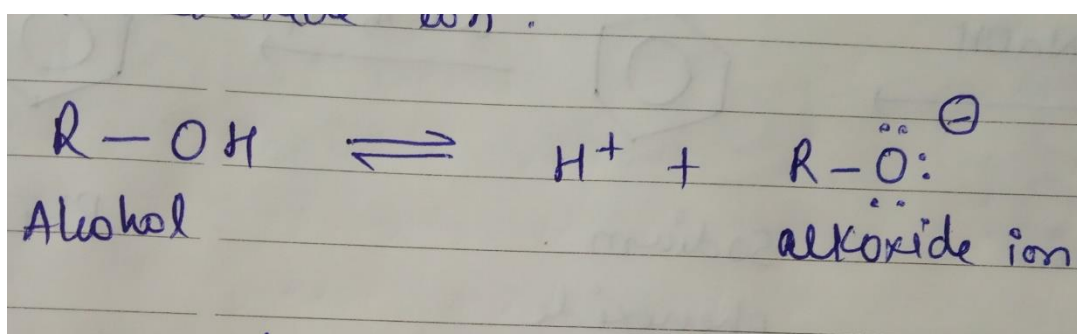
Acidity of Phenols

When phenols are treated with aqueous solutions of hydroxides, they give their salts.

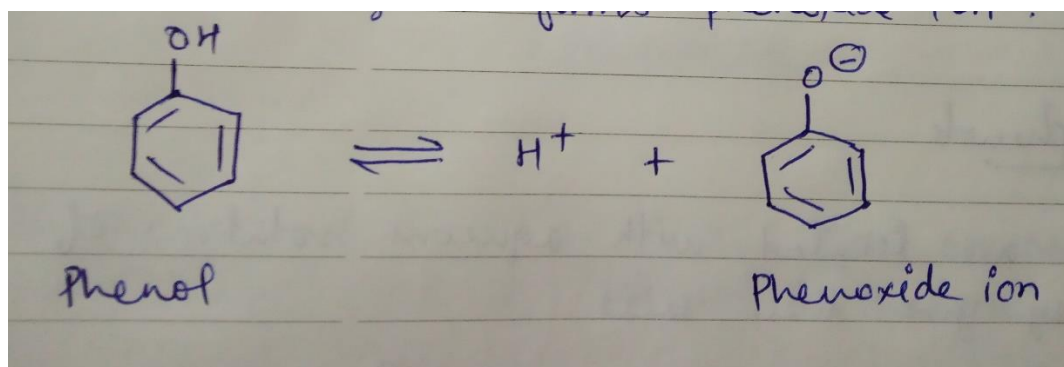


And the salt formed when treated with mineral acids gives back the phenol. Therefore, phenols are considered stronger acids than the water. Generally, phenols have K_a value around 10^{-10} , so they are comparatively more acidic than the alcohols which have K_a values around 10^{-16} - 10^{-18} . Phenols do not form salts with bicarbonates like sodium bicarbonate but salts of phenols give back the phenol on reaction with carboxylic acids. This shows that phenols are weaker acids than the carboxylic acids ($K_a = 10^{-5}$).

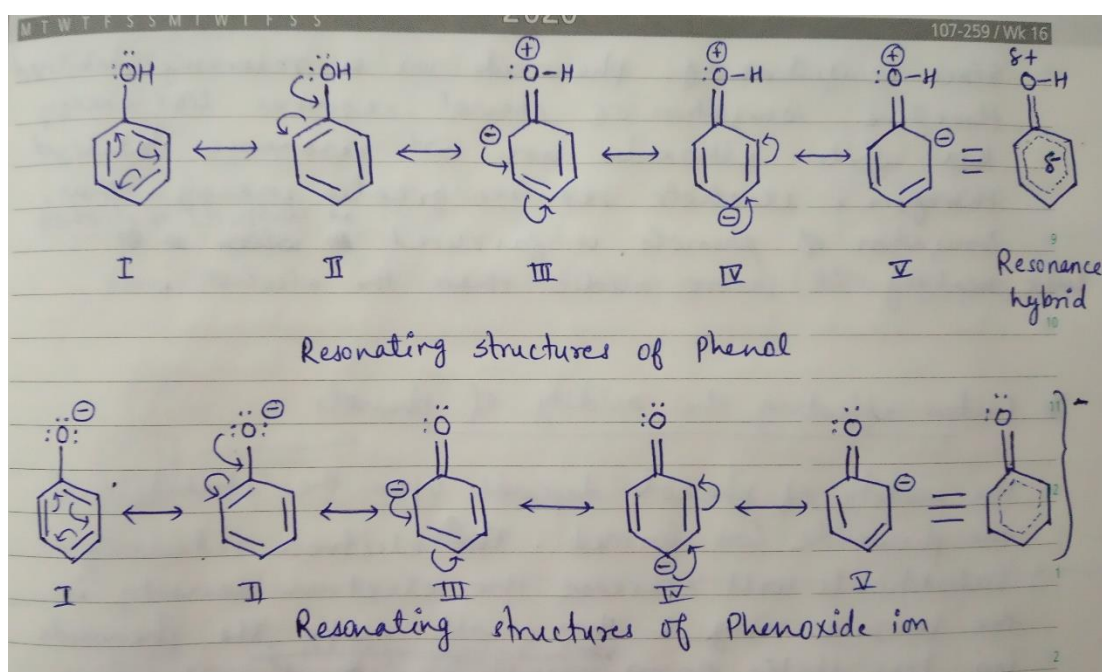
Phenols are more acidic than alcohols this can be explained on the basis of their structures. In alcohols an -OH group is attached to an alkyl group while in phenols -OH group is attached to an aromatic ring. Alcohols on ionization gives alkoxide ions.



Phenols on ionization forms phenoxide ion.



Both phenol and phenoxide ion possess an aromatic ring therefore, they will have resonating structures shown as follows:



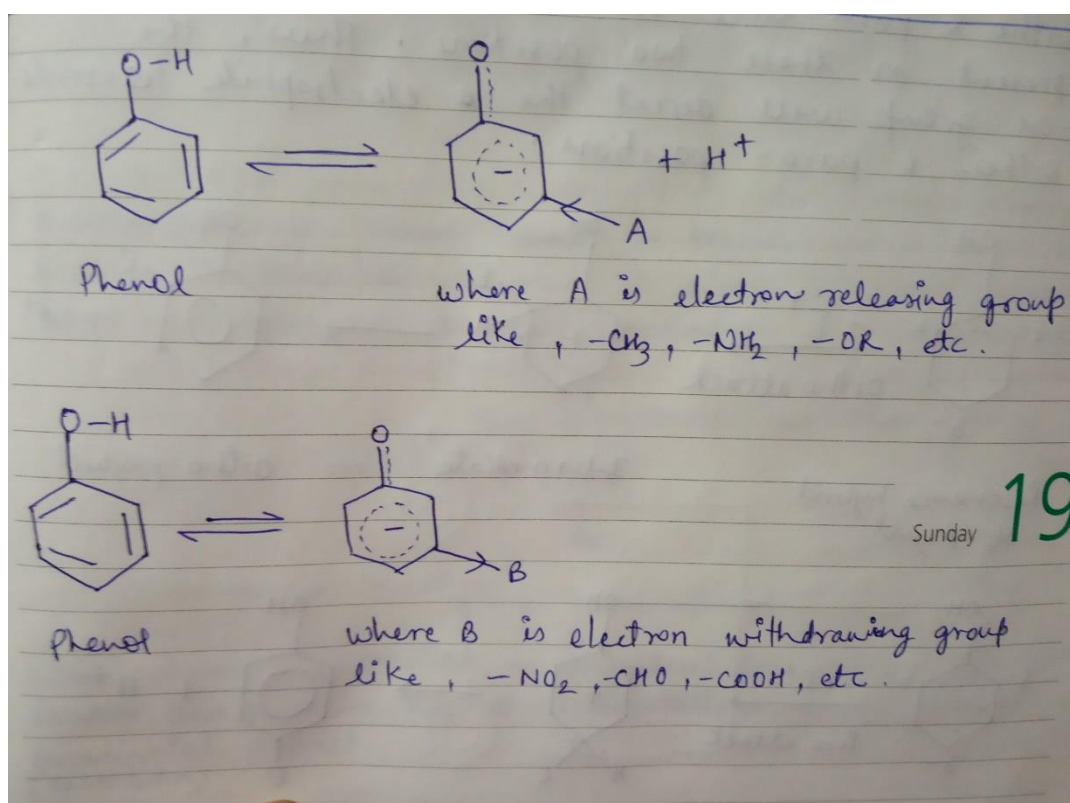
Both phenol and phenoxide ion has five resonating structures among which both have two structures (I and II) in Kekule form. The remaining resonating structures of phenol have charge separation while in the resonating structures of its phenoxide ion there is no charge separation that is, it has only negative charge. Since, the charge separation requires energy therefore, the energy of phenol is greater than that of the phenoxide ion. So, phenol is less stable than the phenoxide ion. Hence, the equilibrium will shift towards right side making the release of a proton easy.

Since, phenoxide ion is resonance stabilized therefore, ionization of phenol requires less energy while alkoxides are not resonance stabilized so, they

require greater energy. Thus, the ionization of phenols is much more favoured than the alcohols that's why phenols are more acidic than the alcohols.

Factors affecting the acidity of phenols

The acidity of phenols depends upon the stability of the phenoxide ion formed. Electron releasing substituents will increase the electron density in the benzene ring and thus decreasing the stability of phenoxide anion which will decrease the acidity of phenol. On the other hand electron withdrawing substituents will pull the electrons from the benzene ring towards itself therefore, it will disperse the negative charge of the phenoxide anion thus increases the stability of the phenoxide anion hence the acidity of phenol.



Reactions of Phenols

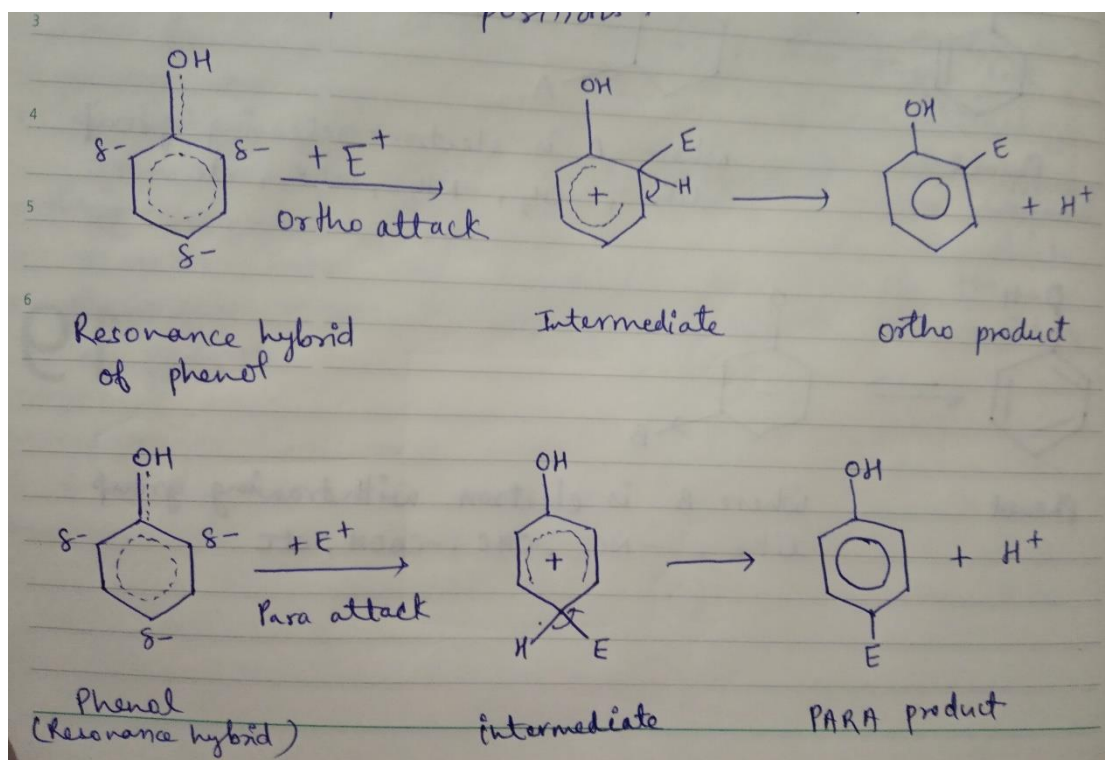
Directive influence of - OH group and electrophilic substitution reactions

As it is seen from the resonating structures of phenol that the non-bonding electrons of the - OH group is delocalized over the whole molecule thus, making it an electron rich system hence activating the ring system towards electrophilic substitution.

From the resonating structures of phenol, it can be seen that the electron rich positions are the ortho and para since the negative charge is present on these

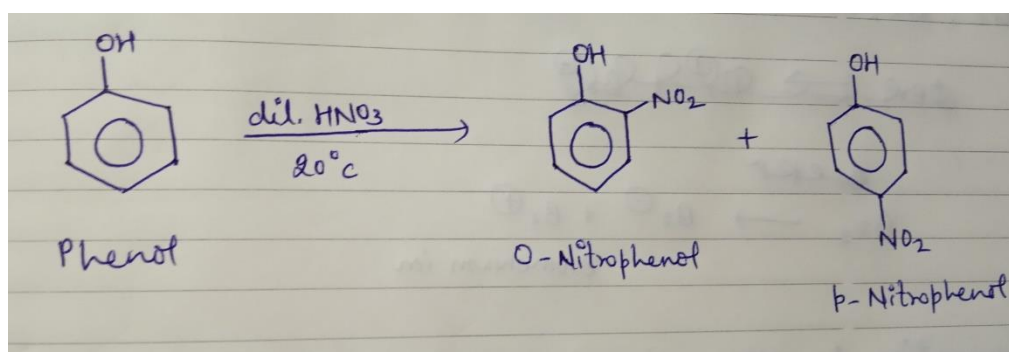
References: Organic Chemistry, R.T. Morrison, R.N. Boyd and S.K. Bhattacharjee, Pearson, 7th Edition and advance Organic Chemistry, Bahl and Bahl, S.Chand & Company Ltd.

two positions. Hence, the -OH group of phenol will direct the electrophile towards the ortho and para positions.



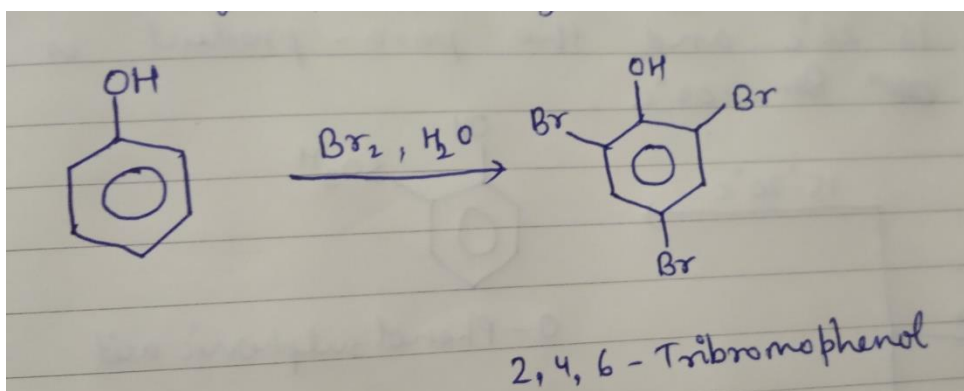
Phenol undergoes the following electrophilic substitution reactions:

- 1) Nitration: when phenols are treated with dilute nitric acid, ortho- and para- nitrophenols are formed. Here, the nitronium ion acts as an electrophile.

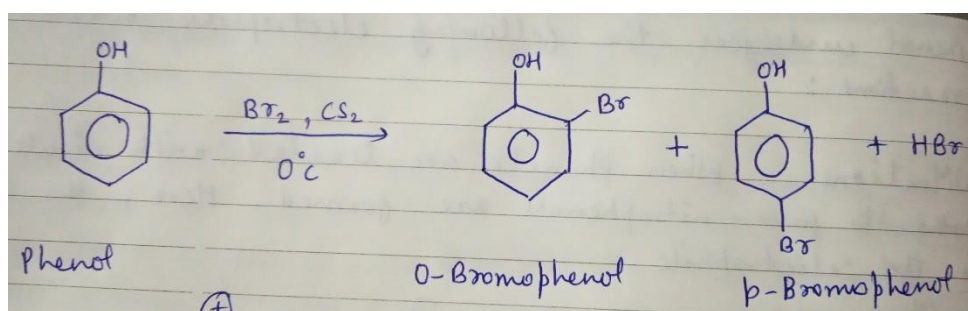


- 2) Halogenation: When phenol is treated with excess of aqueous solution of bromine it gives 2,4,6-tribromophenol. Since, -OH group is a good activator.

References: Organic Chemistry, R.T. Morrison, R.N. Boyd and S.K. Bhattacharjee, Pearson, 7th Edition and advance Organic Chemistry, Bahl and Bahl, S.Chand & Company Ltd.



When phenols are treated with calculated amount of bromine dissolved in CS_2 , it gives mono brominated product.



Here, bromonium ion (Br^+) acts as an electrophile.

- 3) Sulphonation: When phenols are treated with concentrated sulphuric acid it gives ortho and para phenol sulphonic acids. Here, HSO_3^+ ion acts as an electrophile.

Phenols give ortho- substituted product at low temperature that is at 15° - 20°C and para product is formed at 100°C .

