

PHENOLS

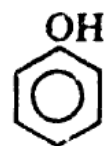
Department of Pharmaceutical Chemistry

Dr. Husam Hamza

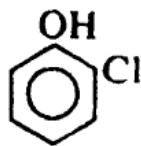


Structure and nomenclature

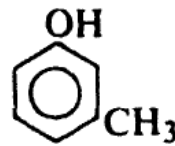
- Phenols are compounds of the general formula **ArOH**, where Ar is phenyl, substituted phenyl, or one of the other aryl groups (e.g., naphthyl)
- Phenols differ from alcohols in having the -OH group attached directly to an aromatic ring
- generally named as derivatives of the simplest member of the family, **phenol**, The **methylphenols** are given the special name of **cresols**



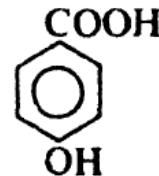
Phenol



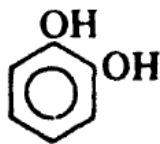
o-Chlorophenol



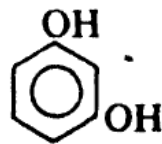
m-Cresol



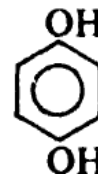
p-Hydroxybenzoic acid



Catechol.



Resorcinol



Hydroquinone



Salicylic acid

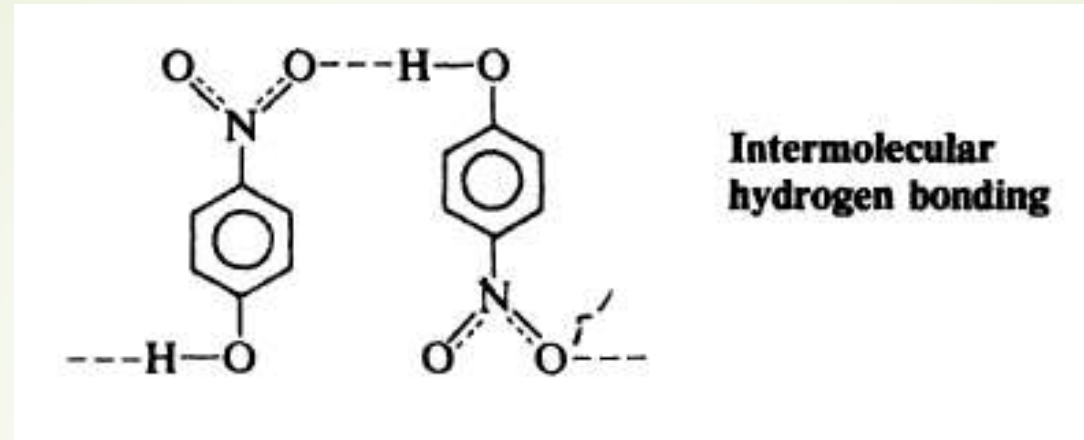
Physical properties

- The simplest phenols are liquids or low-melting solids
- because of hydrogen bonding, they have quite high boiling points
- somewhat soluble in water (9 g per 100 g of water), presumably because of hydrogen bonding with the water; most other phenols are essentially insoluble in water.

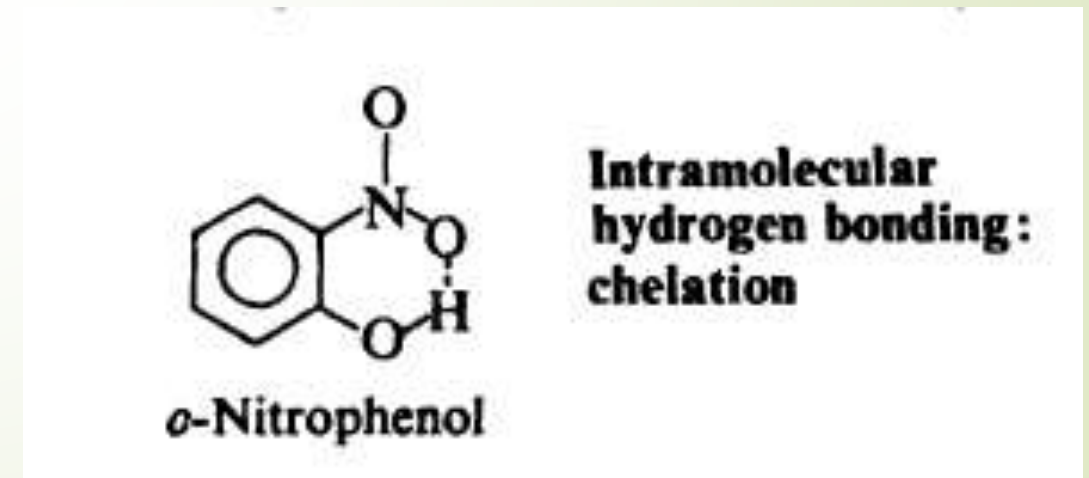
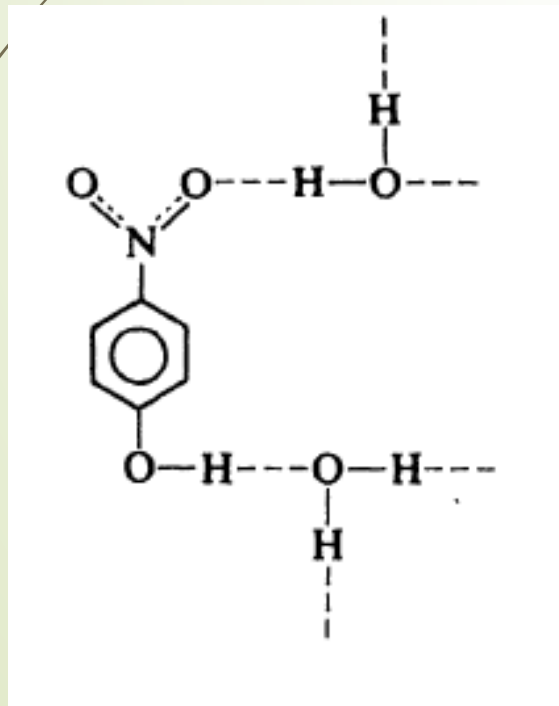
PROPERTIES OF THE NITROPHENOLS

	B.p., °C at 70 mm	Solub., g/100 g H ₂ O	
<i>o</i> -Nitrophenol	100	0.2	Volatile in steam
<i>m</i> -Nitrophenol	194	1.35	Non-volatile in steam
<i>p</i> -Nitrophenol	<i>dec.</i>	1.69	Non-volatile in steam

- *m*- and *p*-isomers. They have very high boiling points because of intermolecular hydrogen bonding

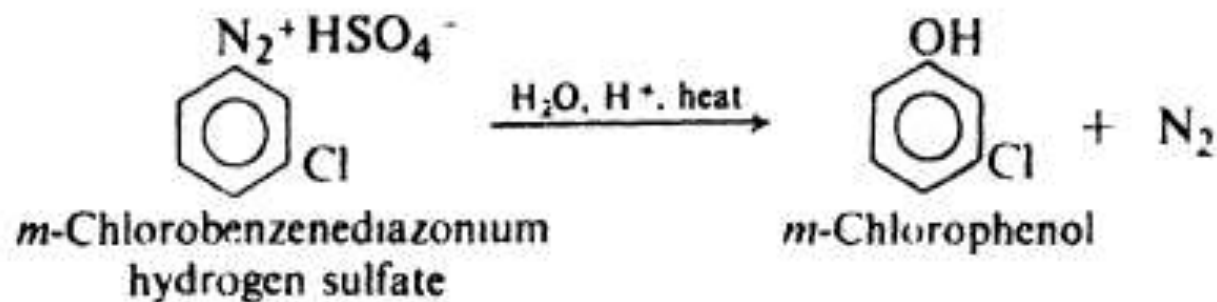


- Their solubility in water is due to hydrogen bonding with water molecules



Preparation

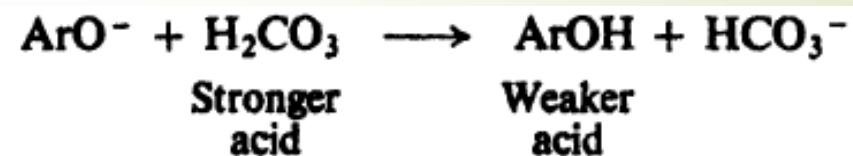
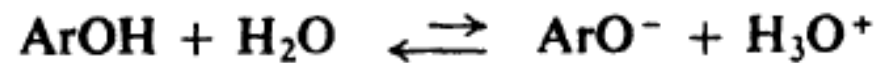
1. Hydrolysis of diazonium salts.



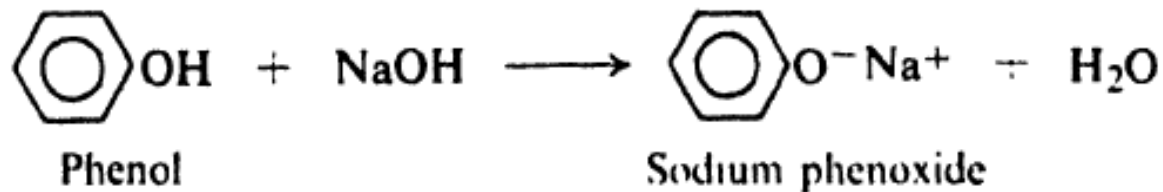
Reactions

1. Acidity. Salt formation.

- Phenols are converted into their salts by aqueous hydroxides, but not by aqueous bicarbonates

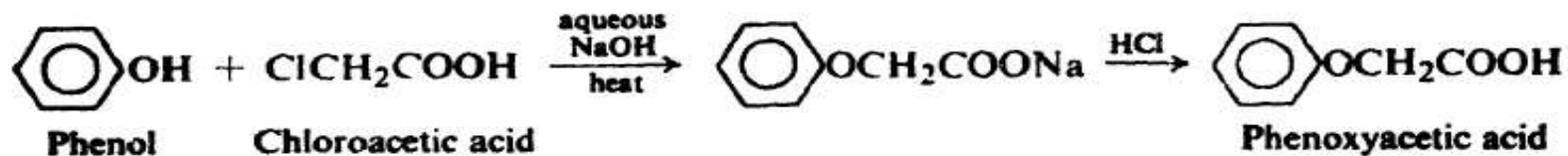
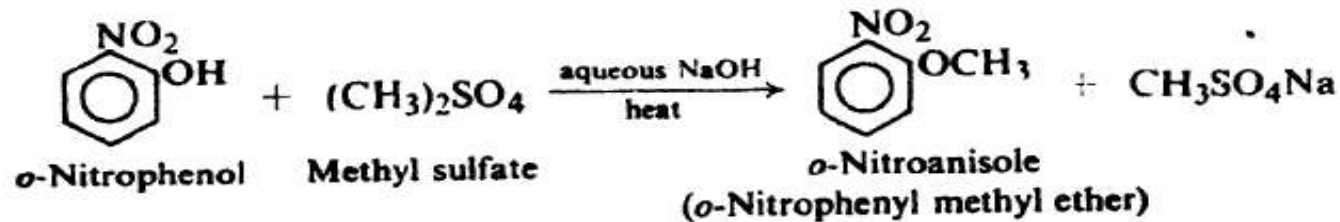
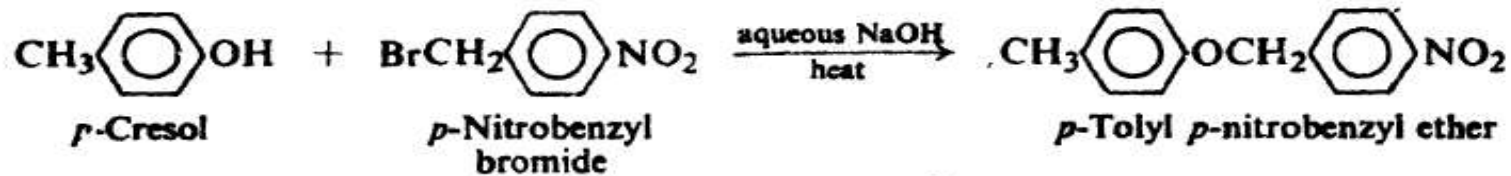
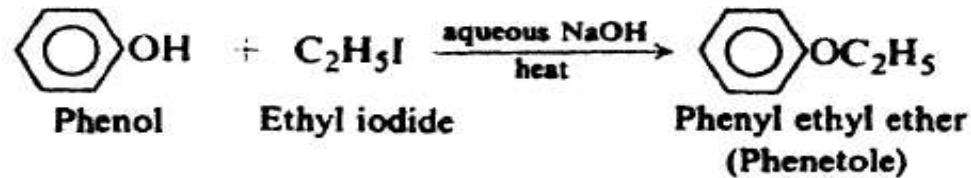
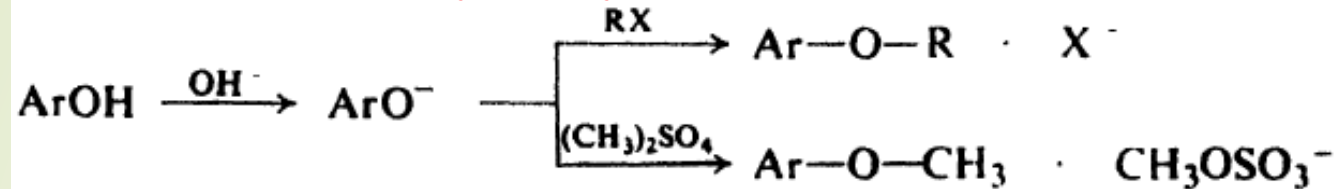


- Phenols stronger acids than water, but considerably weaker acids than the carboxylic acids



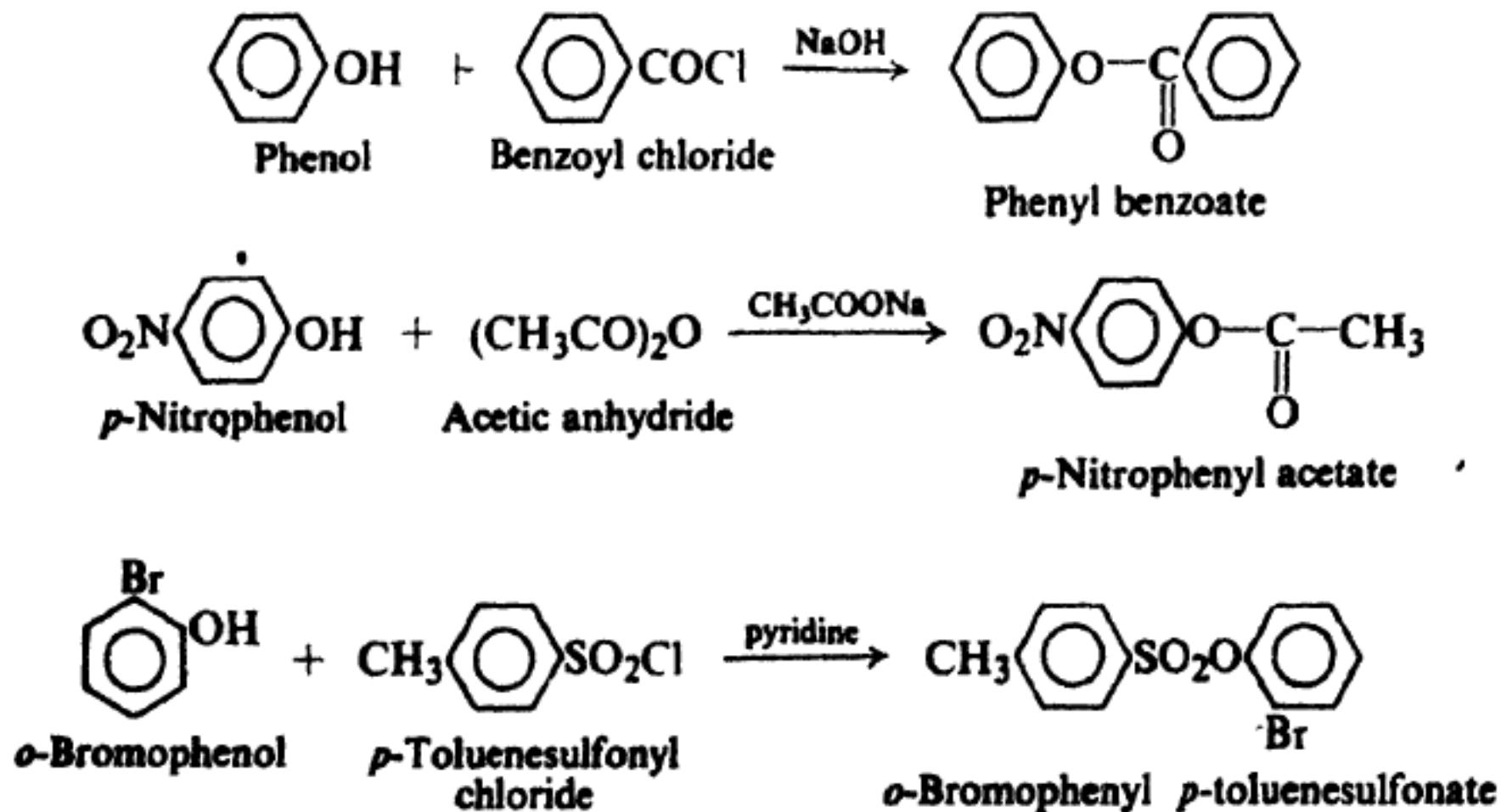
2. Ether formation. Williamson synthesis.

- It can be used to make unsymmetrical ethers as well as symmetrical ethers, and aryl alkyl ethers



3. Ester formation.

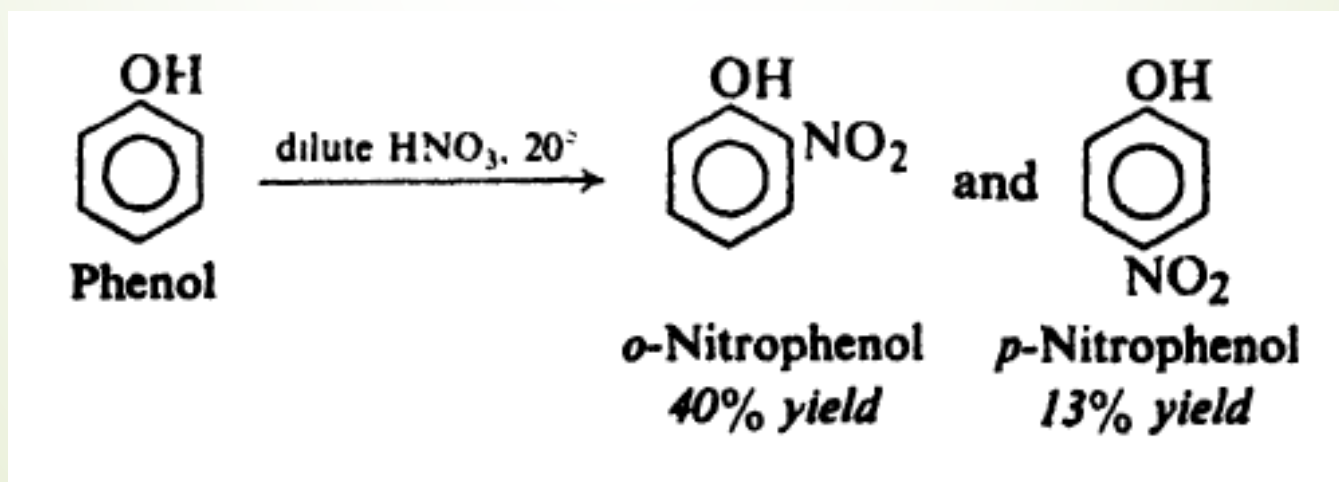
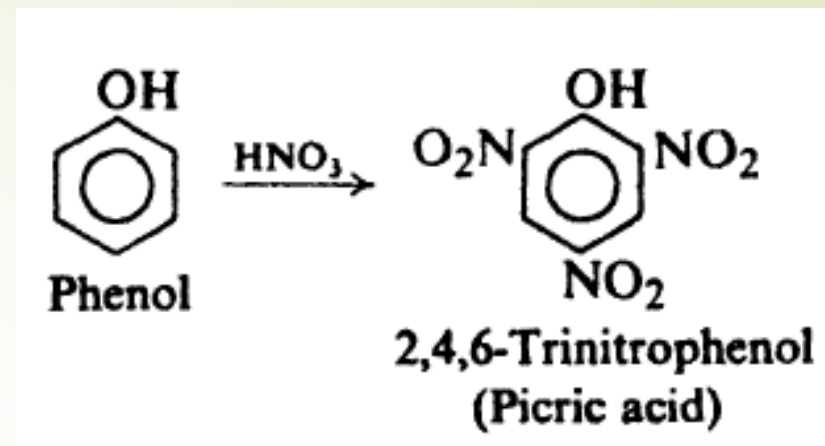
- Phenols are usually converted into their esters by the action of acids, acid chlorides, or anhydrides



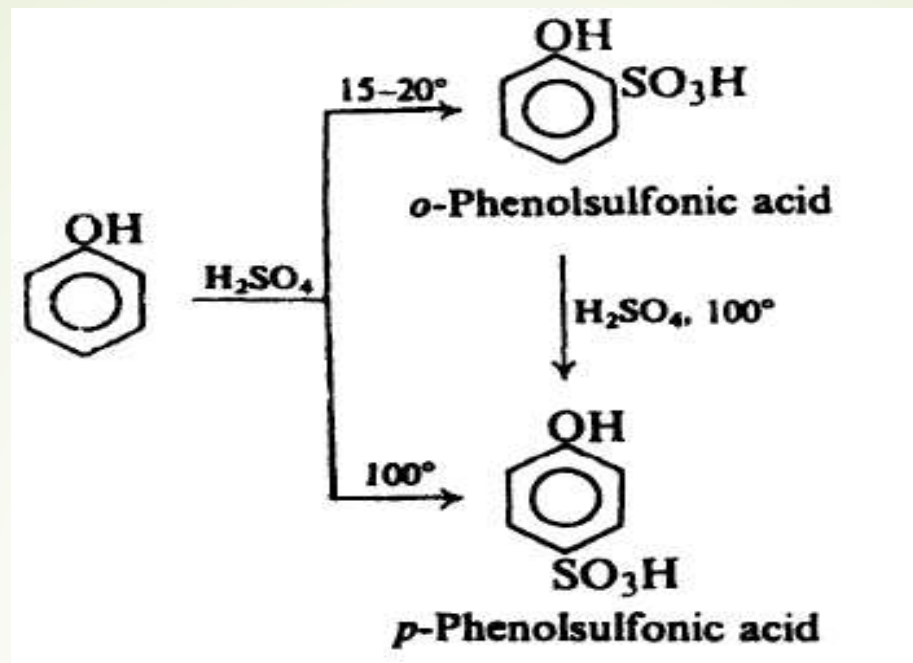
4. Ring substitution.

(a) Nitration.

- Phenol is converted by concentrated nitric acid into 2,4,6-trinitrophenol (picric acid)
- To obtain mononitrophenols, it is necessary to use dilute nitric acid at a low temperature

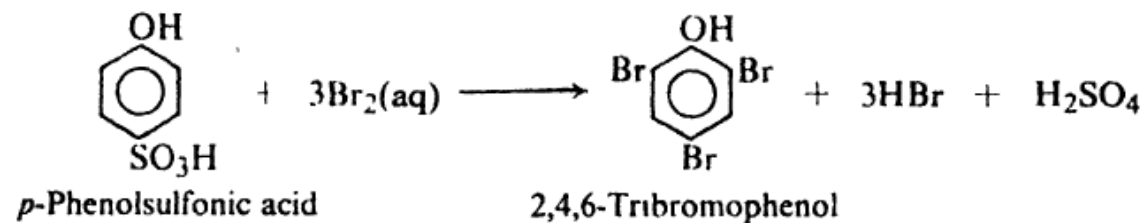
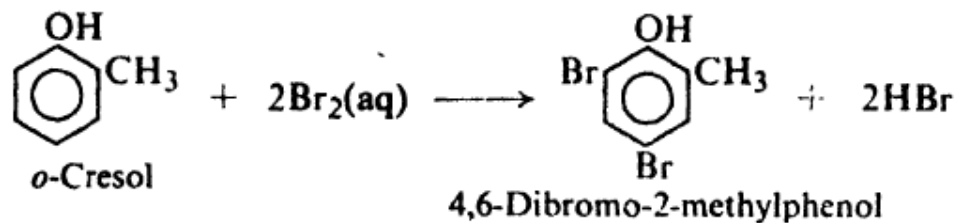


(b) Sulfonation.

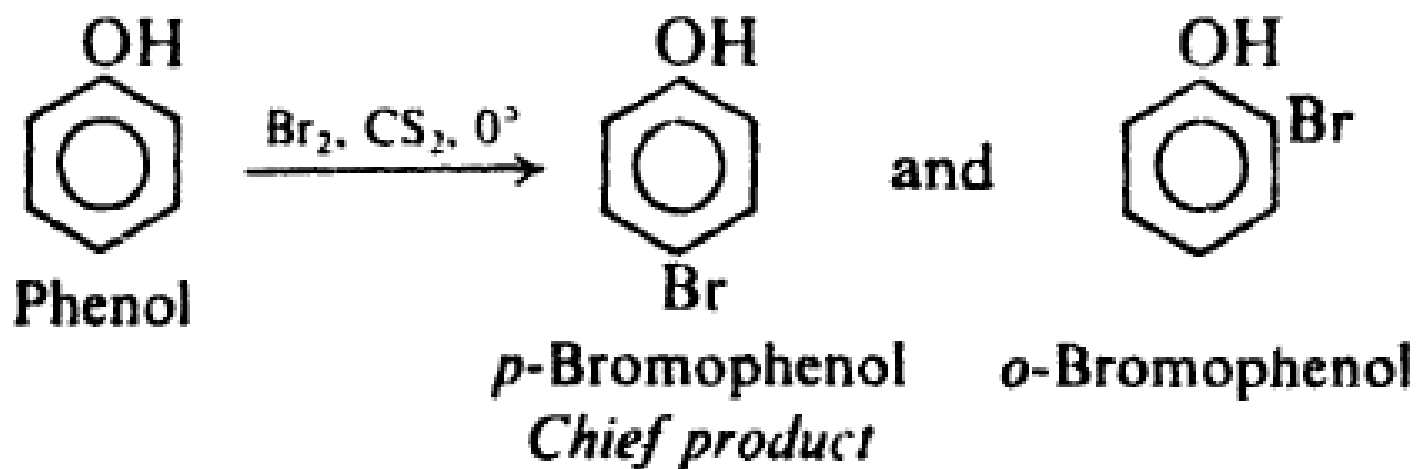


(c) Halogenation.

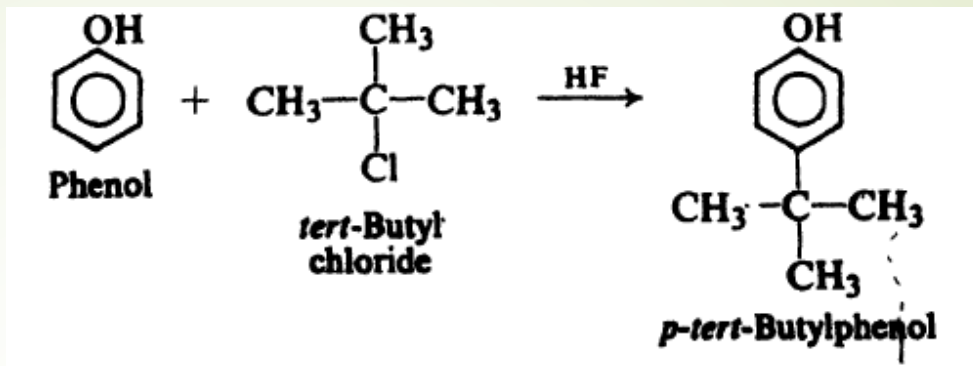
- Treatment of phenols with aqueous solutions of bromine results in replacement of every hydrogen ortho or para to the OH group



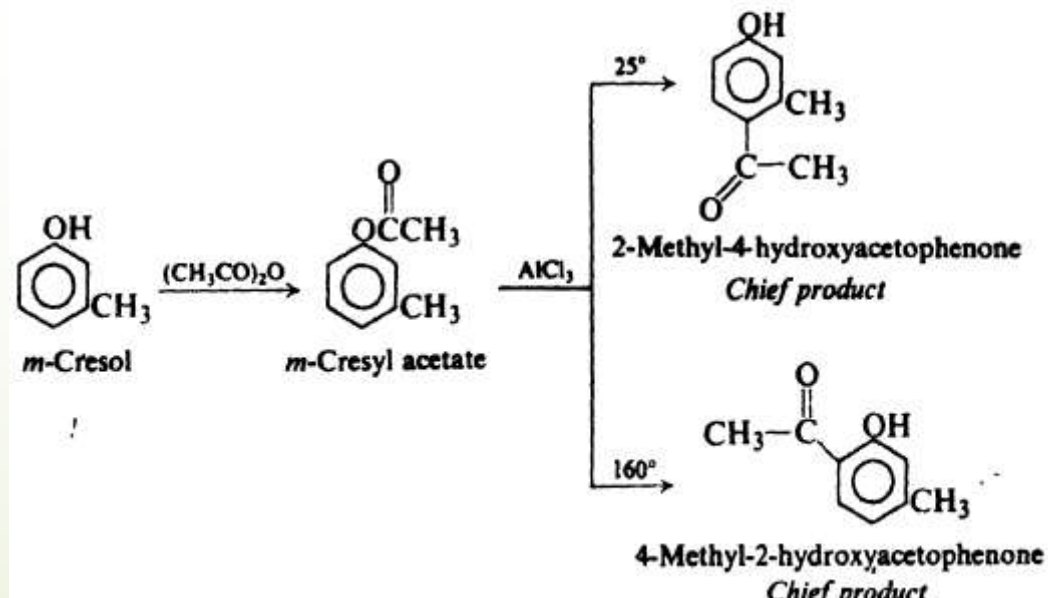
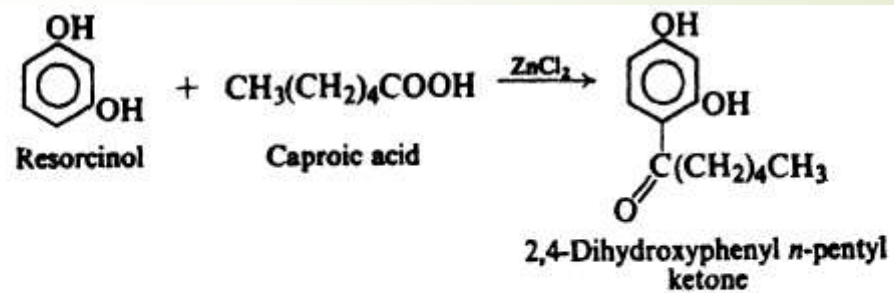
- If halogenation is carried out in a solvent of low polarity, such as chloroform, carbon tetrachloride, or carbon disulfide, reaction can be limited to monohalogenation. For example:



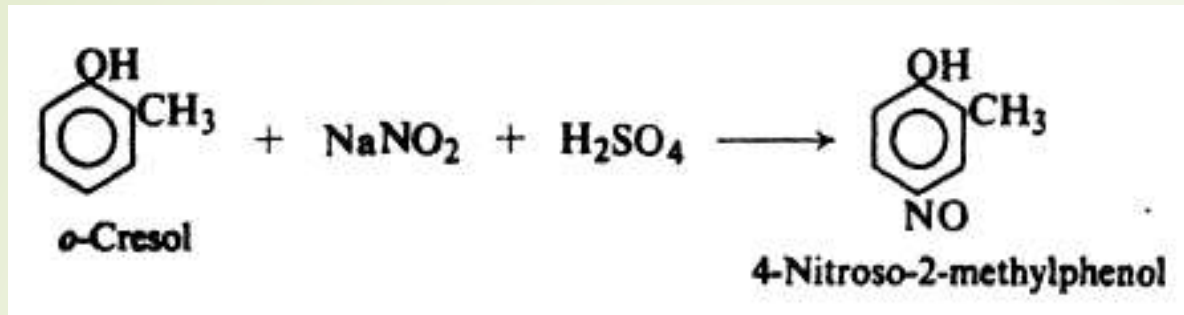
(d) Friedel-Crafts alkylation.



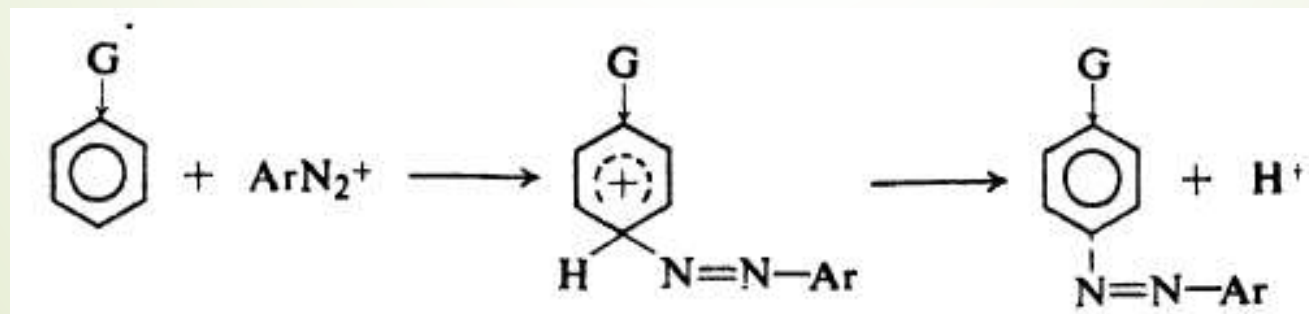
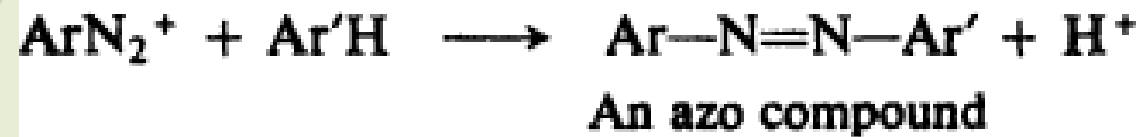
(e) Friedel-Crafts acylation. Fries rearrangement



(f) Nitrosation.



(g) Coupling with diazonium salts.



(h) Carboxylation- Kolbe reaction

- Treatment of the salt of a phenol with carbon dioxide brings about substitution of the carboxyl group, -COOH, for hydrogen of the ring. This reaction is known as the **Kolbe reaction**

