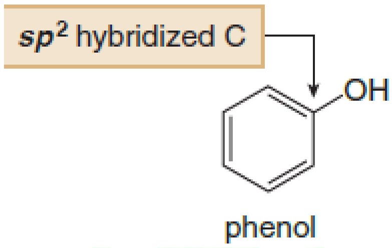
كلية التربية للعلوم الصرفة	الكلية
قسم الكيمياء	القسم
Organic chemistry	المادة باللغة الانجليزية
الكيمياء العضوية	المادة باللغة العربية
المرحلة الثانية	المرحلة الدراسية
د. عمر جمال مهدي العسافي	اسم التدريسي
Phenols	عنوان المحاضرة باللغة الانجليزية
الفينول	عنوان المحاضرة باللغة العربية
الخامسة	رقم المحاضرة
Organic Chemistry 6ed , William H. Brown, Christopher S. Foote, Brent L. Iverson, Eric V. Anslyn, Bruce M. Novak, 2012	المصادر والمراجع
Organic Chemistry 3ed , Janice Gorzynski Smith, 2011	
Organic Chemistry" by Jonathan Clayden, Nick Greeves, and Stuart Warren	

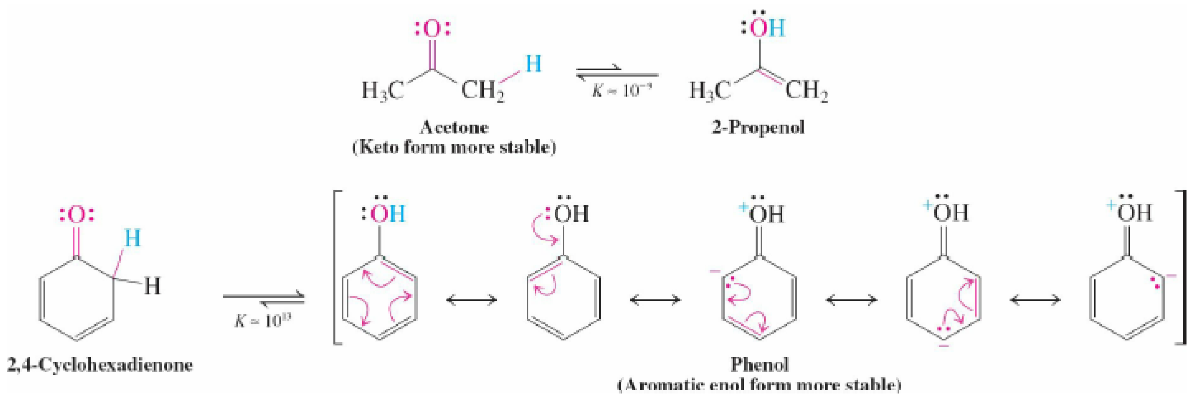
Phenols are compounds that have a hydroxyl group bonded directly to a benzene or benzenoid ring. The parent compound of this group, C6H5OH, called simply phenol, is an important industrial chemical. Many of the properties of phenols are analogous to those of alcohols.



The π system of the benzene ring overlaps with an occupied p orbital on the oxygen atom, a situation resulting in delocalization similar to that found in benzylic anions .

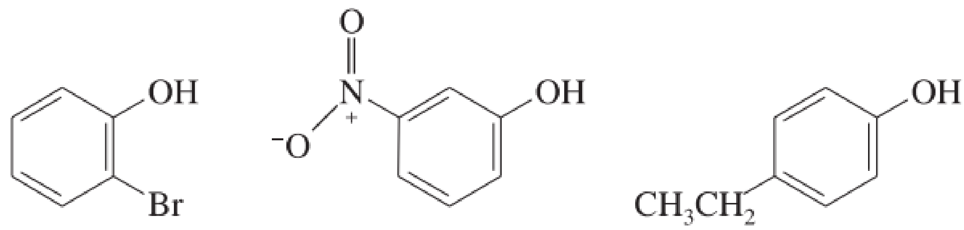
As one result of this extended conjugation, phenols possess an unusual, enolic structure. Recall that enols are usually unstable: They tautomerize easily to the corresponding ketones because of the relatively strong carbonyl bond. Phenols, however, prefer the enol to the keto form because the aromatic character of the benzene ring is preserved.

Keto and Enol Forms of Acetone and Phenol

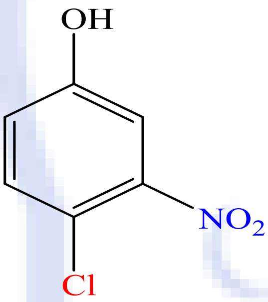


2. Nomenclature

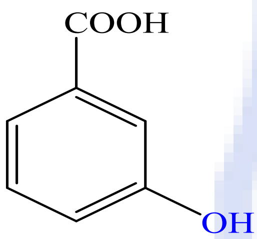
Because the phenol structure involves a benzene ring, the terms ortho (1,2-disubstituted), meta (1,3-disubstituted), and para (1,4-disubstituted) are often used in the common names.



IUPAC name:	2-bromophenol	3-nitrophenol	4-ethylphenol
common name:	*ortho*-bromophenol	*meta*-nitrophenol	*para*-ethylphenol

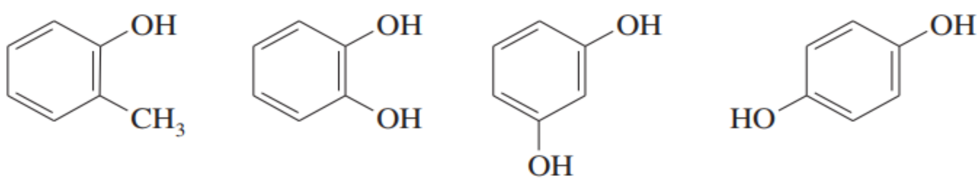


4-chloro-3-nitrophenol



3-hydroxybenzoic acid

The three dihydroxy derivatives of benzene may be named as 1,2-, 1,3-, and 1,4-benzenediol, respectively, but each is more familiarly known by the common name indicated in parentheses below the structures shown here. These common names were permissible IUPAC names prior to the 2004 recommendations.



IUPAC name:	2-methylphenol	benzene-1,2-diol	benzene-1,3-diol	benzene-1,4-diol
common name:	*ortho*-cresol	catechol	resorcinol	hydroquinone

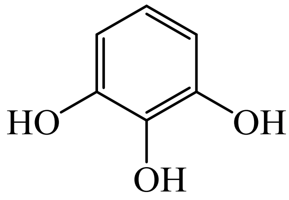
PROBLEM: Write structural formulas for each of the following compounds:

(a) Pyrogallol (1,2,3-benzenetriol)

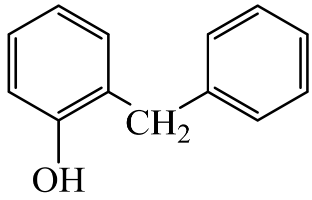
(b) *o*-Benzylphenol

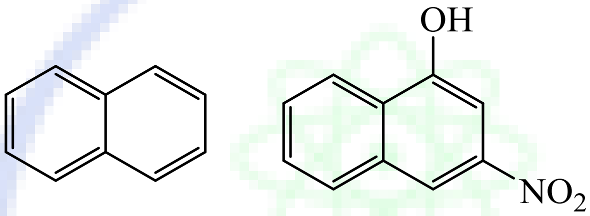
(c) 3-Nitro-1-naphthol

Solution:-

a) 

(1,2,3-benzenetriol)
Pyrogallol

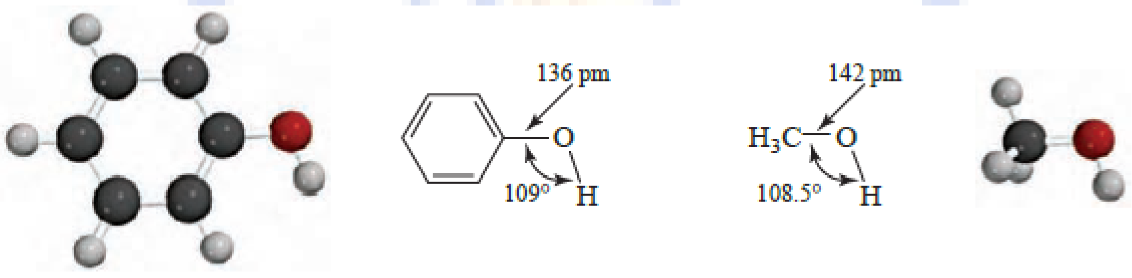
b) 

c) 

3-Nitro-1-naphthol

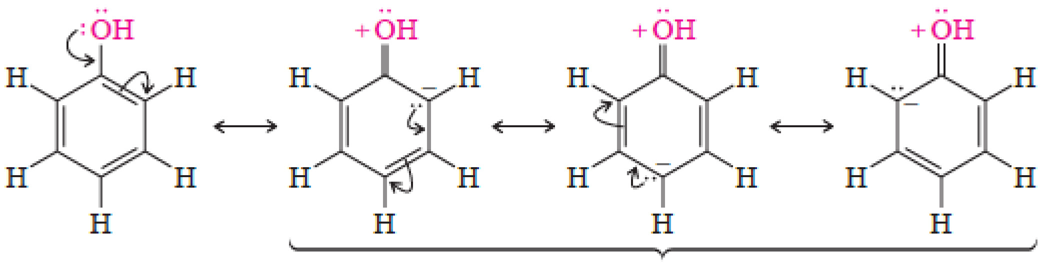
3. Structure and Bonding

Phenol is planar, with angle of 109, almost the same as the tetrahedral angle and not much different from the 108.5 angle of methanol:



Phenol Methanol

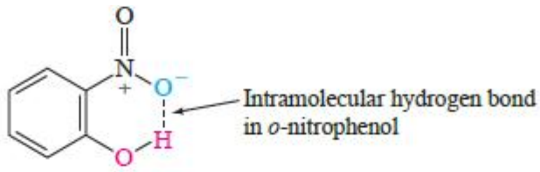
bonds to sp2-hybridized carbon are shorter than those to sp3-hybridized carbon, and the case of phenols is no exception. The carbon–oxygen bond distance in phenol is slightly less than that in methanol. In resonance terms, the shorter carbon–oxygen bond distance in phenol is attributed to the partial double-bond character that results from conjugation of the unshared electron pair of oxygen with the aromatic ring.

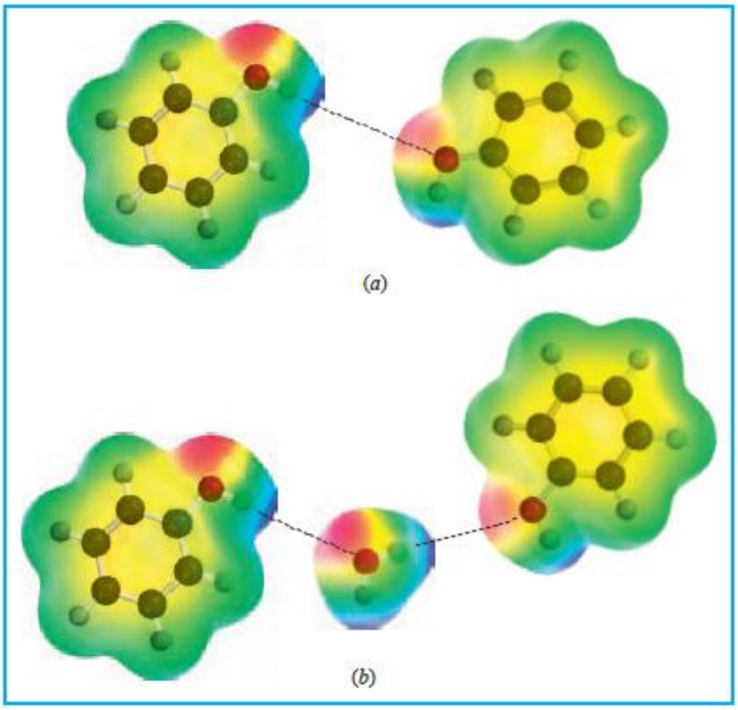


Many of the properties of phenols reflect the polarization implied by the contributing structures. The hydroxyl oxygen is less basic, and the hydroxyl proton more acidic, in phenols than in alcohols. Electrophilic aromatic substitution in phenols is much faster than in benzene, indicating that the ring, especially at the positions ortho and para to the hydroxyl group, is relatively "electron-rich."

4. Physical Properties

The physical properties of phenols are strongly influenced by the hydroxyl group, which permits phenols to form hydrogen bonds with other phenol molecules and with water . Thus, phenols have higher melting points and boiling points and are more soluble in water than arenes and aryl halides of comparable molecular weight.



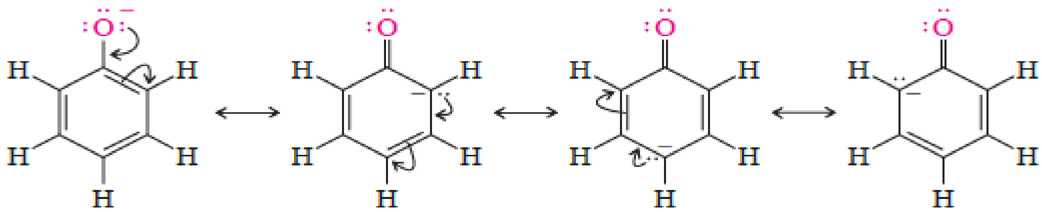


(a) A hydrogen bond between two phenol molecules; (b) hydrogen bonds between water and phenol molecules.

5. Acidity of Phenols

The most characteristic property of phenols is their acidity. Phenols are more acidic than alcohols but less acidic than carboxylic acids. Recall that carboxylic acids have pKa's of approximately 5, whereas the pKa's of alcohols are in the 16–20 range. The pKa for most phenols is about 10. To help us understand why phenols are more acidic than alcohols.

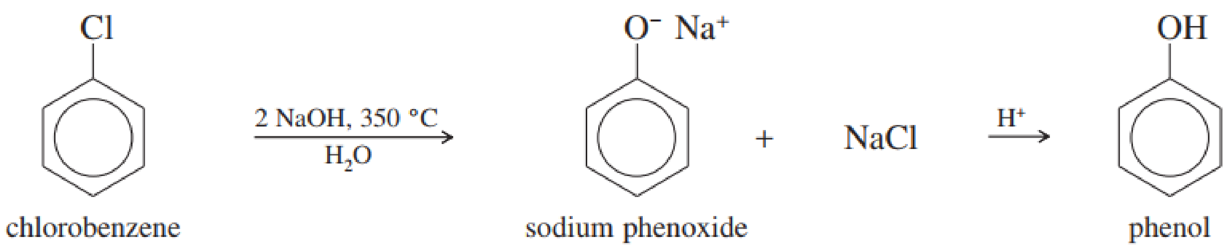
Electron delocalization in phenoxide is represented by resonance among the various contributing structures:



6. Preparation of phenols

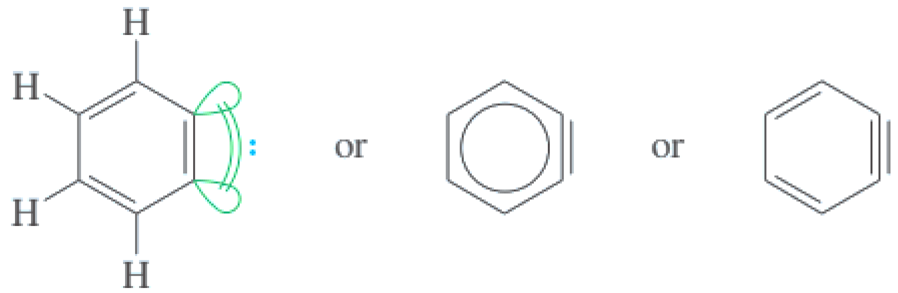
Haloarenes undergo substitution through benzyne intermediates

The addition–elimination mechanism for nucleophilic aromatic substitution requires strong electron-withdrawing substituents on the aromatic ring. Under extreme conditions, however, unactivated halobenzenes react with strong bases. For example, a commercial synthesis of phenol (the "Dow process") involves treatment of chlorobenzene with sodium hydroxide and a small amount of water in a pressurized reactor at 350 °C:

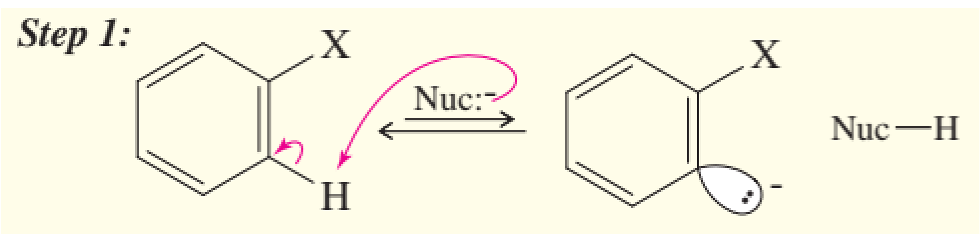


Benzyne Mechanism: Elimination–Addition

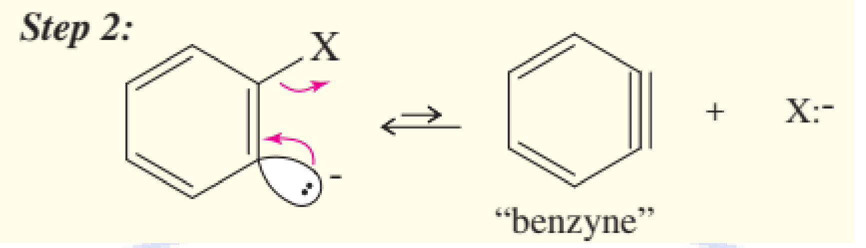
Benzyne: A reactive intermediate in some nucleophilic aromatic substitutions, benzyne is benzene with two hydrogen atoms removed. It can be drawn with a highly strained triple bond in the sixmembered ring



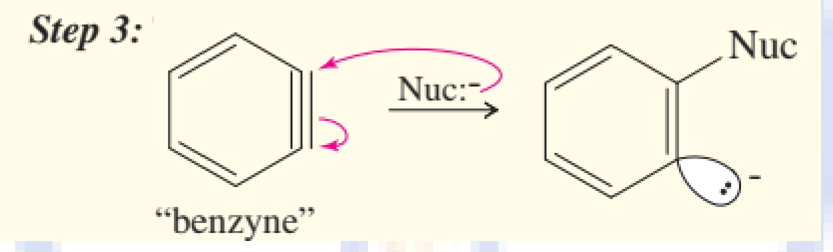
Step 1: Deprotonation adjacent to the leaving group gives a carbanion.



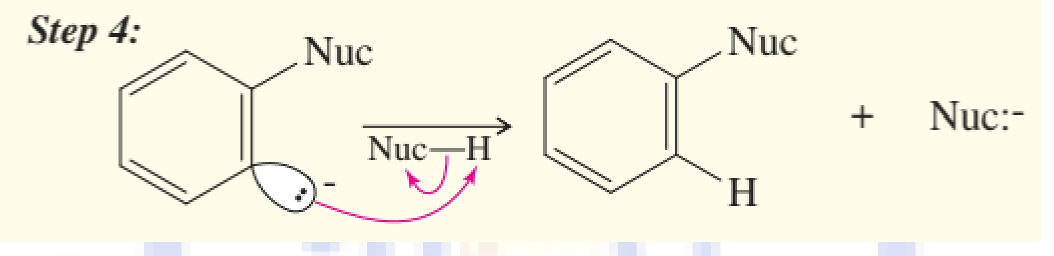
Step 2: The carbanion expels the leaving group to give a "benzyne" intermediate.



Step 3: The nucleophile attacks at either end of the reactive benzyne triple bond.

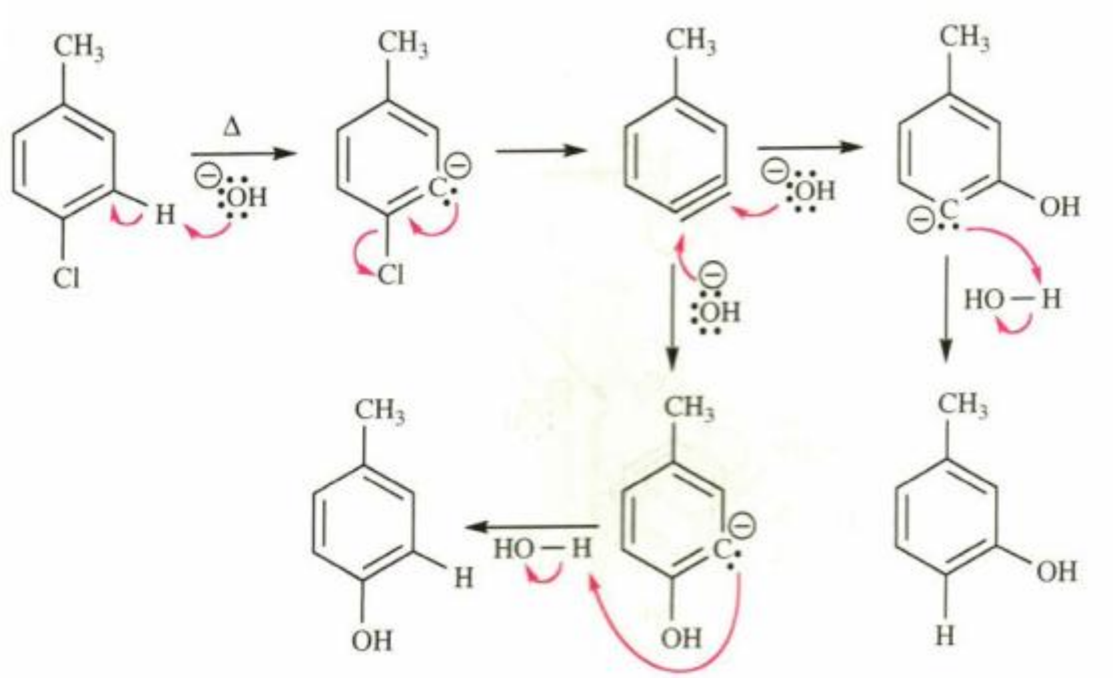


Step 4: Reprotonation gives the product.



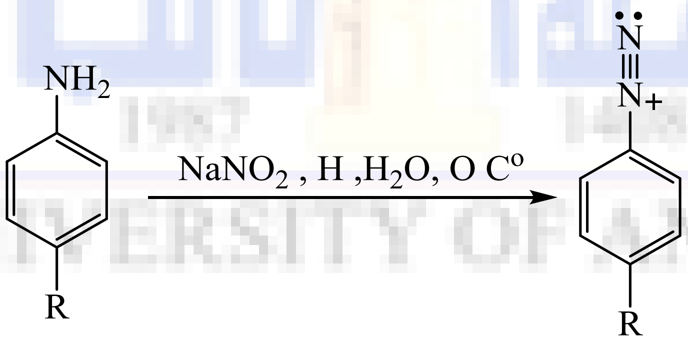
PROBLEM : Propose a mechanism that shows why p-chlorotoluene reacts with sodium hydroxide at 350 °C to give a mixture of p-cresol and m-cresol.

Solution:



Phenols are produced from arenediazonium salts

primary anilines are attacked by cold nitrous acid, in a reaction called diazotization, to give relatively stable, isolable, although still reactive arenediazonium salts. Compared to their alkanediazonium counterparts, these species enjoy resonance stabilization and are prevented from undergoing immediate N2 loss by the high energy of the resulting aryl cations



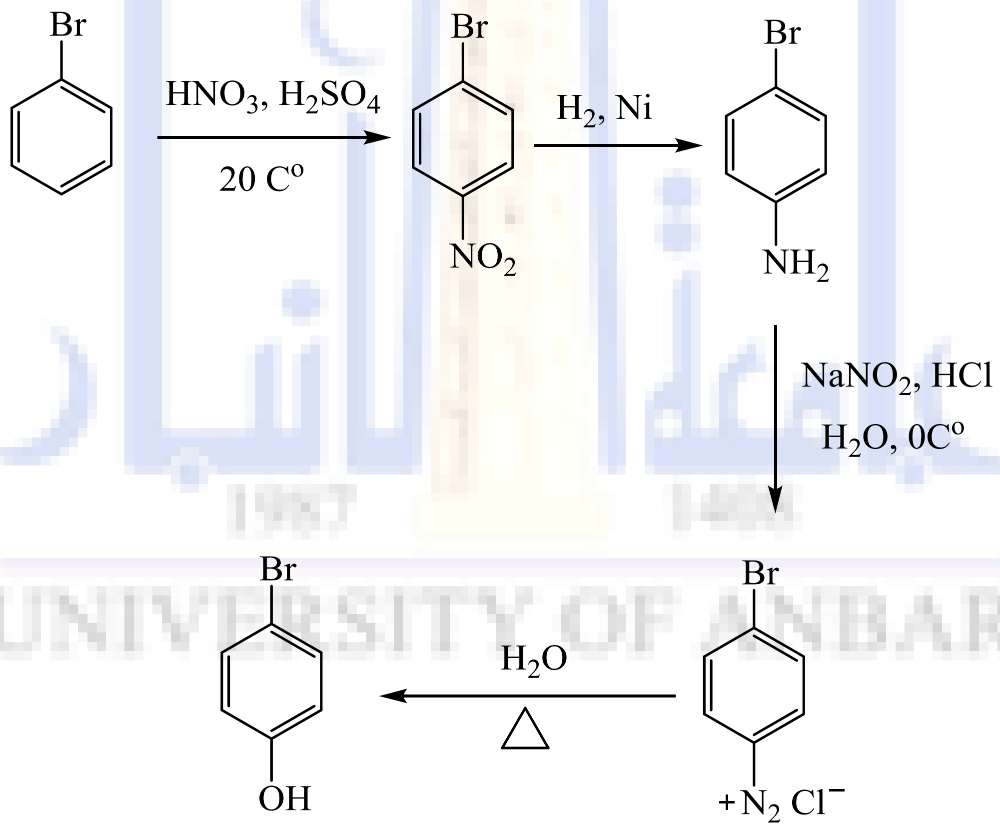
Arenediazonium ion

When arenediazonium ions are gently heated in water, nitrogen is evolved and the resulting aryl cations are trapped extremely rapidly by the solvent to give phenols.

Decomposition of Arenediazonium Salts in Water to Give Phenols

Problem: Starting with bromobenzene, what you need to prepare is parabromophenol.

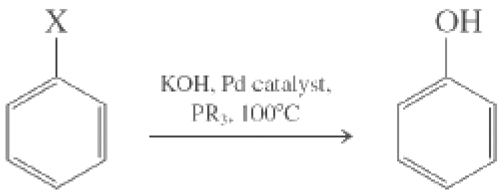
Solution:

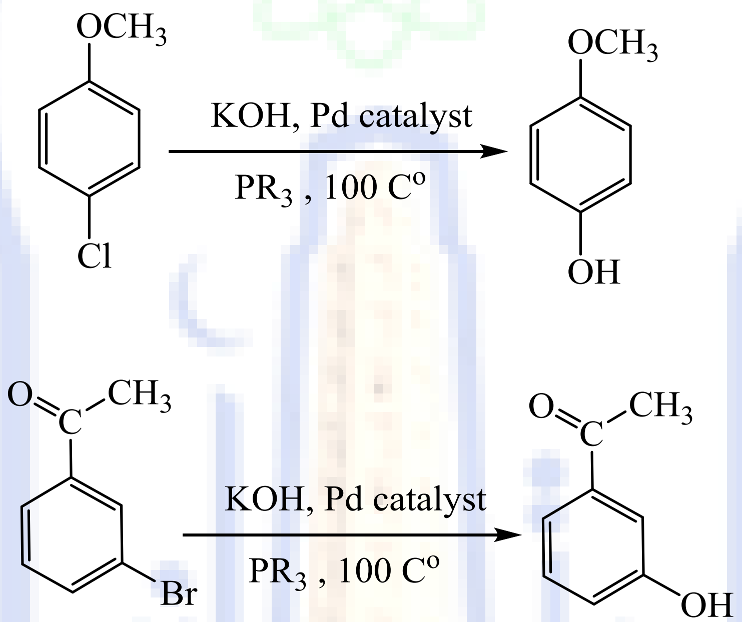


Phenols can be made from haloarenes by Pd catalysis

halobenzenes are resilient to reaction with hydroxide, they enter into such nucleophilic displacements in the presence of Pd salts and added phosphine ligands PR_3.

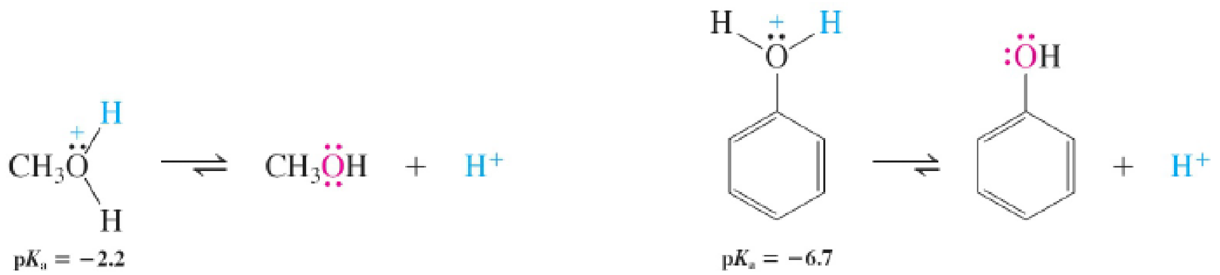
Pd-Catalyzed Phenol Synthesis from Haloarenes



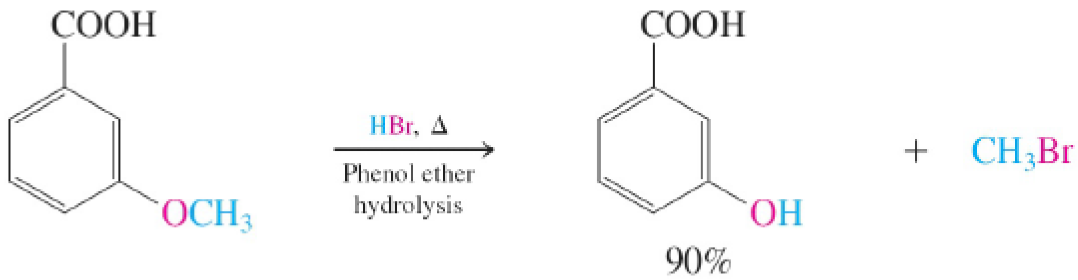


7. Alcohol Chemistry of Phenols

The phenol hydroxy group undergoes several of the reactions of alcohols, such as protonation, Williamson ether synthesis, and esterification. The oxygen in phenols is only weakly basic Phenols are not only acidic but also weakly basic. They (and their ethers) can be protonated by strong acids to give the corresponding phenyloxonium ions. Thus, as with the alkanols, the hydroxy group imparts amphoteric character.

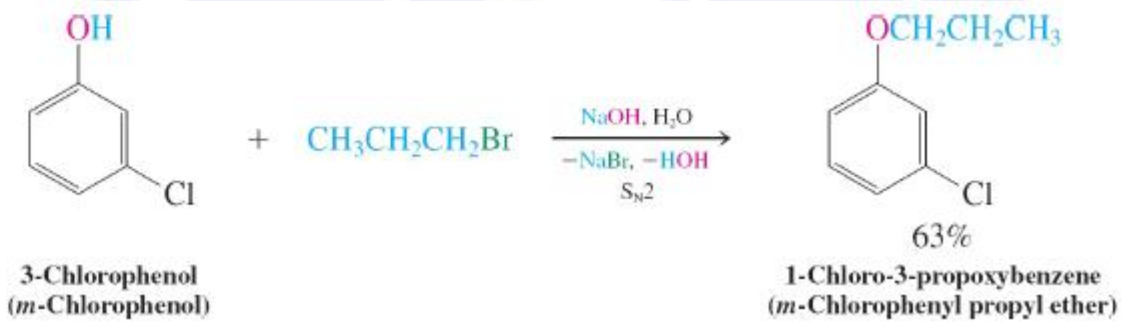


The phenyl– oxygen bond in phenols is very difficult to break. However, after protonation of alkoxybenzenes, the bond between the alkyl group and oxygen is readily cleaved in the presence of nucleophiles like Br− or I− (e.g., from HBr or HI) to give phenol and the corresponding haloalkane.



Alkoxybenzenes are prepared by Williamson ether synthesis

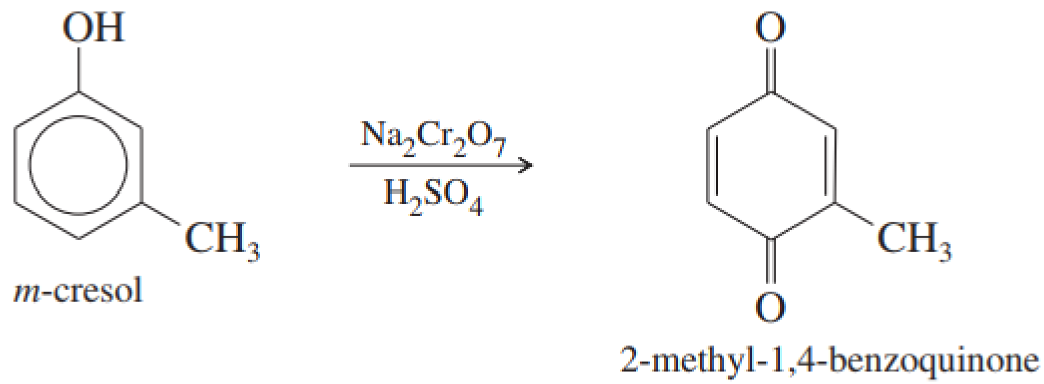
The Williamson ether synthesis permits easy preparation of many alkoxybenzenes. The phenoxide ions obtained by deprotonation of phenols are good nucleophiles. They can displace the leaving groups from haloalkanes and alkyl sulfonates



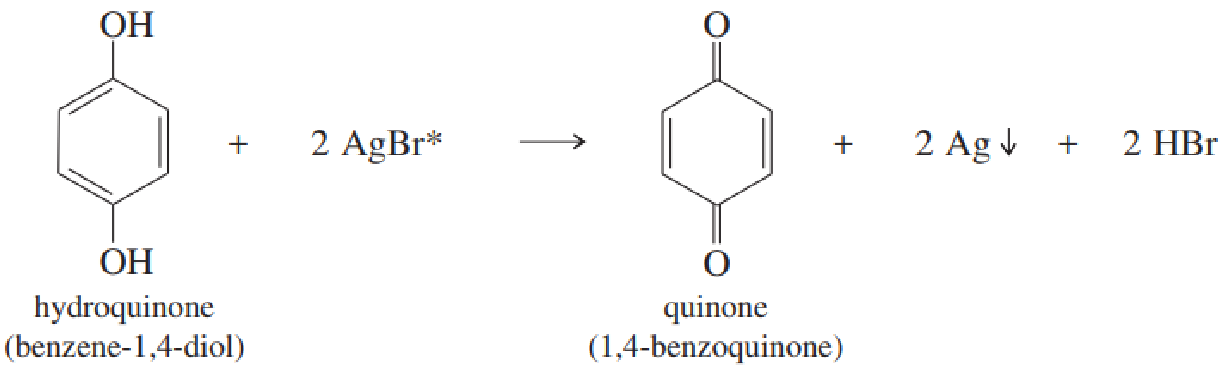
8.Reactions of phenols

Oxidation of Phenols to Quinones

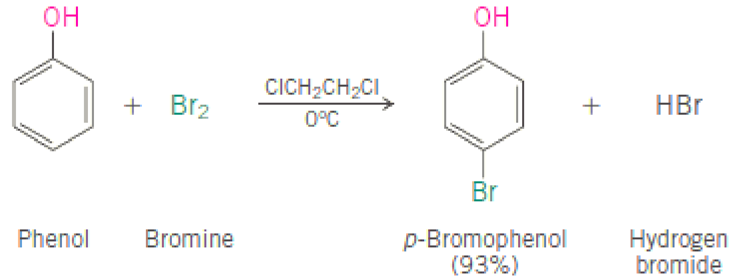
Phenols undergo oxidation, but they give different types of products from those seen with aliphatic alcohols. Chromic acid oxidation of a phenol gives a conjugated 1,4-diketone called a quinone. In the presence of air, many phenols slowly autoxidize to dark mixtures containing quinones.



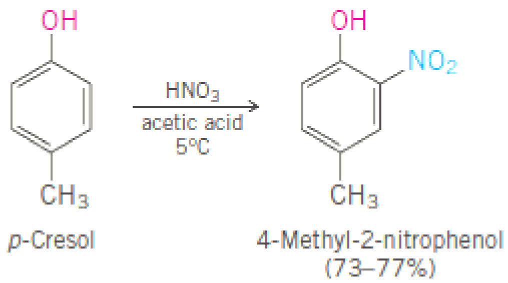
Hydroquinone (benzene-1,4-diol) is easily oxidized because it already has two oxygen atoms bonded to the ring. Even very weak oxidants like silver bromide (AgBr) can oxidize hydroquinone. Silver bromide is reduced to black metallic silver in a lightsensitive reaction: Any grains of silver bromide that have been exposed to light (AgBr*) react faster than unexposed grains .



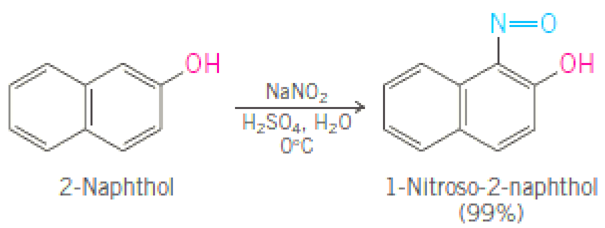
Halogenation Bromination and chlorination of phenols occur readily even in the absence of a catalyst. Substitution occurs primarily at the position para to the hydroxyl group. When the para position is blocked, ortho substitution is observed.



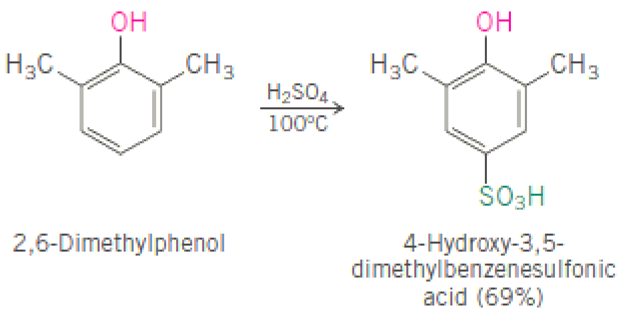
Nitration Phenols are nitrated on treatment with a dilute solution of nitric acid in either water or acetic acid. It is not necessary to use mixtures of nitric and sulfuric acids, because of the high reactivity of phenols.



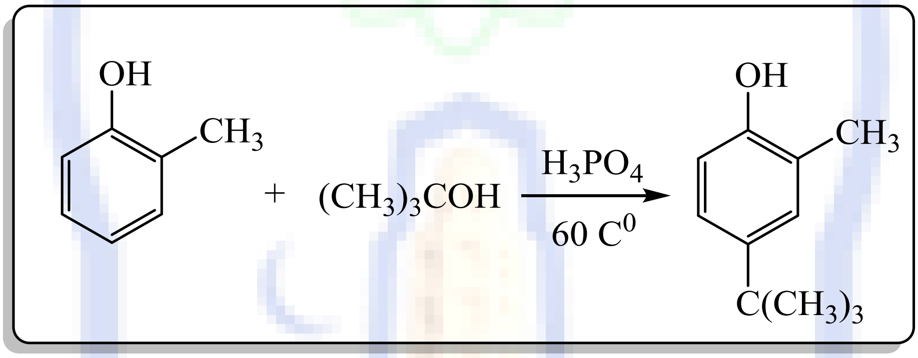
Nitrosation On acidification of aqueous solutions of sodium nitrite, the nitrosyl cation $:N\equiv\overset{+}{O}:$ is formed, which is a weak electrophile and attacks the strongly activated ring of a phenol. The product is a nitroso phenol.



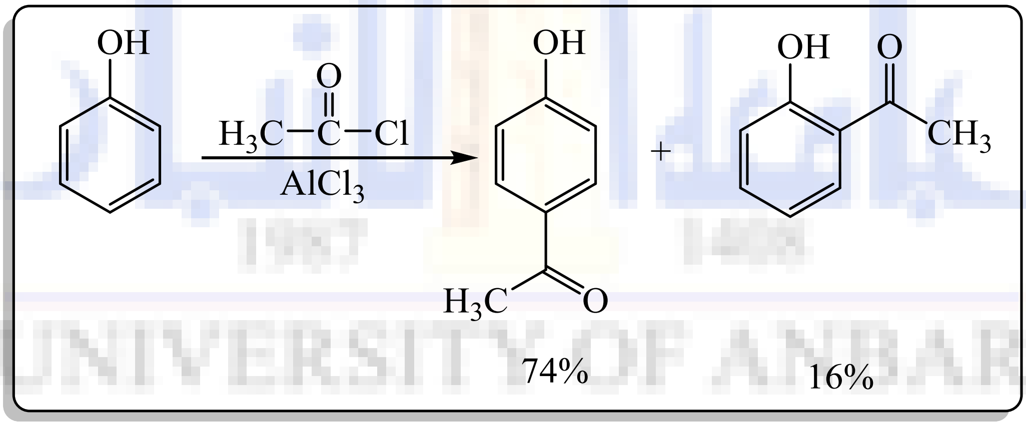
Sulfonation Heating a phenol with concentrated sulfuric acid causes sulfonation of the ring.



Friedel−Crafts alkylation Alcohols in combination with acids serve as sources of carbocations. Attack of a carbocation on the electron-rich ring of a phenol brings about its alkylation



Friedel−Crafts acylation In the presence of aluminum chloride, acyl chlorides and acid anhydrides acylate the aromatic ring of phenols.



PROBLEM

Identify the product in each case.

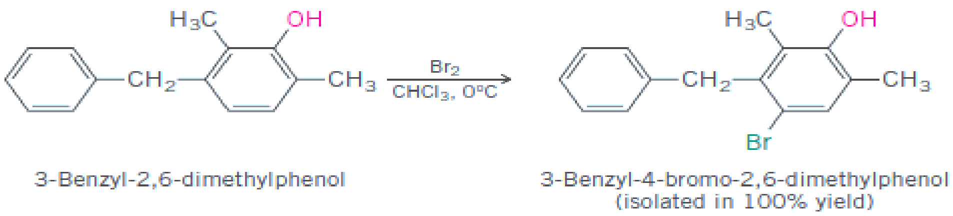
(a) 3-Benzyl-2,6-dimethylphenol treated with bromine in chloroform

(b) 4-Bromo-2-methylphenol treated with 2-methylpropene and sulfuric acid

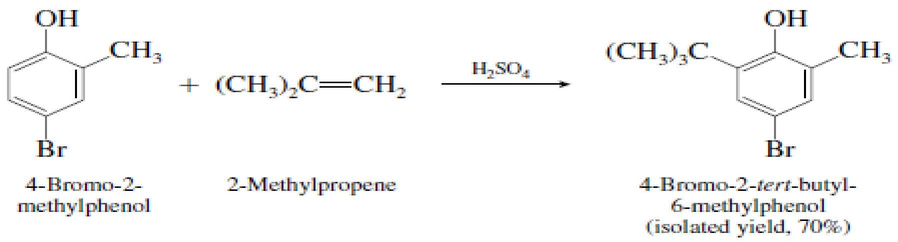
(c) 2-Isopropyl-5-methylphenol (thymol) treated with sodium nitrite and dilute hydrochloric acid
(d) p-Cresol treated with propanoyl chloride and aluminum chloride

Solution:

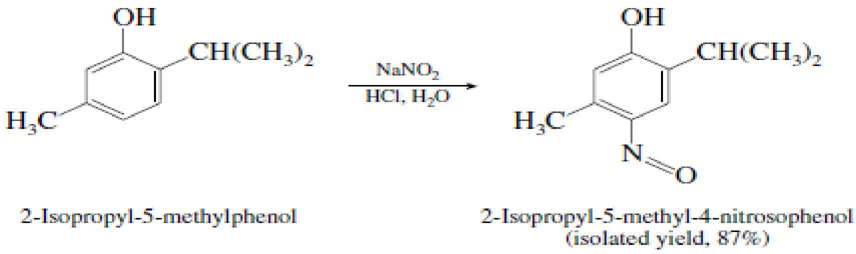
a)



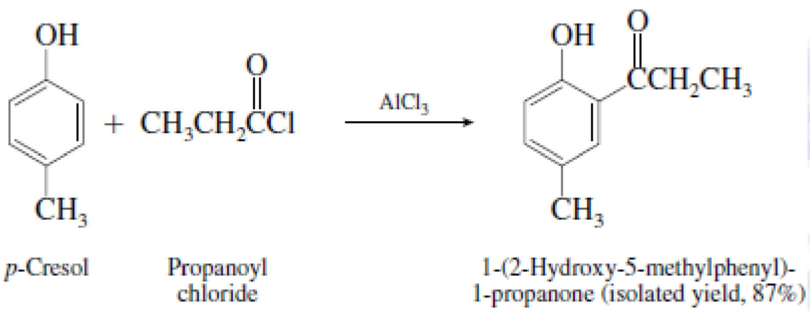
b)



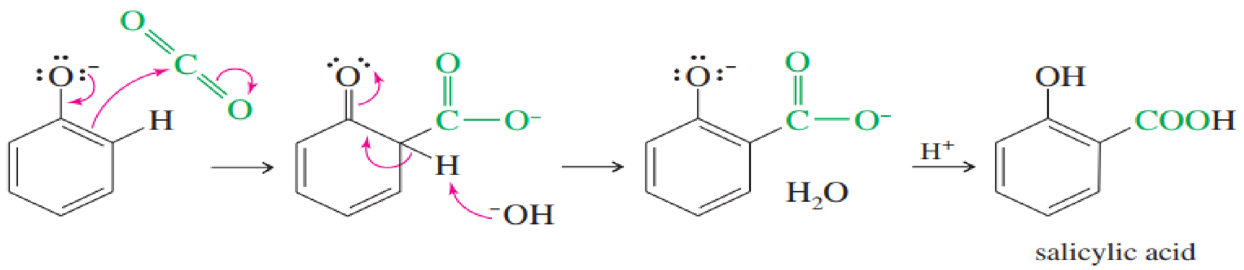
c)



d)

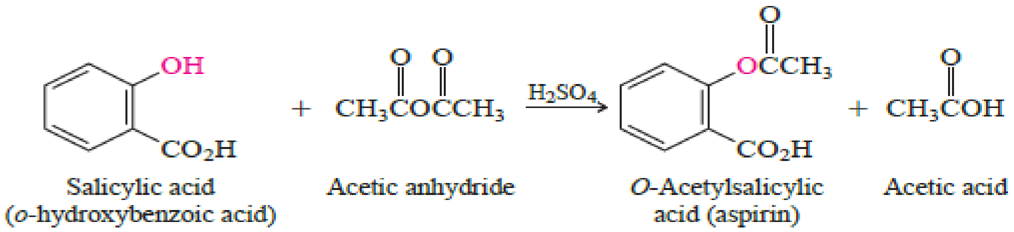


Phenoxide ions are so strongly activated that they undergo electrophilic aromatic substitution with carbon dioxide, a weak electrophile. The carboxylation of phenoxide ion is an industrial synthesis of salicylic acid, which is then converted to aspirin



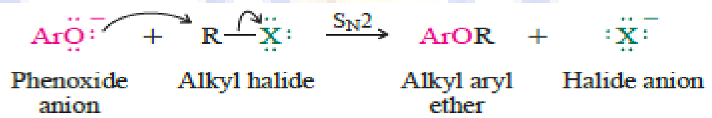
Carboxylation of Phenols: Aspirin and the Kolbe–Schmitt Reaction

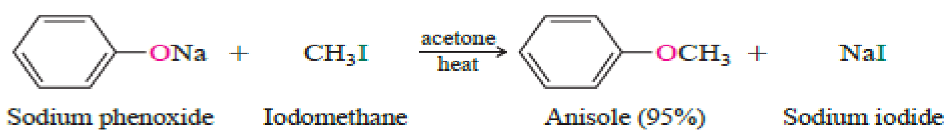
The best known aryl ester is O-acetylsalicylic acid, better known as aspirin. It is prepared by acetylation of the phenolic hydroxyl group of salicylic acid:



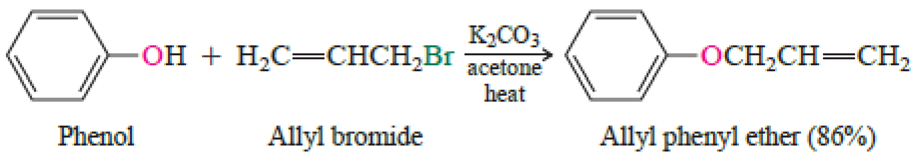
Preparation of Aryl Ethers

Aryl ethers are best prepared by the Williamson method . Alkylation of the hydroxyl oxygen of a phenol takes place readily when a phenoxide anion reacts with an alkyl halide.





As the synthesis is normally performed, a solution of the phenol and alkyl halide is simply heated in the presence of a suitable base such as potassium carbonate:



9. Identification of Phenols – Ferric Chloride Test

Compounds with a phenol group will form a blue, violet, purple, green, or red-brown color upon addition of aqueous ferric chloride according the substation groups. This reaction can be used as a test for phenol groups.