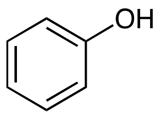
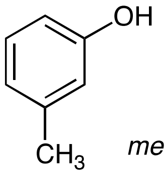
Chapter 23
Phenols

Nomenclature

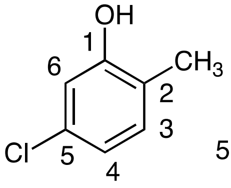
The –OH group takes precedence as the parent phenol.



phenol

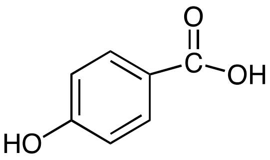


meta-cresol



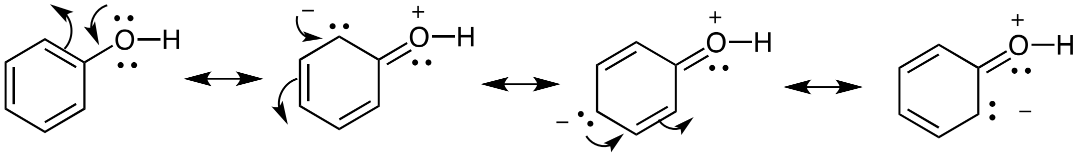
5-chloro-2-methylphenol

Carboxyl and acyl groups take precedence over the –OH group.

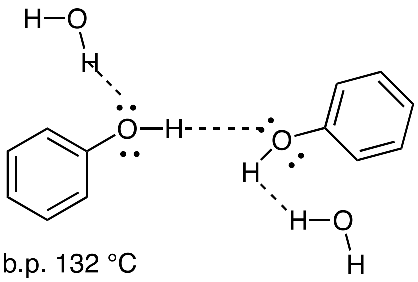


p-hydroxybenzoic acid

The –OH group is a strong electron-donating group through the lone pair.

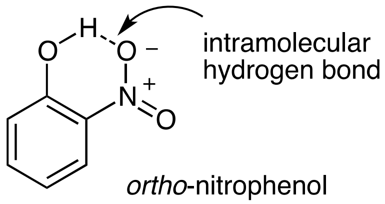


Phenol can hydrogen bond with H_2O and other phenol groups.

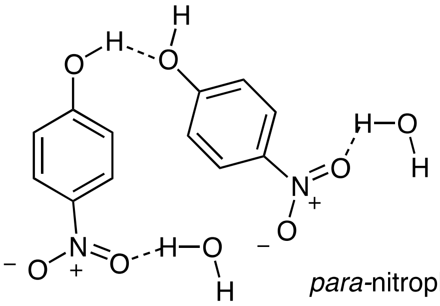


b.p. 132 °C

Ortho-nitrophenol can engage in intramolecular hydrogen bonding and has a lower boiling point and lower water solubility than either the *meta* or *para*-isomers because there is less intermolecular hydrogen bonding and less hydrogen bonding with water.

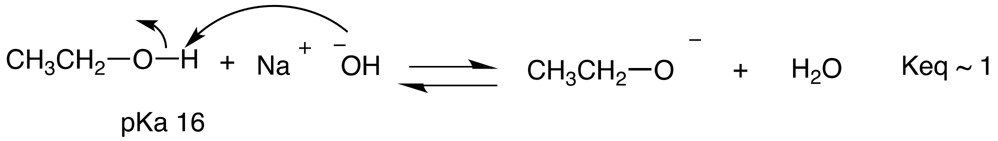


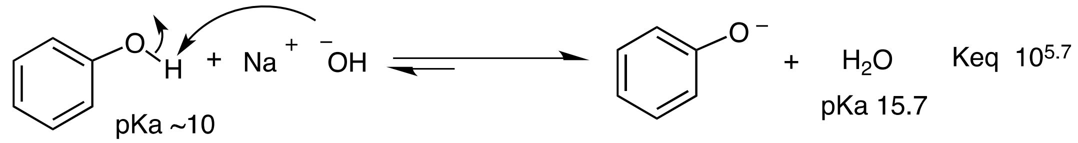
ortho-nitrophenol



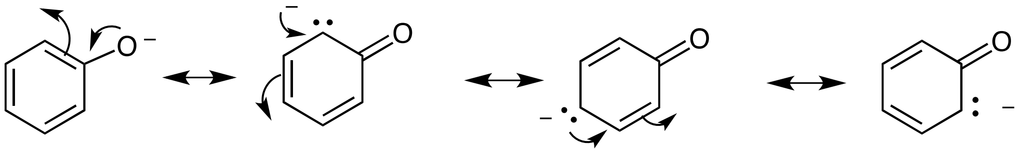
para-nitrophenol

Phenols are much more acidic than regular alcohols. It is completely deprotonated by sodium hydroxide.

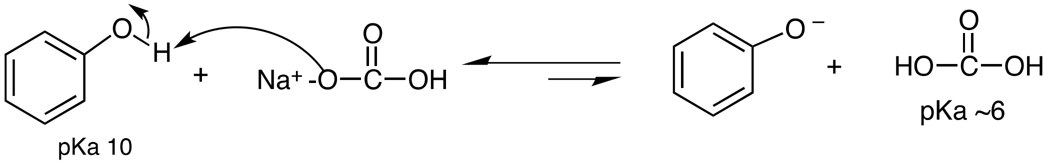




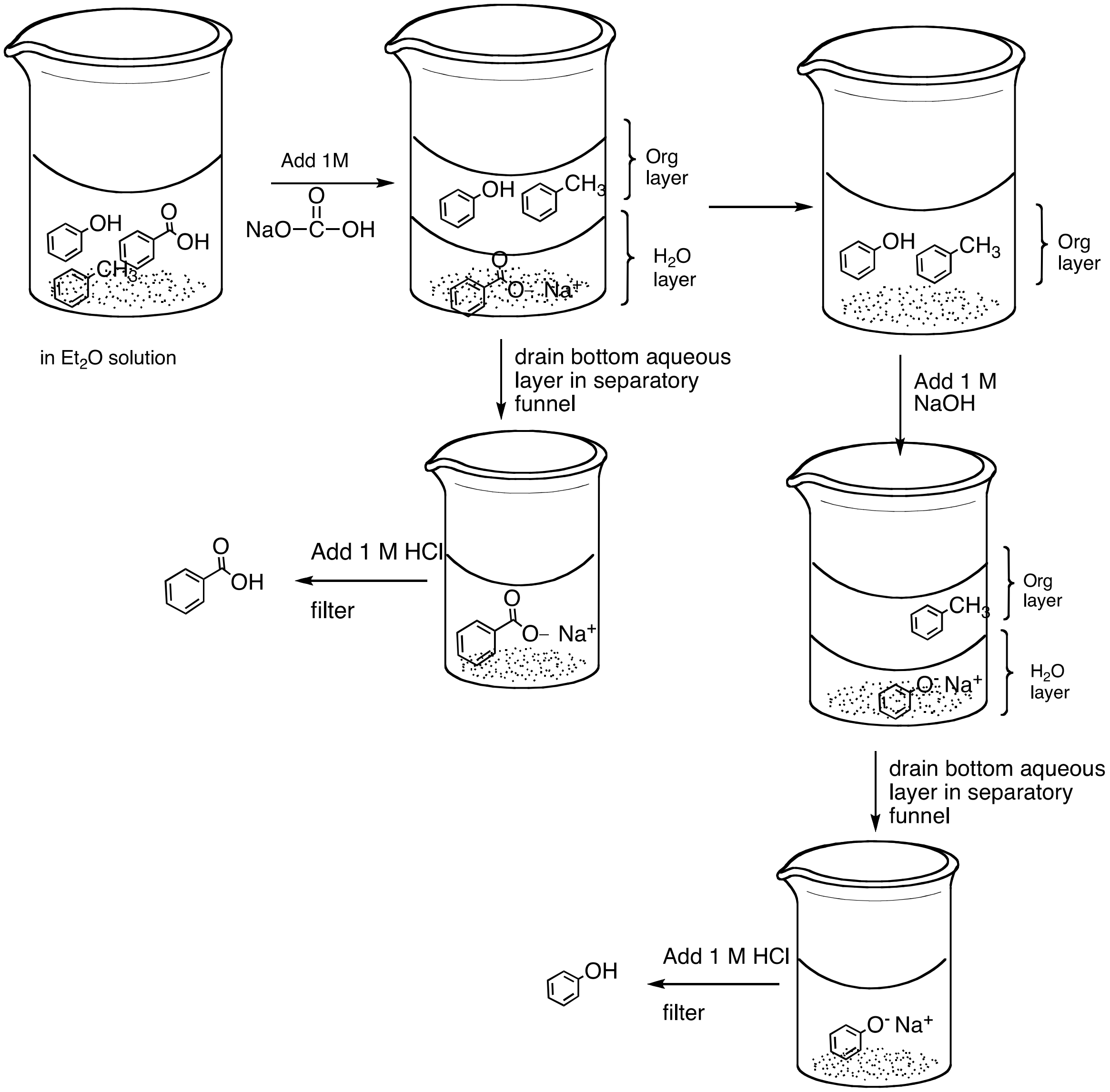
This is due to the fact that the resulting anion is stabilized by resonance donation of the lone pair onto the benzene ring.



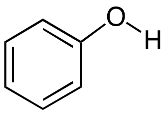
But it is not a strong enough acid to be significantly ionized by sodium bicarbonate.

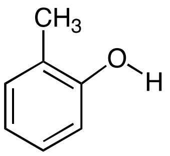


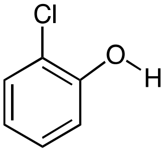
This allows separation of a mixture of phenol, benzoic acid and toluene in diethyl ether using simple acid-base chemistry. The mixture is first treated with a solution of aqueous sodium bicarbonate. This is will deprotonate the benzoic acid, making it soluble in the aqueous layer, while phenol and toluene remain in the organic layer. The aqueous layer is drained off, treated with mild acid to neutralize it and precipitate the benzoic acid as a solid which can be recovered by filtration. The organic layer is then treated with sodium hydroxide, a stronger base, which can deprotonate the phenol but not the toluene. The phenol will be extracted into the aqueous layer where it can be separated from the organic layer. Neutralization with dilute acid will reprotonate the phenol and it can be separated from the aqueous layer extraction with diethyl ether. This just leaves the original organic layer containing the toluene.

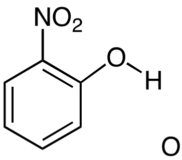


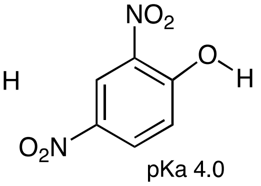
Electron withdrawing groups on the phenol will increase the acidity and donating groups will decrease the acidity.


pKa 10


pKa 10.3

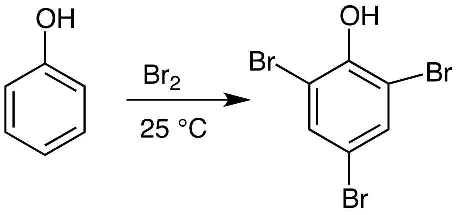

pKa 8.6


pKa 7.2

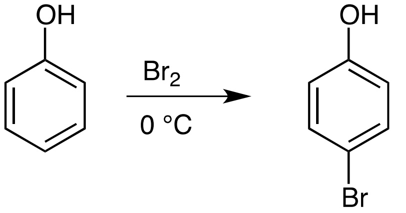

pKa 4.0

Reactions of Phenols

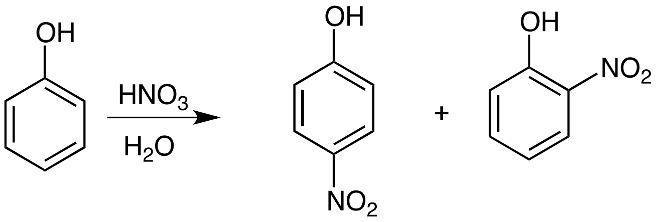
(1) Electrophilic Aromatic Substitution. Phenols are very reactive due to the electron-donation by the hydroxyl lone pair. For bromination, for example, no catalyst is needed and it is hard to stop at mono-bromination. Like with aniline derivatives, the product is usually the 2,4,6-tribromophenol.



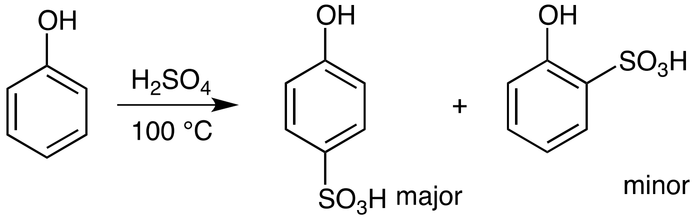
To get mono-bromination, use low temperature. Usually the *para*-isomer is the major product.



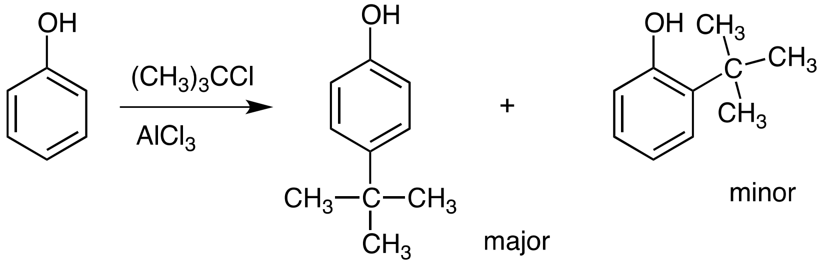
For nitration, nitric acid in water or acetic acid can be used. Sulfuric acid is not needed as a dehydrating agent for the nitric acid. Oxidation of the benzene ring can be a major side reaction.



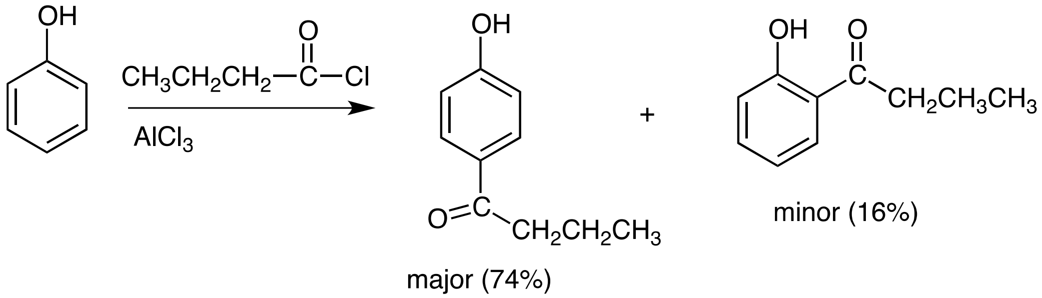
Sulfonation gives mainly the *para*-isomer.



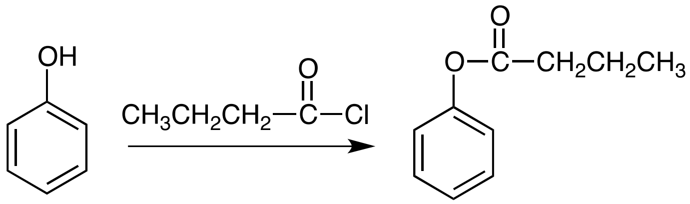
Friedel-Crafts alkylation gives mainly the *para*-isomer.



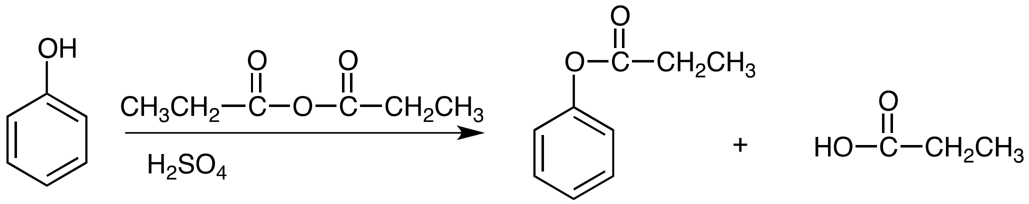
Friedel-Crafts acylation also gives mainly the *para*-isomer.



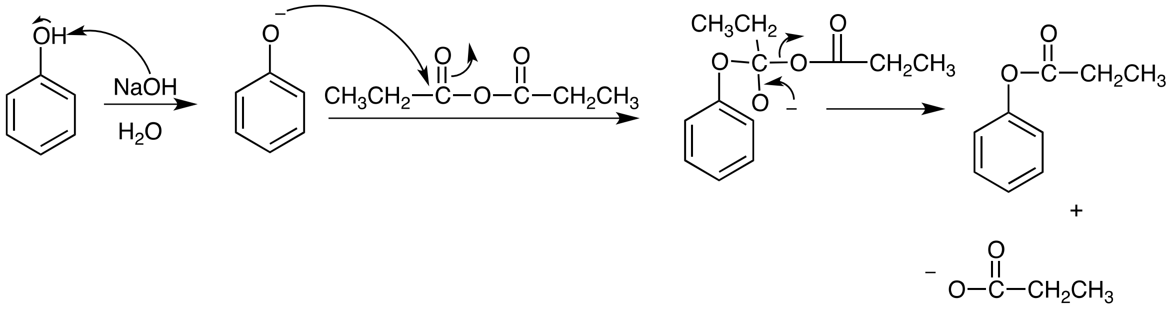
So, in the presence of aluminum trichloride, we see acylation at carbon. In the absence of aluminum trichloride, we see acylation at oxygen.



With anhydrides, acid activation is used and acylation also occurs on oxygen.

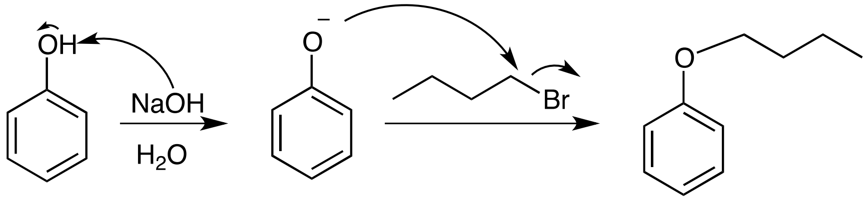


Acylation can also be done in basic conditions with anhydrides. Treatment of the phenol with sodium hydroxide deprotonates the phenol and makes the oxygen a better nucleophile.

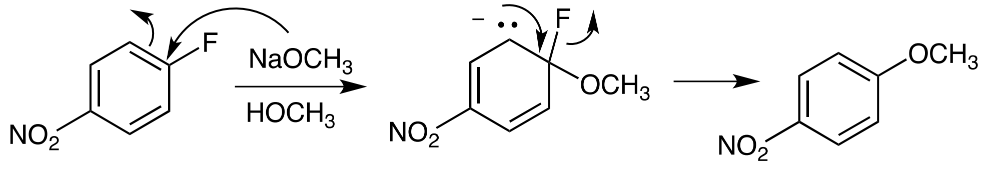


Aryl Ethers

For synthesis of aryl ethers, the phenol must be the nucleophile since there is no nucleophilic substitution at sp^2 carbons.



If there is a strong electron withdrawing group, nucleophilic aromatic substitution can occur through an addition-elimination mechanism.



Cleavage of aryl ethers occurs only on the alkyl side of the ether since there is no nucleophilic substitution at sp^2 carbons.