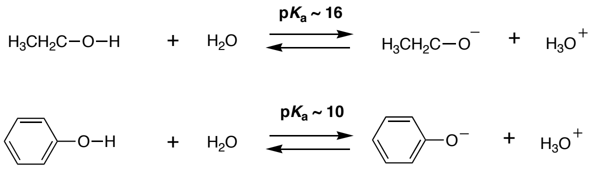
Chapter 24: Phenols. Alcohols contain an OH group bonded to an sp^3-hybridized carbon. Phenols contain an OH group bonded to an sp^2-hybridized carbon of a benzene ring

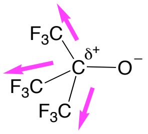
24.1: Nomenclature (please read)
24.2: Structure and Bonding (please read)
24.3: Physical Properties (please read). Like other alcohols the OH group of phenols cab participate in hydrogen bonding with other phenol molecules and to water.

24.4: Acidity of Phenols. Phenols are more acidic than aliphatic alcohols



Factors that influence acidity:
Inductive effect:

	CH_3CH_2OH	FCH_2CH_2OH	F_2CHCH_2OH	F_3CCH_2OH	$(F_3C)_3COH$
pK_a ~	16.0	14.4	13.3	12.4	5.4



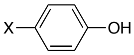
Electron-withdrawing groups make an alcohol a stronger acid by stabilizing the conjugate base (alkoxide)

A benzene ring is generally considered electron withdrawing and stabilizes the negative charge through inductive effects

Resonance effect: the benzene ring stabilizes the the phenoxide ion by resonance delocalization of the negative charge

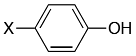
24.5: Substituent Effects on the Acidity of Phenols.

Electron-donating substituents make a phenol less acidic by destabilizing the phenoxide ion (resonance effect)



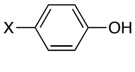
X=	**-H**	**-CH_3**	**-OCH_3**	**-NH_2**
pK_a ~	10	10.3	10.2	10.5

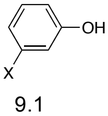
Electron-withdrawing substituents make a phenol more acidic by stabilizing the phenoxide ion through delocalization of the negative charge and through inductive effects.



X=	**-H**	**-Cl**	**-Br**	**-NO_2**
pK_a ~	10	9.4	9.3	7.2

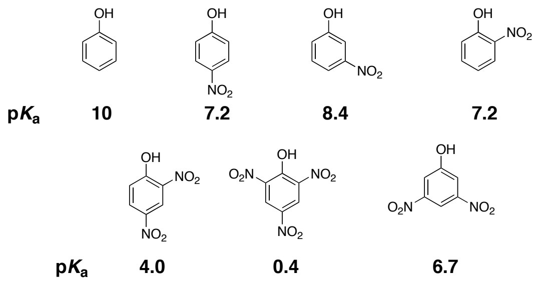
The influence of a substituent on phenol acidity is also dependent on its position relative to the -OH



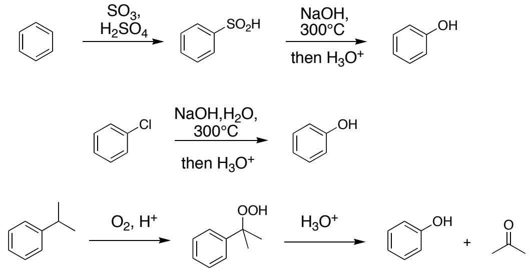


pK_a	X=		
	-Cl	9.4	9.1
	-NO_2	7.2	8.4
	-OCH_3	10.2	9.6
	-CH_3	10.3	10.1

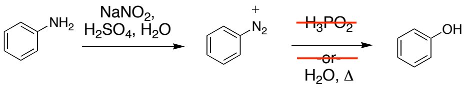
The effect of multiple substituents on phenol acidity is additive.



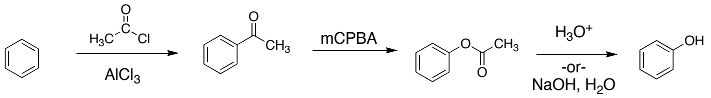
24.6: Sources of Phenols. (Table 24.3)



From aryl diazonium ion

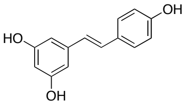


From aryl ketones



24.7: Naturally Occurring Phenols.

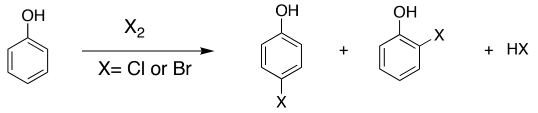
(please read) Phenols are common in nature.



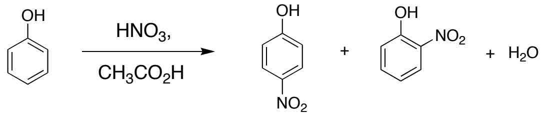
Resveratrol

24.8: Reactions of Phenols: Electrophilic Aromatic Substitution. Table 24.4 (a review from Chapter 12). The hydroxyl group of phenols is a strong activator and *o*-/*p*-director.

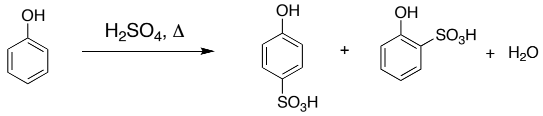
a. Halogenation. Phenols are so activated that they often react with Br_2 and Cl_2 without a catalyst.



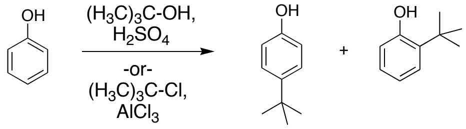
b. Nitration.



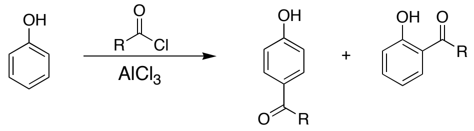
c. Sulfonation.



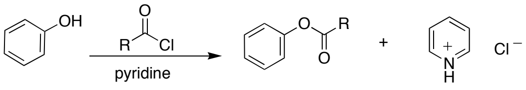
d. Friedel-Crafts alkylation



e. Friedel-Crafts acylation

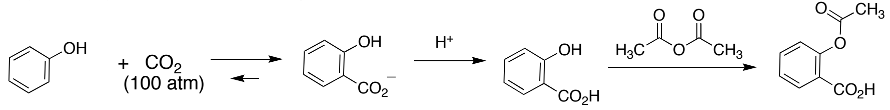


24.9: Acylation of Phenols. In the absence if $AlCl_3$, phenols react with acid chlorides to afford phenyl esters.

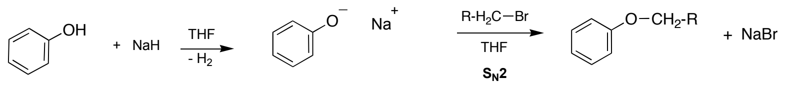


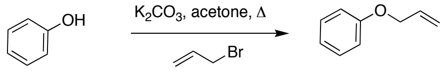
Note: The Fischer esterification works poorly for the preparation of phenyl esters

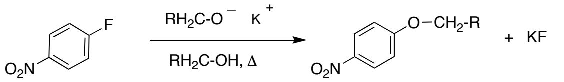
24.10: Carboxylation of Phenols. Aspirin and the Kolbe-Schmitt Reaction. (please read) Synthesis of salicylic acid (*o*-hydroxybenzoic acid) from phenol.



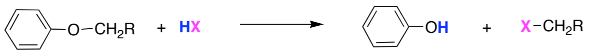
24.11: Preparation of Aryl Ethers. The phenoxide ion is a good nucleophile and reacts with 1° and 2° alkyl halides and tosylates afford aryl ethers (Williamson ether synthesis)



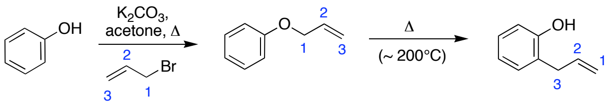




24.12: Cleavage of Aryl Ethers by Hydrogen Halides. Aryl alkyl ethers can be cleaved by HX to give phenols.

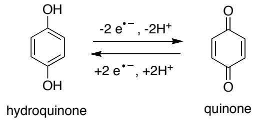


24.13: Claisen Rearrangement. Thermal rearrangement of an aryl allyl ether to an *o*-allyl phenol.

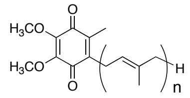


The Claisen rearrangement involves a concerted, pericyclic mechanism, which is related to the Diels-Alder reaction

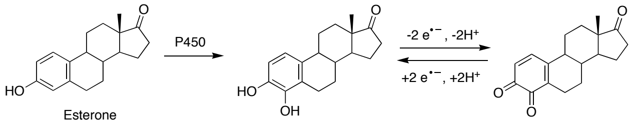
24.14 Oxidation of Phenols: Quinones (please read)



hydroquinone quinone



Coenzyme Q_n (Ubiquinone)

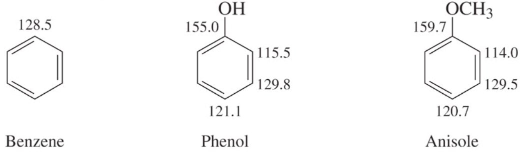


24.15: Spectroscopic Analysis of Phenols. Largely the same as for alcohols (Ch 15.14).

IR: broad O-H stretch ~3600 cm^{-1}. C-O single bond stretch is ~1200-1250 cm^{-1}, which is shifted from that of aliphatic alcohols (1000-1200 cm^{-1}).

^1H NMR: Like aliphatic alcohols, the O-H proton resonance is observed over a large chemical shift range as a broad singlet.

^{13}C NMR: The *sp^2*-carbon directly attached to the OH has a chemical shift of ~150-160 ppm.



^{13}C Chemical shifts δ (ppm)