

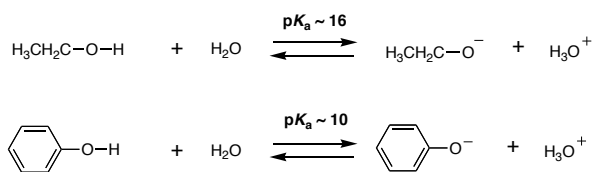
Chapter 22: Phenols. Alcohols contain an OH group bonded to an sp^3 -hybridized carbon. Phenols contain an OH group bonded to an sp^2 -hybridized carbon of a benzene ring

22.1: Nomenclature (please read)

22.2: Structure and Bonding (please read)

22.3: Physical Properties (please read). Like other alcohols the OH group of phenols can participate in hydrogen bonding with other phenol molecules and to water.

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

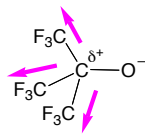


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Factors that influence acidity:

Inductive effect:

	$\text{CH}_3\text{CH}_2\text{OH}$	$\text{FCH}_2\text{CH}_2\text{OH}$	$\text{F}_2\text{CHCH}_2\text{OH}$	$\text{F}_3\text{CCH}_2\text{OH}$	$(\text{F}_3\text{C})_3\text{COH}$
$\text{p}K_a \sim$	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

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Resonance effects: the benzene ring stabilizes the the phenoxide ion through resonance delocalization of the negative charge

22.5: Substituent Effects on the Acidity of Phenols.


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

					
$pK_a \sim$	X=	-H	-CH ₃	-OCH ₃	-NH ₂
		10	10.3	10.2	10.5

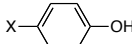
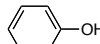
(Table 22.2, p. 918)

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Electron-withdrawing substituents make a phenol more acidic by stabilizing the phenoxide ion through delocalization of the negative charge and through inductive effects. (Table 22.2, p. 918)

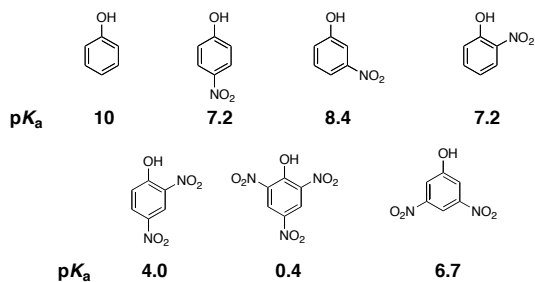
					
$pK_a \sim$	X=	-H	-Cl	-Br	-NO ₂
		10	9.4	9.3	7.2

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

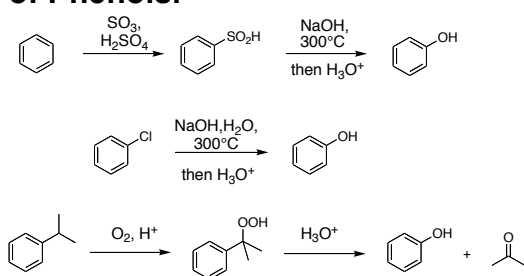
			
pK_a	X=	-Cl	-Cl
		9.4	9.1
	-NO ₂	7.2	8.4
	-OCH ₃	10.2	9.6
	-CH ₃	10.3	10.1

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The effect of multiple substituents on phenol acidity is additive.

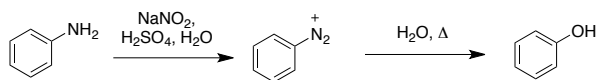


22.6: Sources of Phenols.

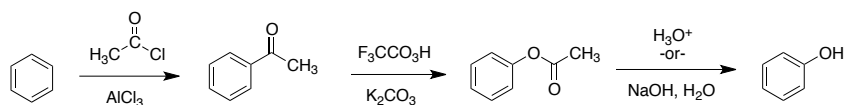


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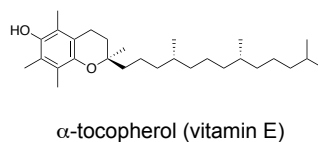
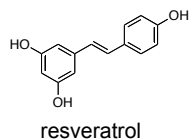
From aryl diazonium ion



From aryl ketones



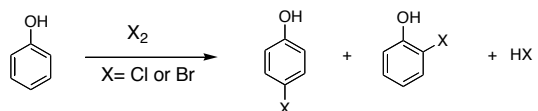
22.7: Naturally Occurring Phenols. (please read) Phenols are common in nature.



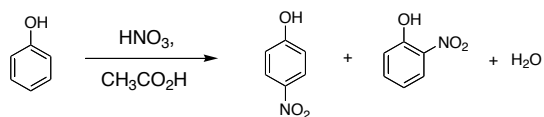
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22.8: Reactions of Phenols: Electrophilic Aromatic Substitution. (Table 22.3, p. 922; a review from Chapter 12). The hydroxyl group of phenols is a strong activator and *o*-/*p*-director.

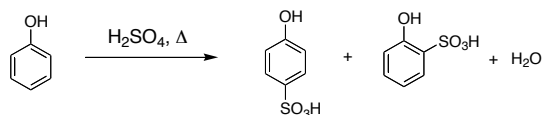
a. Halogenation. Phenols are so highly activated that they often react with Br_2 and Cl_2 without a catalyst.



b. Nitration.

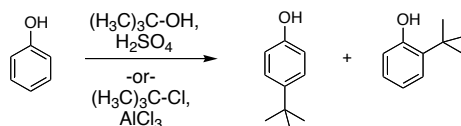


c. Sulfonation.

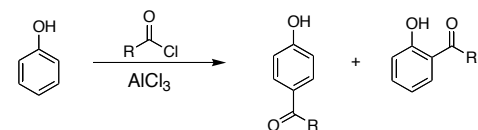


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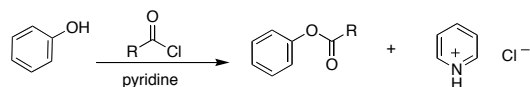
d. Friedel-Crafts alkylation



e. Friedel-Crafts acylation



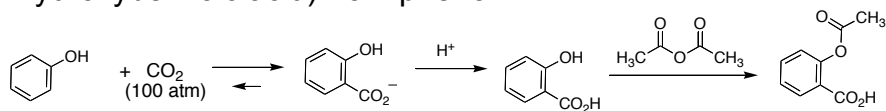
22.9: Acylation of Phenols. In the absence of AlCl_3 , phenols react with acid chlorides to afford phenyl esters.



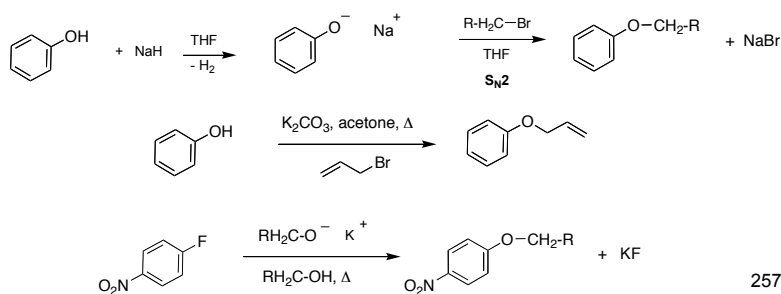
Note: The Fischer esterification works poorly for the preparation of phenyl esters

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

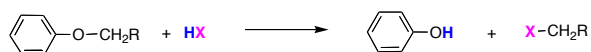


22.11: Preparation of Aryl Ethers. The phenoxide ion is a good nucleophile and reacts with 1° and 2° alkyl halides and tosylates to afford aryl ethers (Williamson ether synthesis).

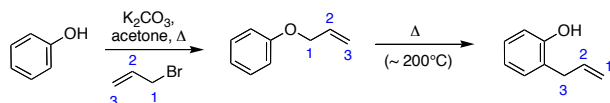


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22.12: Cleavage of Aryl Ethers by Hydrogen Halides. Aryl alkyl ethers can be cleaved by HX to give phenols.



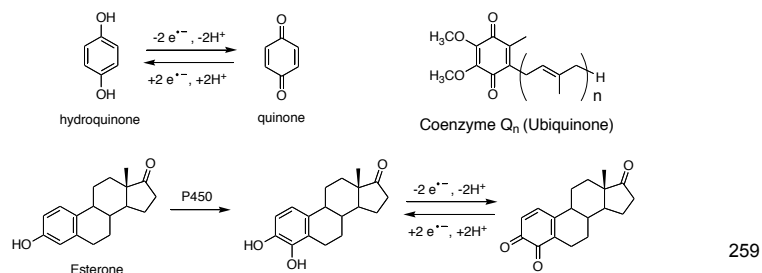
22.13: Claisen Rearrangement. Thermal rearrangement of an aryl allyl ether to an *o*-allyl phenol.



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

22.14 Oxidation of Phenols: Quinones (please read)

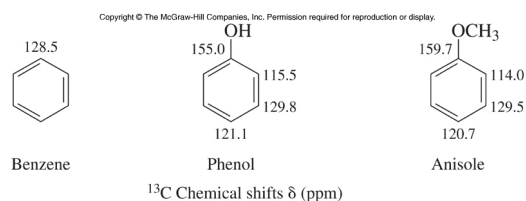


22.15: Spectroscopic Analysis of Phenols. Largely the same as for alcohols (Ch 15.14).

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

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

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



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