

CH 318 N

LECTURE 21

Textbook Assignment: Chapter 21

Homework (for credit): POW 10 posted

Today's Topics: Benzene & Its Reactions

Notice & Announcements:

ORGANIC LECTURE SERIES

Benzene & Aromaticity

Concept of Aromaticity

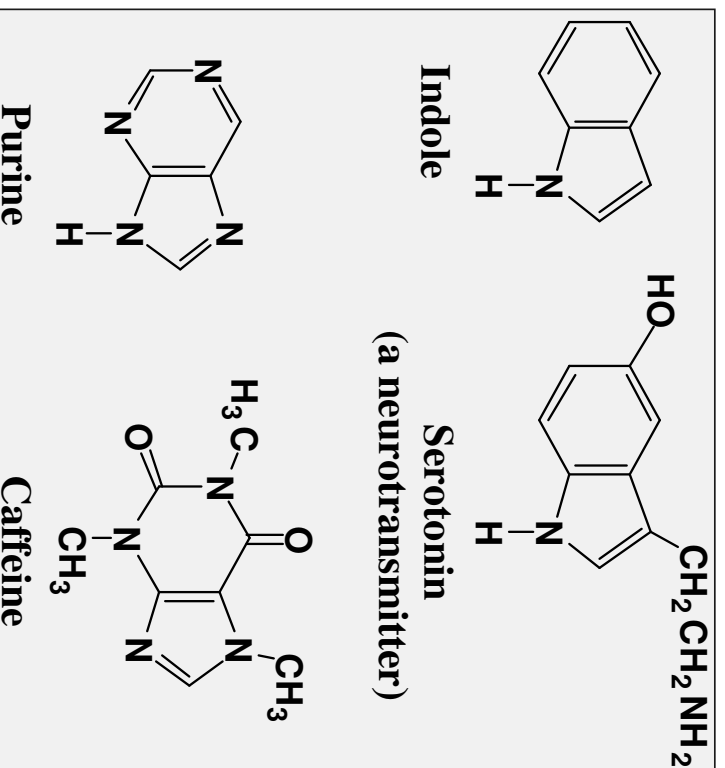
The underlying criteria for aromaticity were recognized in the early 1930s by Erich Hückel, based on molecular orbital (MO) calculations

To be aromatic, a compound must:

1. be cyclic
2. have one p orbital on each atom of the ring
3. be planar or nearly planar so that there is continuous or nearly continuous overlap of all p orbitals of the ring
4. have a closed loop of $(4n + 2) \pi$ electrons in the cyclic arrangement of p orbitals

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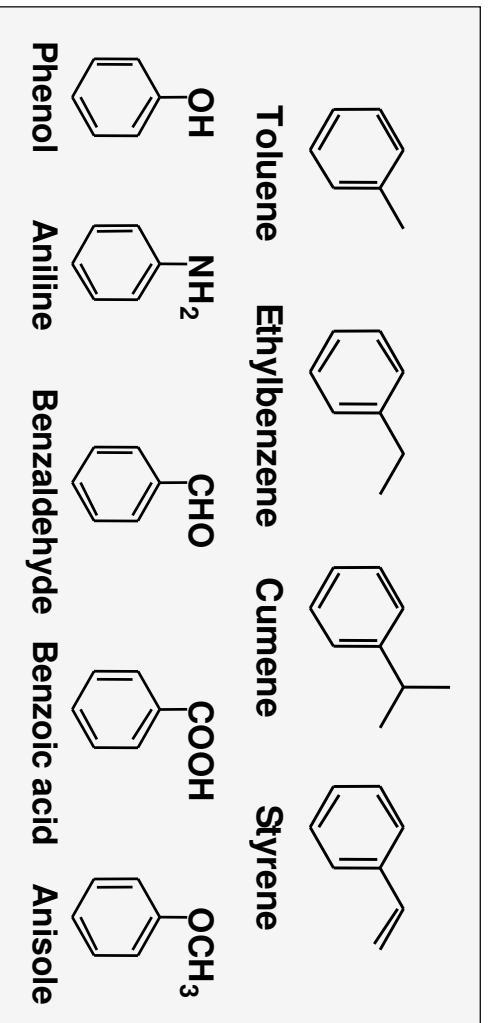
Other Heterocyclics



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Nomenclature-Monosubstituted

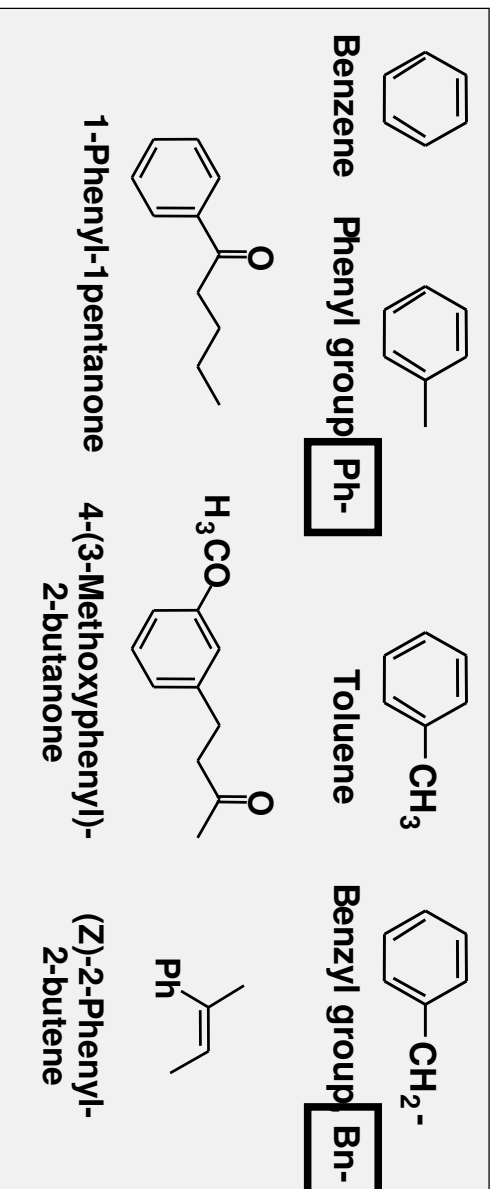
- Monosubstituted alkylbenzenes are named as derivatives of benzene
 - many common names are retained



(commit to memory)

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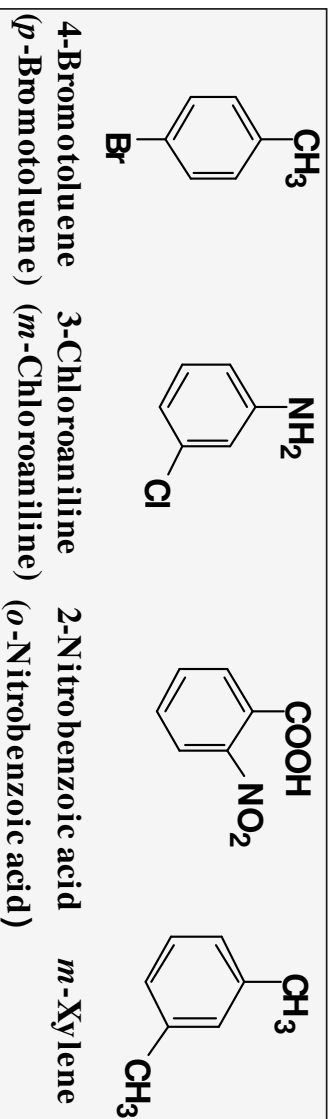
Benzyl and phenyl groups:



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Disubstituted Benzenes

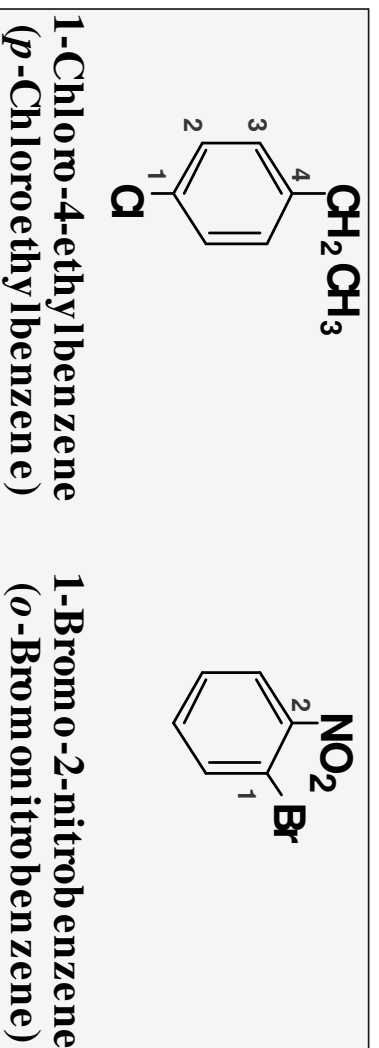
- Locate two groups by numbers or by the locators ortho (1,2-), meta (1,3-), and para (1,4-)
 - where one group imparts a special name, name the compound as a derivative of that molecule



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Disubstituted Benzenes

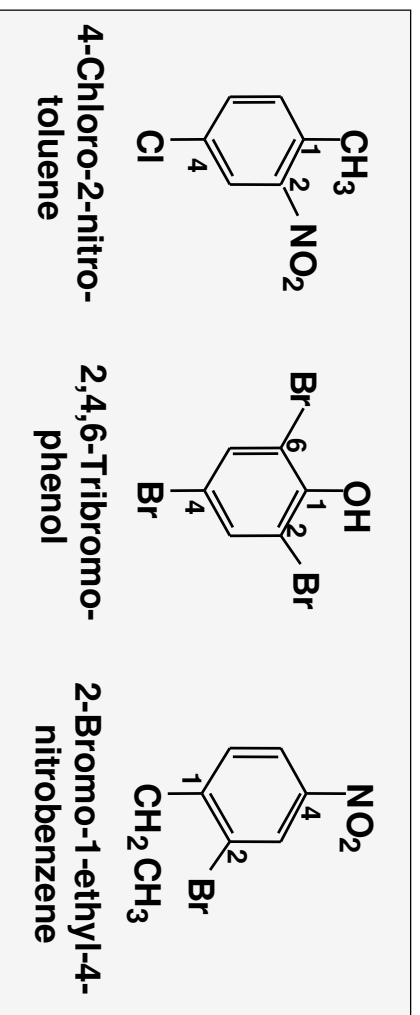
where neither group imparts a special name, locate the groups and **list them in alphabetical order**



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Polysubstituted Derivatives

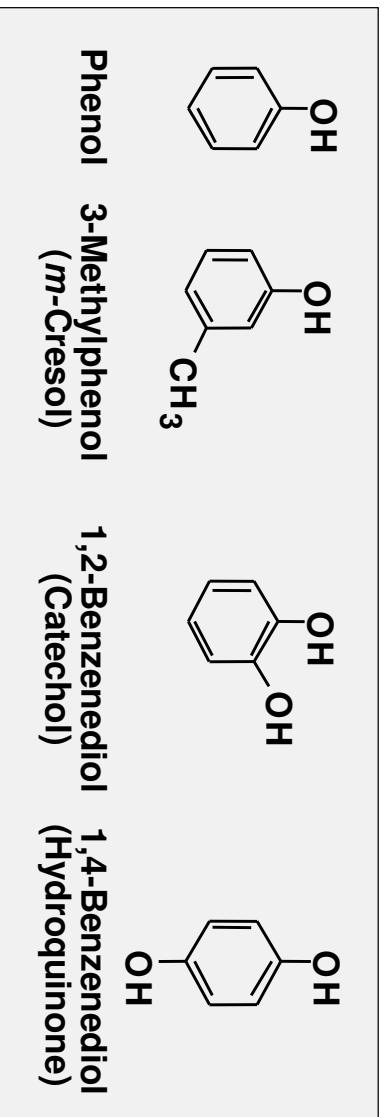
- if one group imparts a special name, name the molecule as a derivative of that compound
- if no group imparts a special name, list them in alphabetical order, giving them the lowest set of numbers



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Phenols

- The functional group of a phenol is an -OH group bonded to a benzene ring

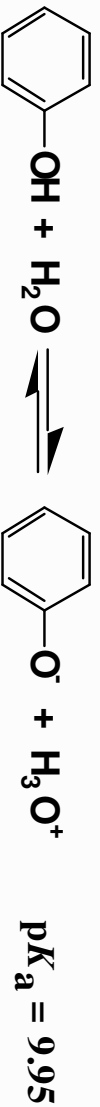


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Acidity of Phenols

- Phenols are significantly more acidic than alcohols, compounds that also contain the OH group

Phenoxide:

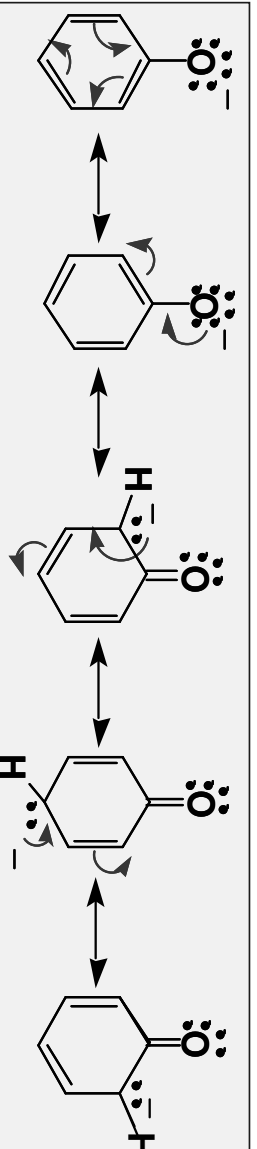


Ethoxide

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Acidity of Phenols

—the greater acidity of phenols compared with alcohols is due to the greater stability of the phenoxide ion relative to an alkoxide ion



These 2 Kekulé structures are equivalent

These three contributing structures delocalize the negative charge onto carbon atoms of the ring

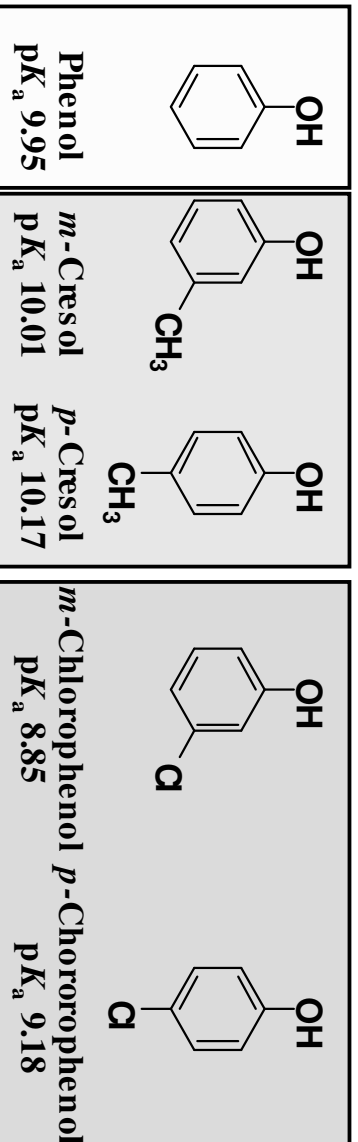
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Acidity of Phenols

Alkyl and halogen substituents effect

acidities by inductive effects:

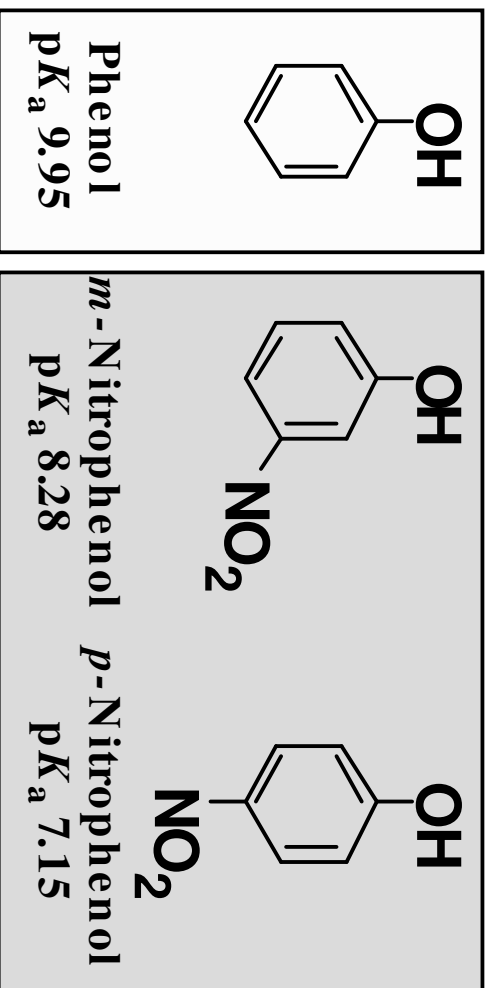
- alkyl groups are electron-releasing
- halogens are electron-withdrawing



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Acidity of Phenols

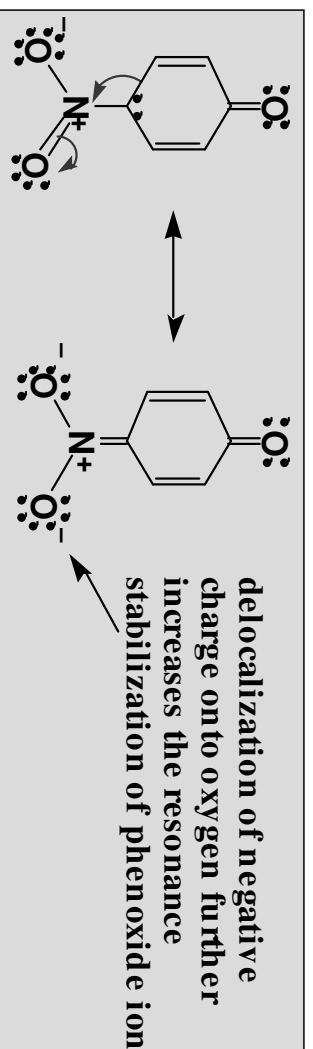
- nitro groups increase the acidity of phenols by both an electron-withdrawing inductive effect and a resonance effect



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Acidity of Phenols

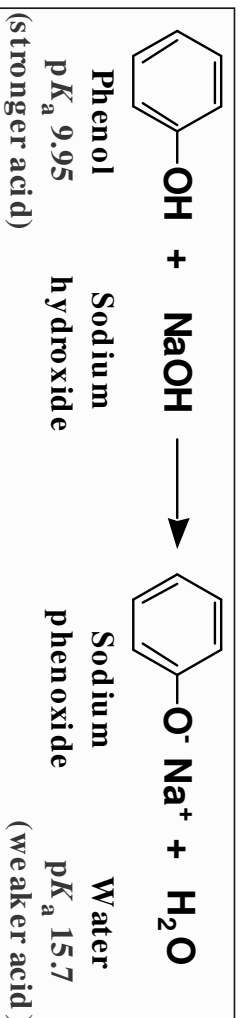
- part of the acid-strengthening effect of $-\text{NO}_2$ is due to its electron-withdrawing inductive effect
- in addition, $-\text{NO}_2$ substituents in the ortho and para positions help to delocalize the negative charge



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Acidity of Phenols

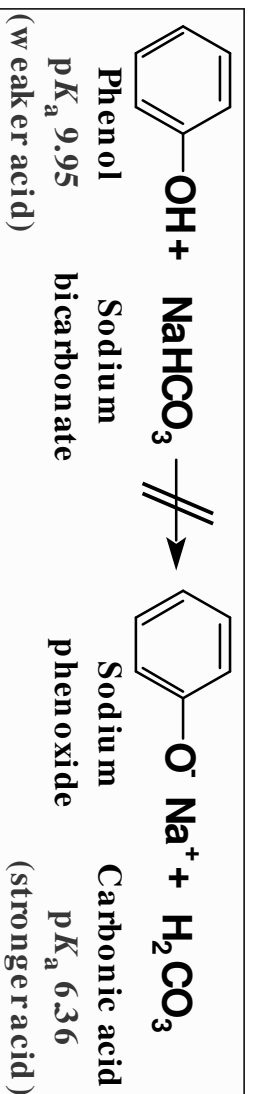
- Phenols are weak acids and react with strong bases to form water-soluble salts
 - water-insoluble phenols dissolve in $\text{NaOH}(\text{aq})$



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Acidity of Phenols

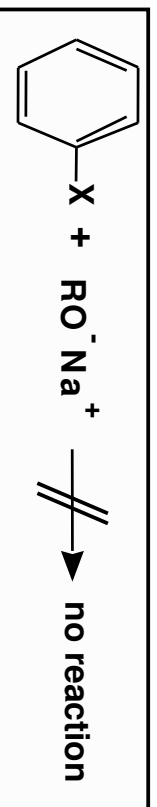
–most phenols do not react with weak bases such as NaHCO_3 ; they do not dissolve in aqueous NaHCO_3



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Alkyl-Aryl Ethers

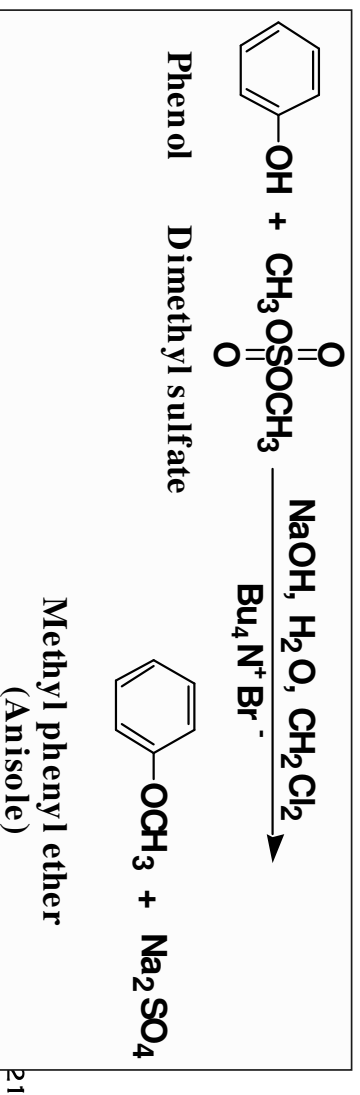
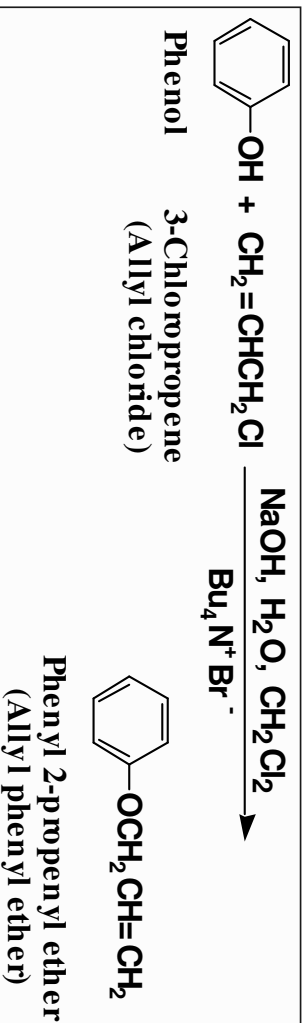
- Alkyl-aryl ethers can be prepared by the Williamson ether synthesis
 - but only using phenoxide salts and haloalkanes
 - haloarenes are unreactive to $\text{S}_{\text{N}}2$ reactions



- The following two examples illustrate
 - the use of a phase-transfer catalyst
 - the use of dimethyl sulfate as a methylating agent

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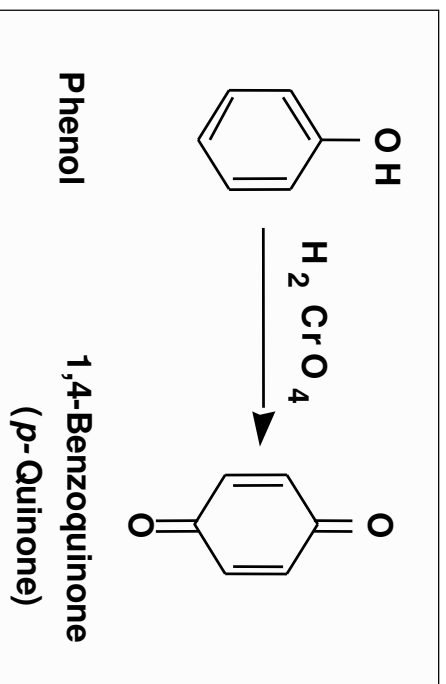
Alkyl-Aryl Ethers



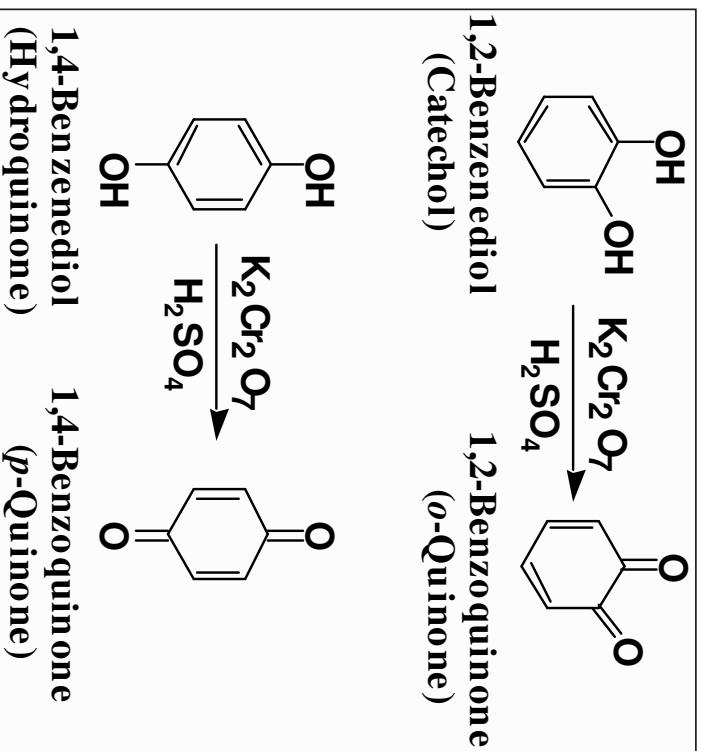
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Quinones

- Because of the presence of the electron-donating -OH group, phenols are susceptible to oxidation by a variety of strong oxidizing agents



Quinones

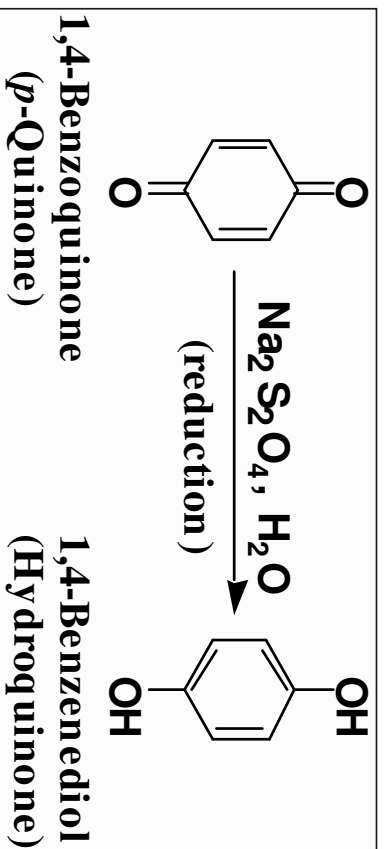


Not responsible for mechanism

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Quinones

Perhaps the most important chemical property of quinones is that they are readily reduced to hydroquinones:

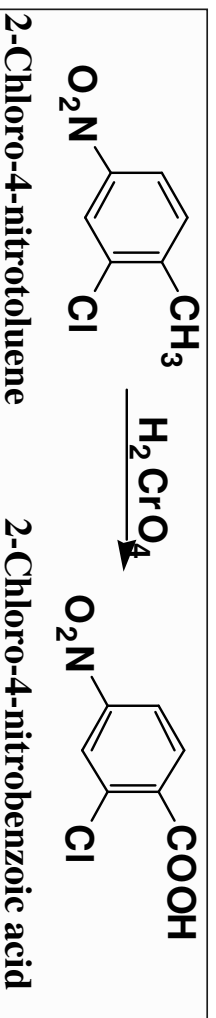


Not responsible for mechanism

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Benzylic Oxidation

- Benzene is unaffected by strong oxidizing agents such as H_2CrO_4 and KMnO_4
 - halogen and nitro substituents are also unaffected by these reagents
 - an alkyl group with at least one hydrogen on its benzylic carbon is oxidized to a carboxyl group

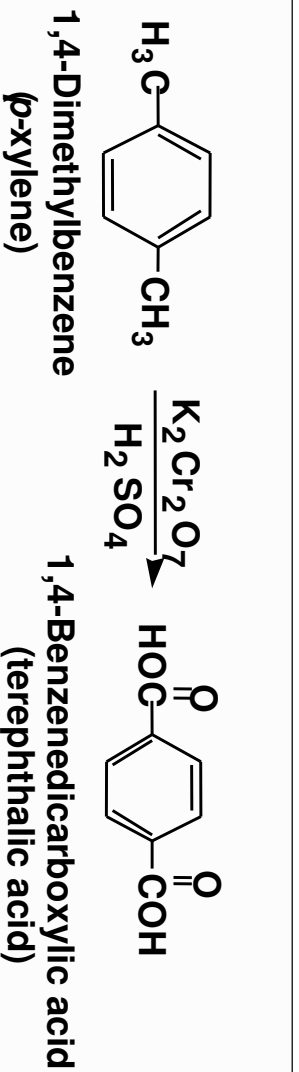


Not responsible for mechanism

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Benzylic Oxidation

- if there is more than one alkyl group on the benzene ring, each is oxidized to a -COOH group

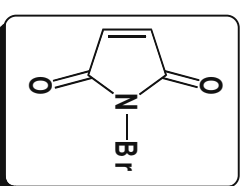
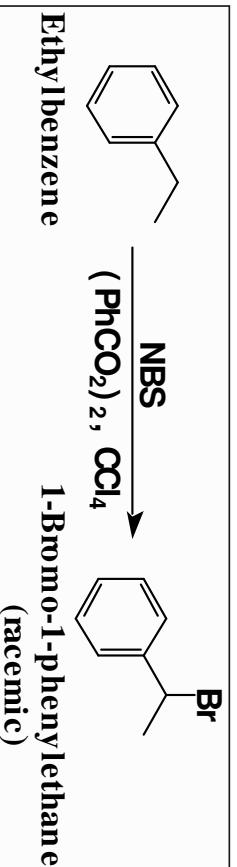
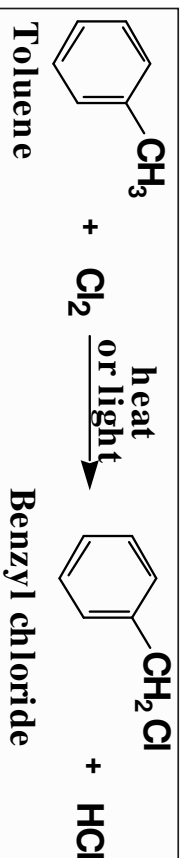


Not responsible for mechanism

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Benzylic Chlorination

- Chlorination (and bromination) occurs by a radical mechanism

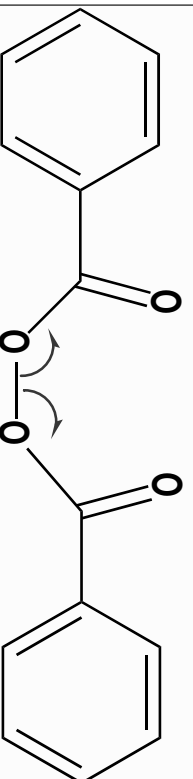


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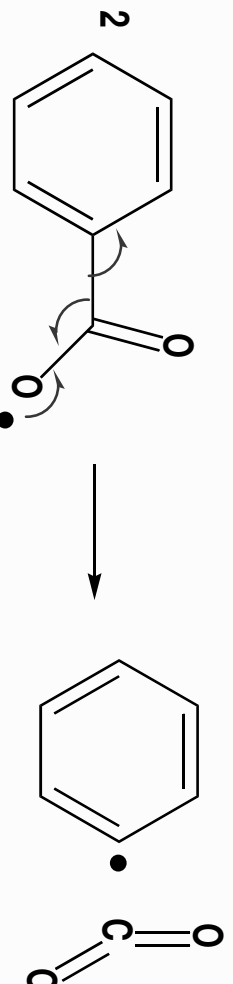
Benzoyl Peroxide as a Radical initiator

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Benzoyl Peroxide



$h\nu$
 or
 Δ

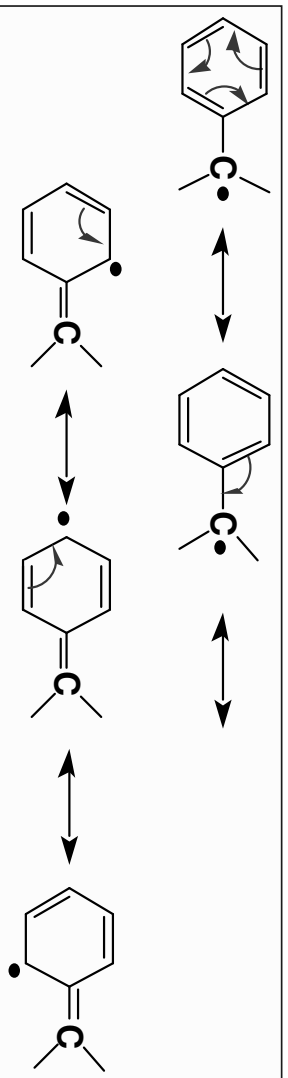


Phenyl Radical

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Benzylic Reactions

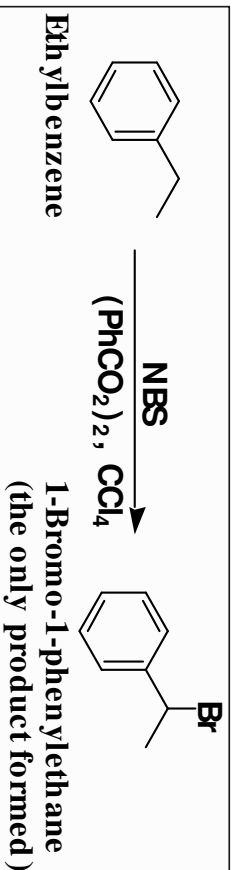
- **Benzylic radicals** (and cations also) are easily formed because of the resonance stabilization of these intermediates
 - the benzyl radical is a hybrid of five contributing structures



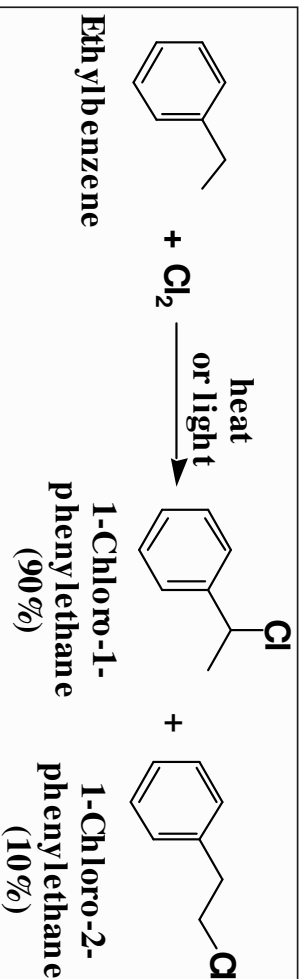
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Benzylic Halogenation

- benzylic bromination is highly regioselective



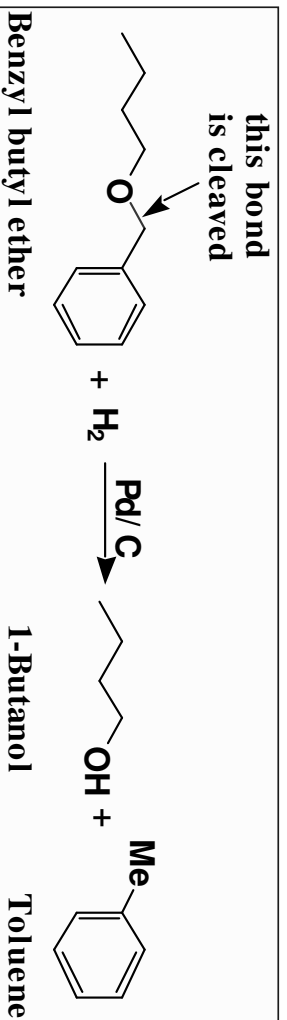
- benzylic chlorination is less regioselective



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Hydrogenolysis

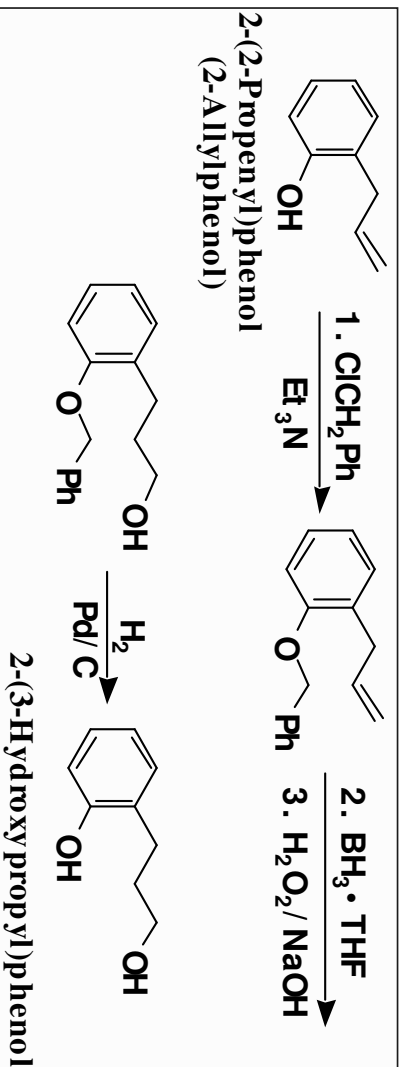
- Hydrogenolysis: cleavage of a single bond by H_2
 - among ethers, benzylic ethers are unique in that they are cleaved under conditions of catalytic hydrogenation



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Benzyl Ethers

- The value of benzyl ethers is as protecting groups for the OH groups of alcohols and phenols
 - to carry out hydroboration/oxidation of this alkene, the phenolic -OH must first be protected; it is acidic enough to react with BH_3 and destroy the reagent



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