

Benzene & Aromaticity

Chapter 21

1

Concept of Aromaticity

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

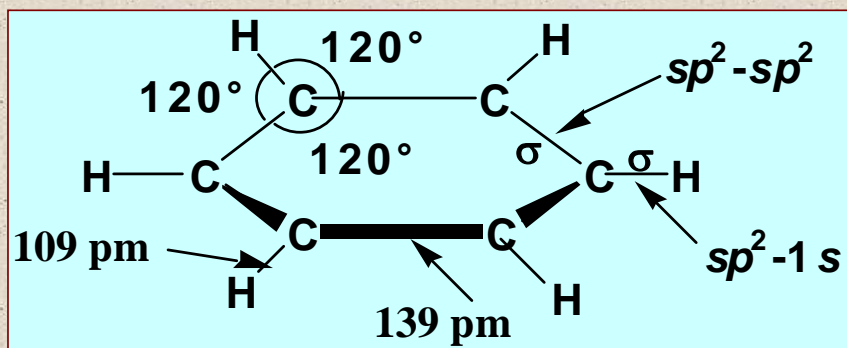
To be aromatic, a compound must:

- 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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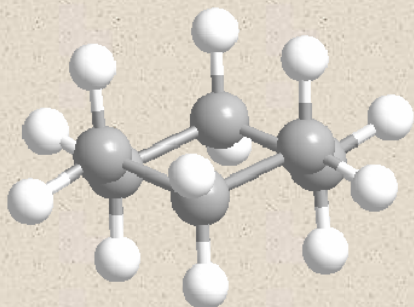
Benzene - Resonance Model

- The concepts of hybridization of atomic orbitals and the theory of resonance, developed in the 1930s, provided the first adequate description of benzene's structure
 - the carbon skeleton is a regular hexagon
 - all C-C-C and H-C-C bond angles 120°

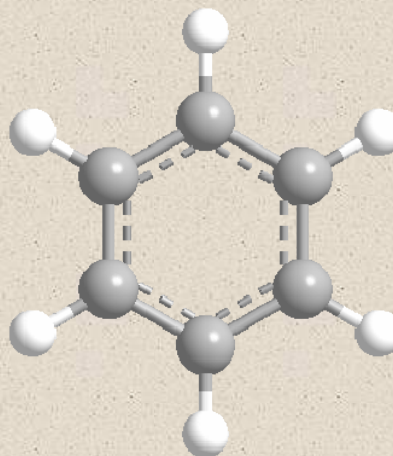


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Cyclohexane-Chair conformation



Benzene- "flat" unsaturated system

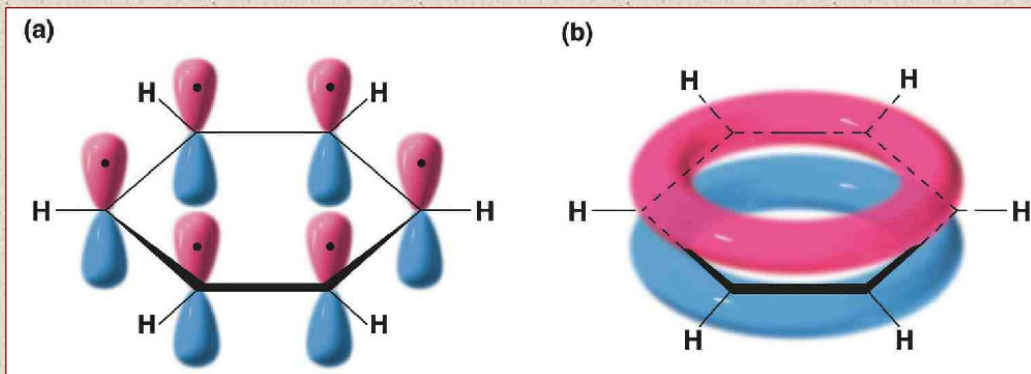


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Benzene – Molecular Orbitals

The π system of benzene:

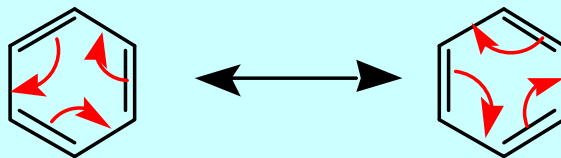
1. the carbon framework with the six $2p$ orbitals
2. overlap of the parallel $2p$ orbitals forms one torus above the plane of the ring and another below it
3. this orbital represents the lowest-lying pi-bonding molecular orbital



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Benzene - Resonance Model

- Benzene is represented as a hybrid of two equivalent Kekulé structures
 - each makes an equal contribution to the hybrid and thus the C-C bonds are neither double nor single, but something in between



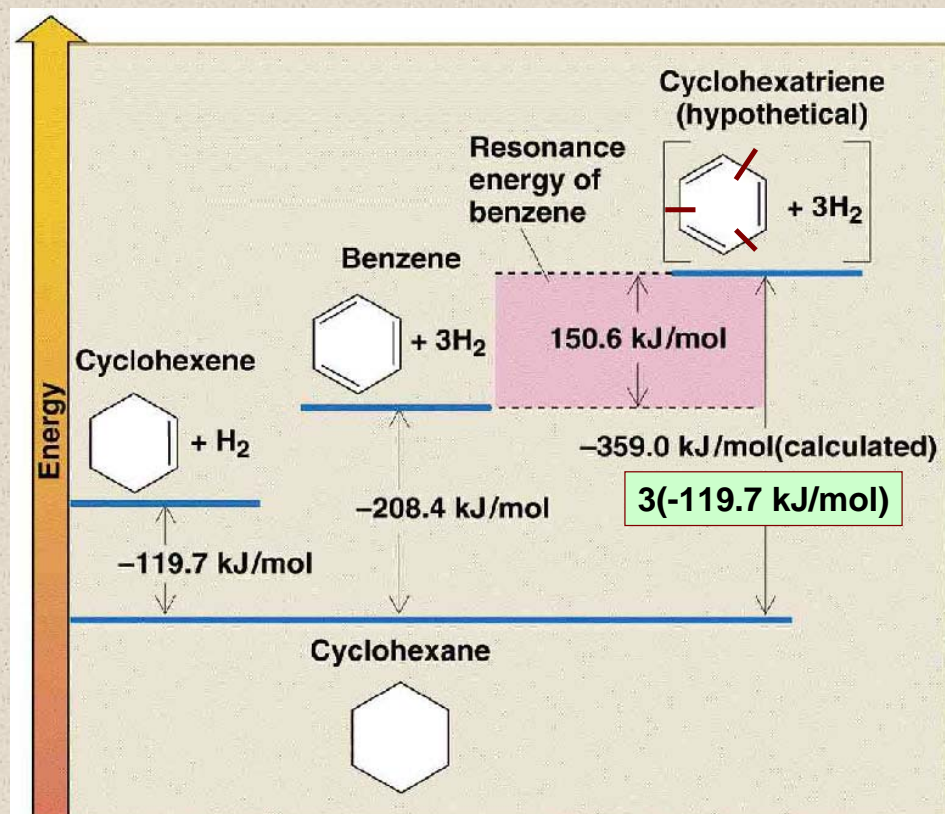
Benzene as a hybrid of two equivalent contributing structures

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Benzene - Resonance Model

- **Resonance energy:** the difference in energy between a resonance hybrid and the most stable of its hypothetical contributing structures in which electrons are localized on particular atoms and in particular bonds
 - one way to estimate the resonance energy of benzene is to compare the **heats of hydrogenation** of benzene and cyclohexene

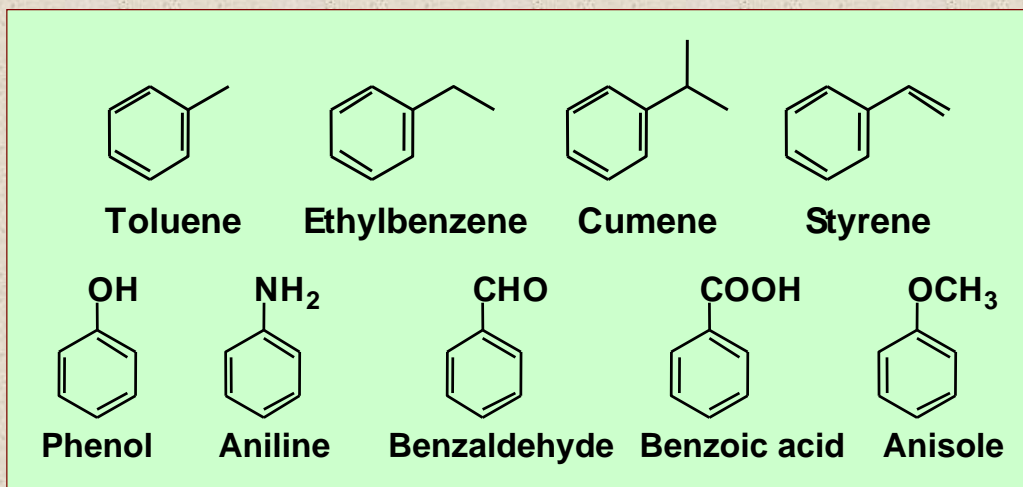
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Nomenclature-Monosubstituted

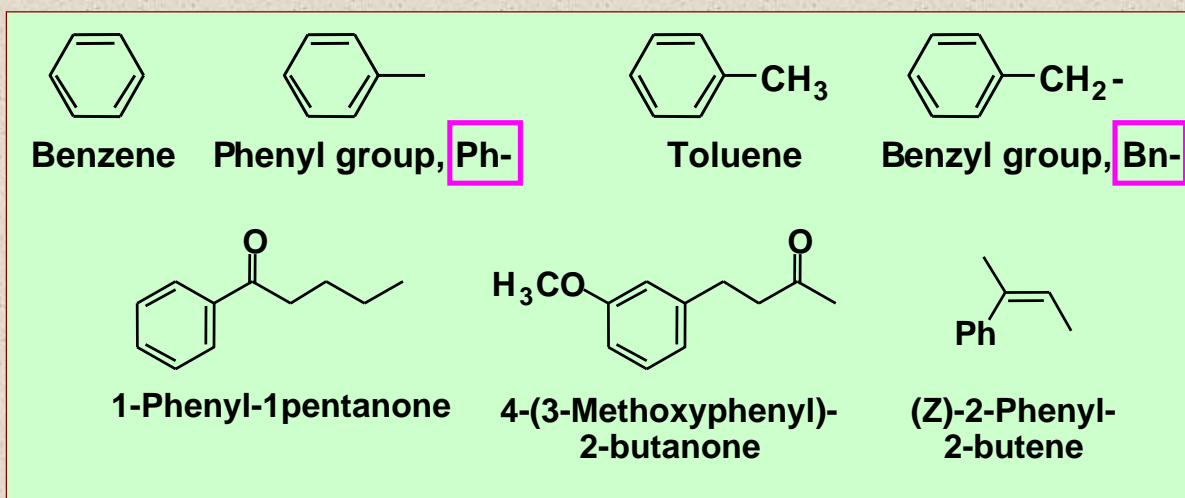
- Monosubstituted alkylbenzenes are named as derivatives of benzene
 - many common names are retained



(commit to memory)

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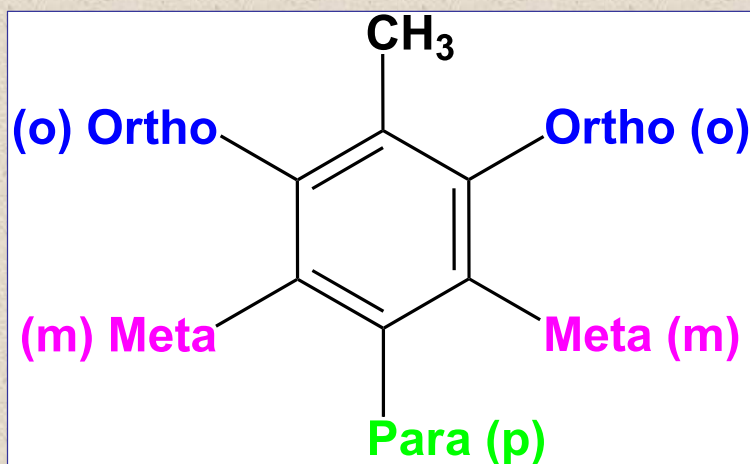
Benzyl and phenyl groups:



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Disubstituted Benzenes

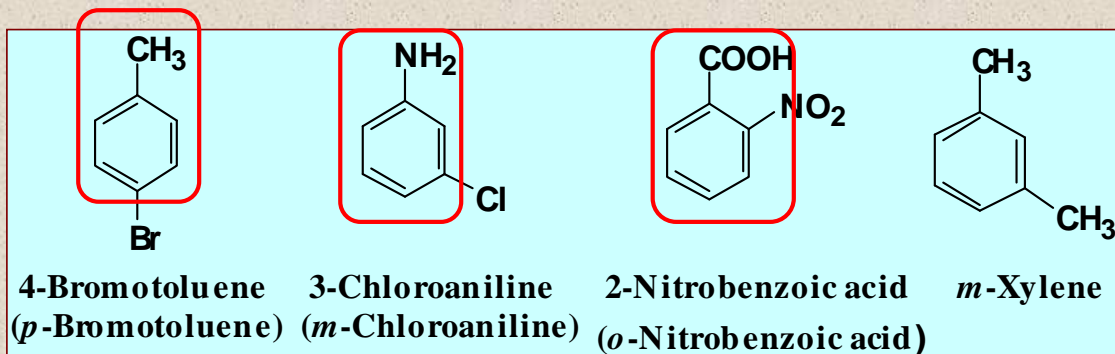
- Locate two groups by numbers or by the locators **ortho** (1,2-), **meta** (1,3-), and **para** (1,4-)



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Disubstituted Benzenes

- where one group imparts a special name, name the compound as a derivative of that molecule:



Toluene is
the parent
name

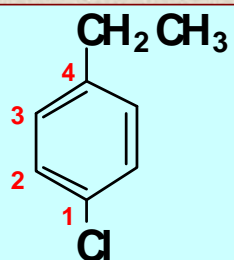
Aniline is
the parent
name

Benzoic Acid
is the parent
name

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Disubstituted Benzenes

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



1-Chloro-4-ethylbenzene
(*p*-Chloroethylbenzene)

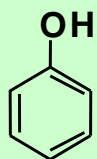


1-Bromo-2-nitrobenzene
(*o*-Bromonitrobenzene)

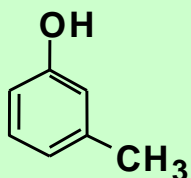
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Phenols

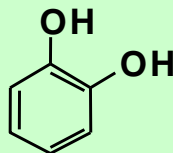
- The functional group of a phenol is an -OH group bonded to a benzene ring



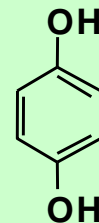
Phenol



3-Methylphenol
(*m*-Cresol)



1,2-Benzenediol
(Catechol)



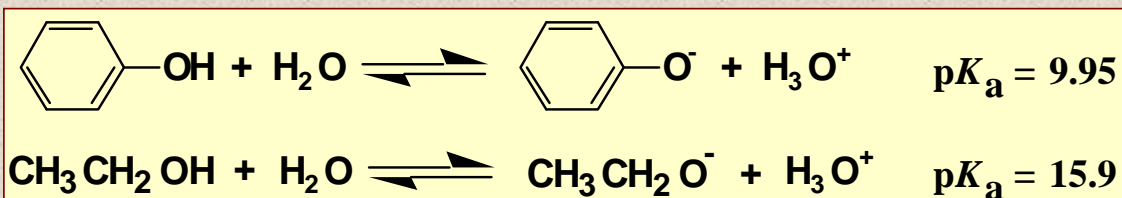
1,4-Benzenediol
(Hydroquinone)

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Acidity of Phenols

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

Phenoxide:

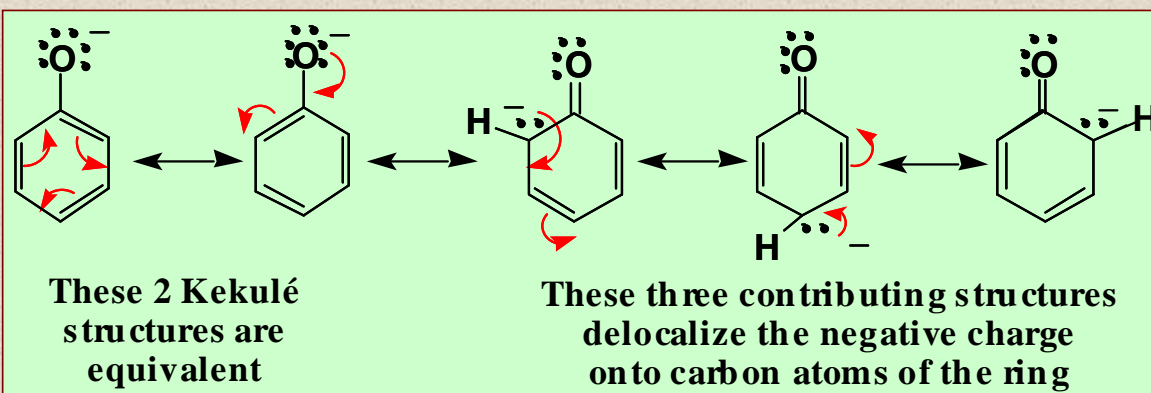


Ethoxide

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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:

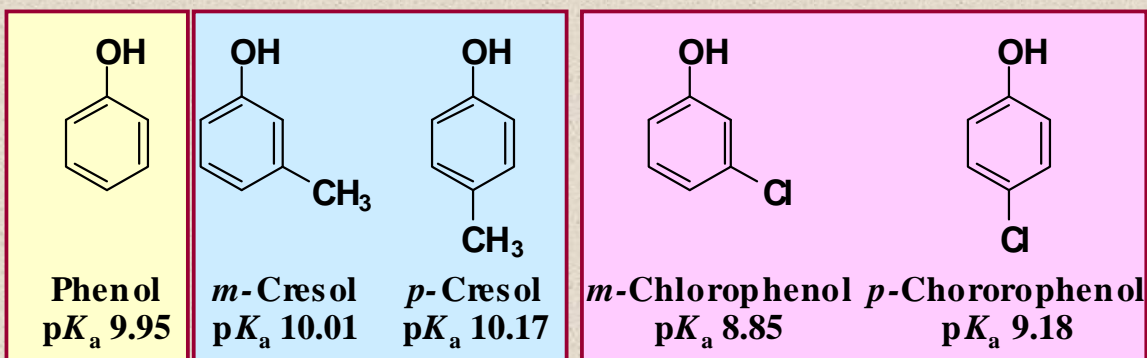


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Acidity of Phenols

Alkyl and halogen substituents effect acidities by inductive effects:

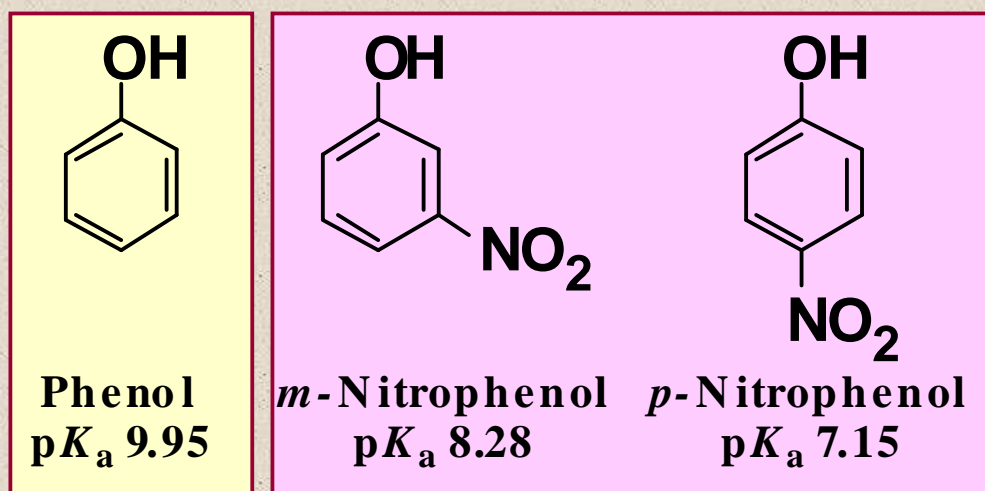
- alkyl groups are electron-releasing
- halogens are electron-withdrawing



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Acidity of Phenols

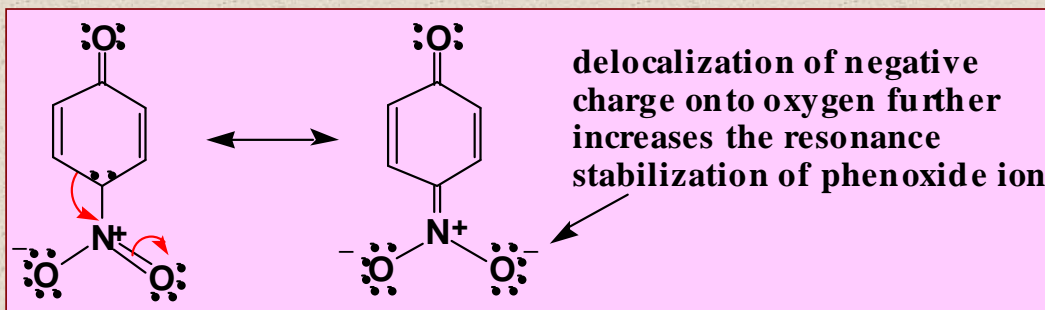
- nitro groups increase the acidity of phenols by **both an electron-withdrawing inductive effect and a resonance effect**



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Acidity of Phenols

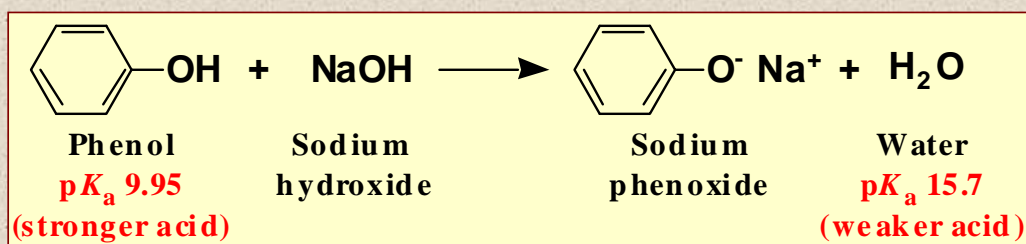
- part of the acid-strengthening effect of $-\text{NO}_2$ is due to its electron-withdrawing inductive effect
- in addition, $-\text{NO}_2$ substituents in the ortho and para positions help to delocalize the negative charge



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Acidity of Phenols

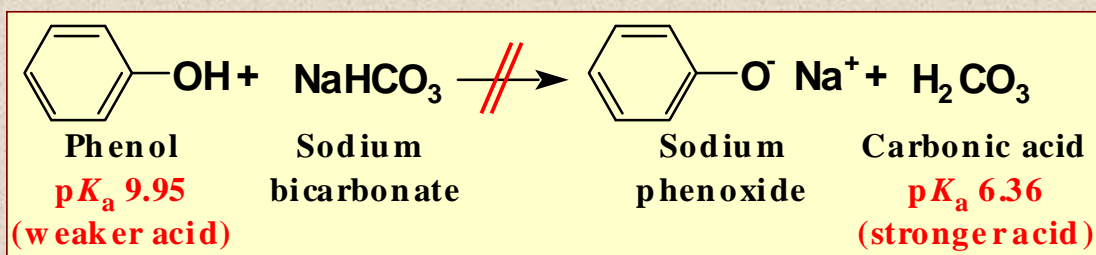
- Phenols are weak acids and react with strong bases to form water-soluble salts
 - water-insoluble phenols dissolve in $\text{NaOH}(\text{aq})$



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Acidity of Phenols

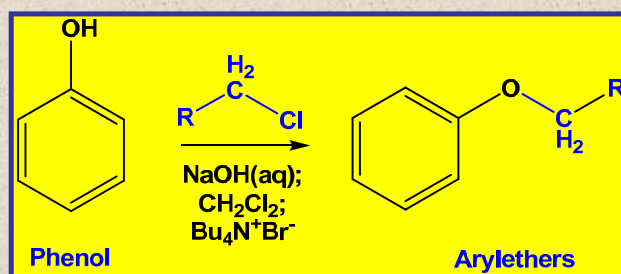
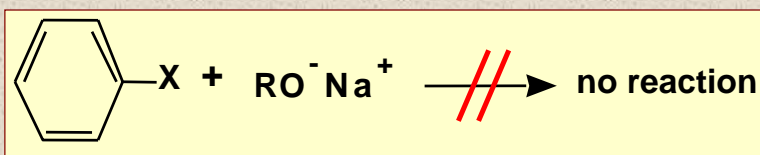
- most phenols do not react with weak bases such as NaHCO_3 ; they do not dissolve in aqueous NaHCO_3



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Alkyl-Aryl Ethers

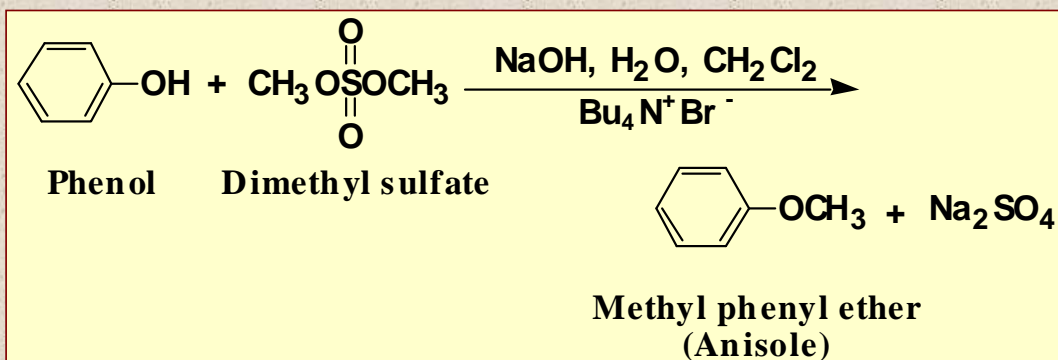
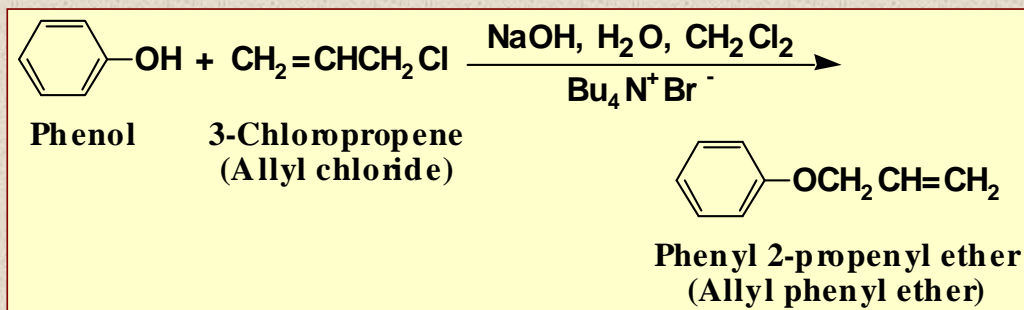
- Alkyl-aryl ethers can be prepared by the Williamson ether synthesis
 - but only using phenoxide salts and haloalkanes
 - haloarenes are unreactive to $\text{S}_{\text{N}}2$ reactions



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The following two examples illustrate

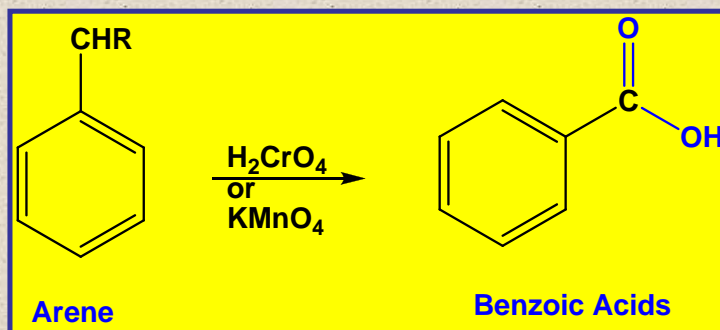
1. the use of a phase-transfer catalyst
2. the use of dimethyl sulfate as a methylating agent



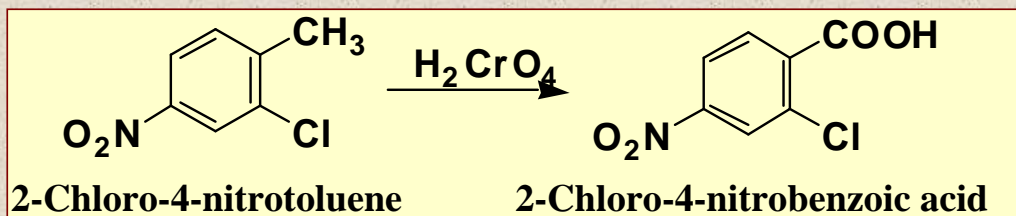
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Benzylic Oxidation

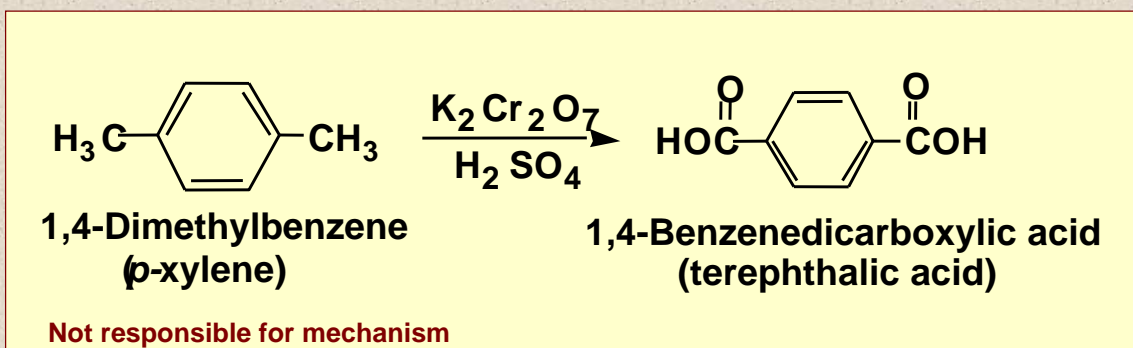
- Benzene is unaffected by strong oxidizing agents such as H_2CrO_4 and KMnO_4
 - halogen and nitro substituents are also unaffected by these reagents
 - an alkyl group with at least one hydrogen on its benzylic carbon is oxidized to a carboxyl group



Benzylic Oxidation

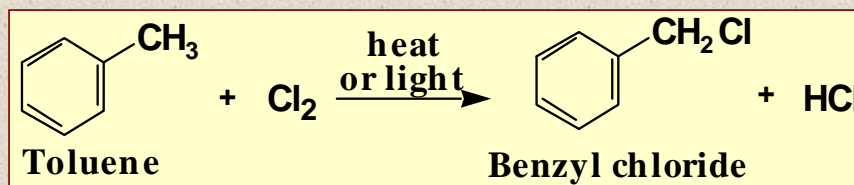
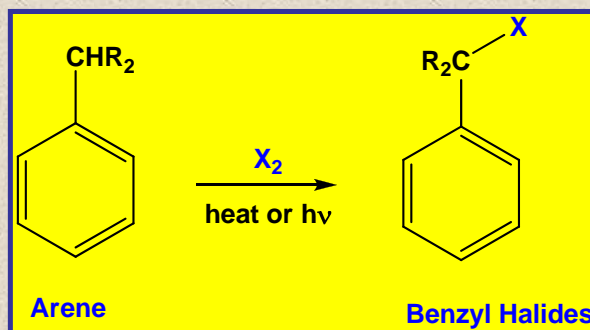


- if there is more than one alkyl group on the benzene ring, each is oxidized to a -COOH group



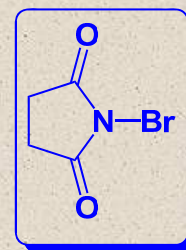
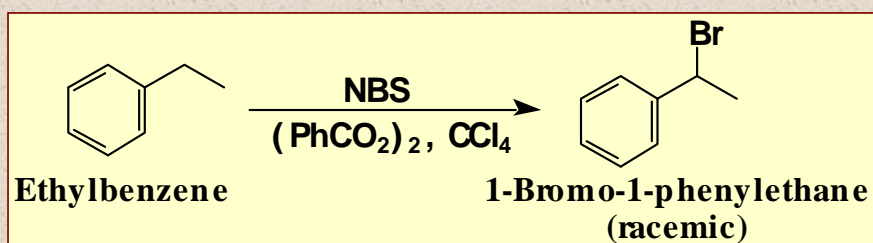
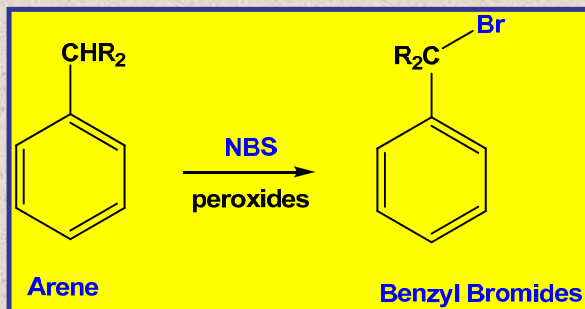
Benzylic Chlorination

- Chlorination (and bromination) occurs by a radical mechanism



Benzylic Bromination

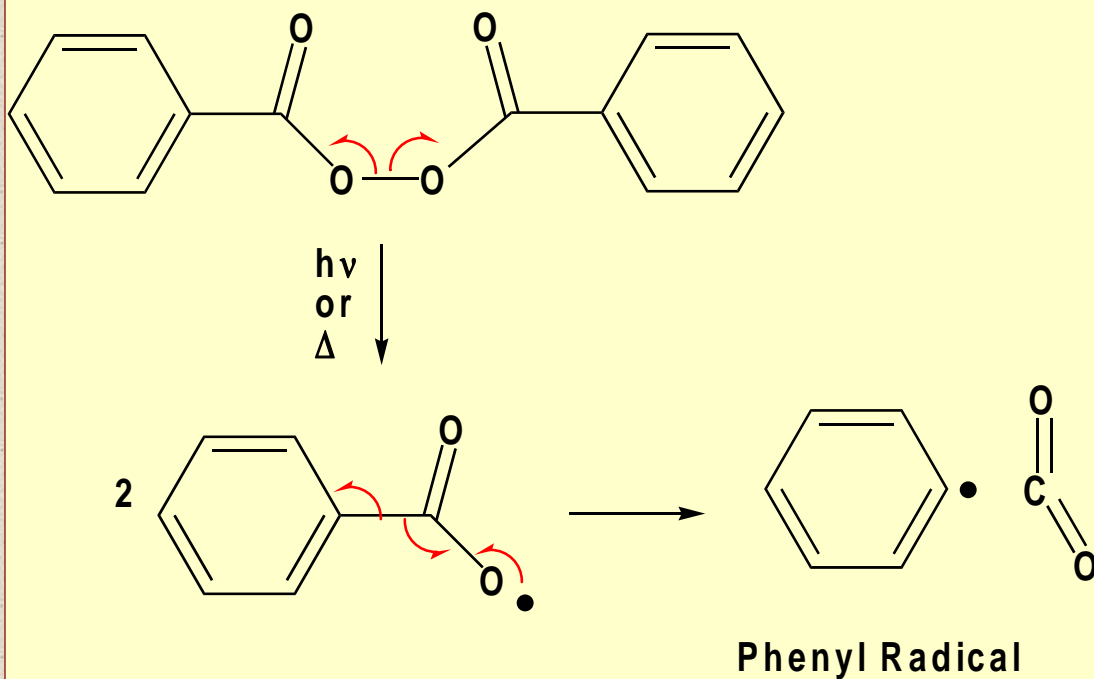
- Bromination can be conducted with NBS:



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Benzoyl Peroxide as a Radical initiator

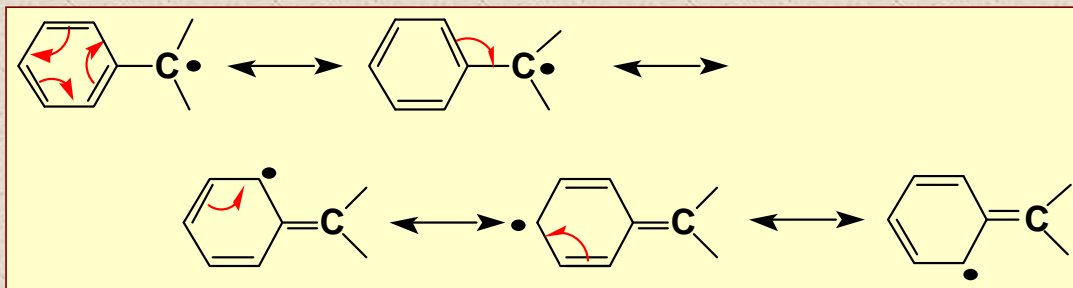
Benzoyl Peroxide



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Benzylic Reactions

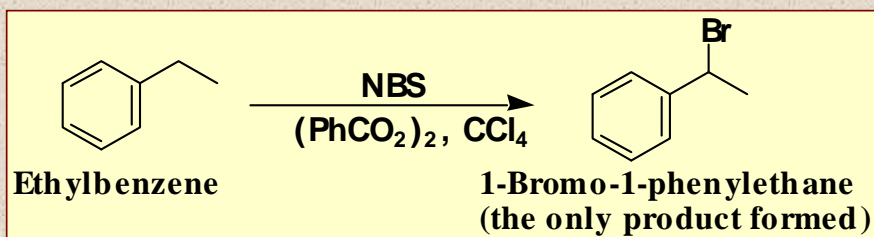
- **Benzylic radicals** (and cations also) are easily formed because of the resonance stabilization of these intermediates
 - the benzyl radical is a hybrid of five contributing structures



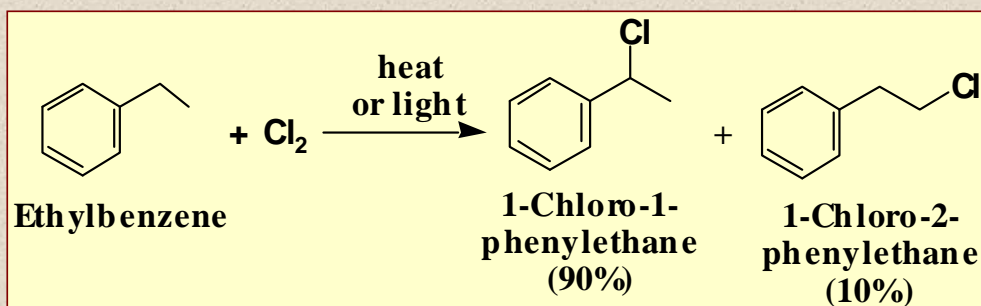
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Benzylic Halogenation

- **benzylic bromination** is highly regioselective



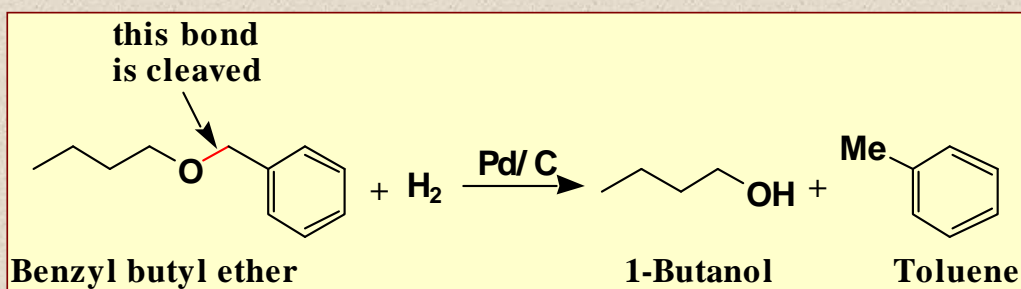
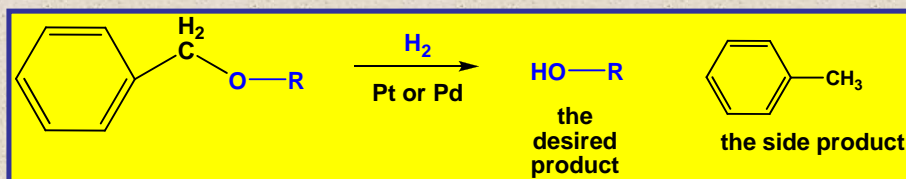
- **benzylic chlorination** is less regioselective



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Hydrogenolysis

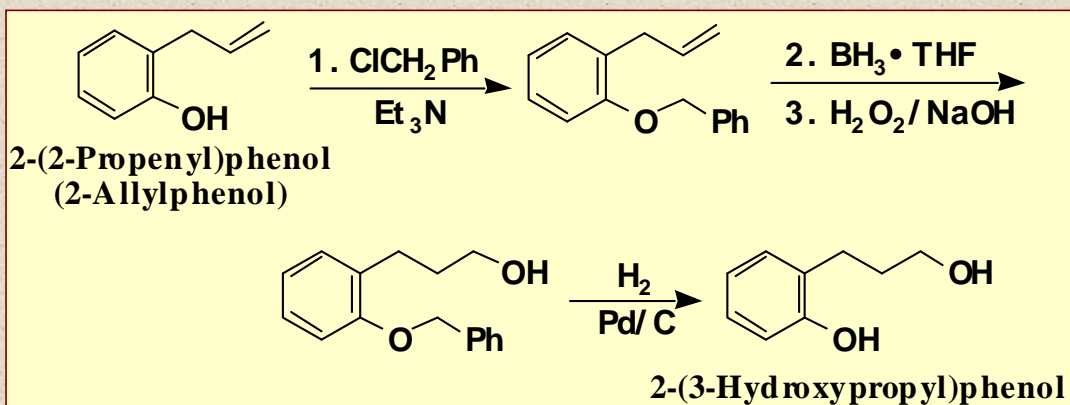
- **Hydrogenolysis:** cleavage of a single bond by H_2
 - among ethers, benzylic ethers are unique in that they are cleaved under conditions of catalytic hydrogenation



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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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