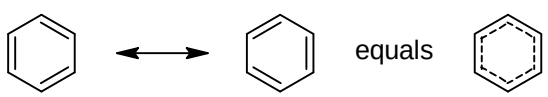
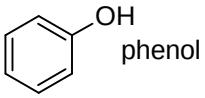
Chapter 9 – Benzene and its Derivatives

This chapter covers a special hydrocarbon group: the benzene ring. This ring is always viewed as a *resonance hybrid* and relatively *unreactive*. Substituents around the ring change the ring's reactivity and chapter 9 discusses these "substituent effects" in detail.





A *phenol* is a benzene ring that is substituted with a hydroxyl group, –OH. Phenols are weak acids (typical pK_a ~10) falling between alcohols (pK_a ~18) and carboxylic acids (pK_a ~5). Phenols are found in diverse compounds such as vitamin E, BHT (a synthetic anti-oxidant added to food), and urushiol, the "itch" in poison ivy.

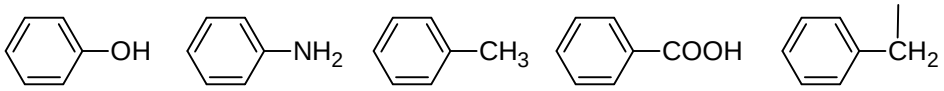
After you finish studying this chapter, you should be able to do the following:

1 Identify cyclic unsaturated molecules that might be aromatic
2 Predict how aromaticity affects molecular energy

- Sample problems: 9.10-9.11
- Key background:
  - orbital hybridization
  - orbital overlap model of covalent bonding
  - resonance theory (what is a *resonance hybrid*? a *resonance contributor*? what does ↔ mean?)

3 Write and interpret IUPAC names for molecules based on benzene
4 Write and interpret IUPAC names for *special* molecules related to benzene: *phenol, aniline, toluene, benzoic acid*
5 Describe relationship between two benzene ring positions as *ortho (o), meta (m),* or *para (p)*
6 Identify *benzyl* groups in a molecular formula

- Sample problems: 9.12-9.16
- Key background:
  - You do *not* need to know how to name polycyclics (*naphthalene, anthracene, etc.*) or heterocyclics (*pyridine, furan, etc.*)
  - Useful structures:



phenol aniline toluene benzoic acid benzyl group

7 Predict the *relative* acidity of phenols, alcohols, carboxylic acids & oxonium ions; predict the *relative* basicity of their conjugate bases

- Sample problems: 9.34-9.38
- Key background:
  - *relative* pK_a's
  - formal charge effect
  - resonance effect

For chapter 9 reactions: 1) if a reaction is marked **[C+ I]**, draw *all* important resonance contributing forms of cation *intermediates* resulting from *ortho, meta,* and *para* attack; 2) if a reaction is marked **[C+ Rct]**, draw carbocation *electrophile* that attacks benzene ring

8 Recognize benzylic CH bonds

9 Draw the *most likely* organic product(s) of a chemical reaction between a *substituted* benzene and the reagents list below

- **$K_2Cr_2O_7$ + H_2SO_4 (oxidation of benzylic CH, 9.5)**
- **[C+ I] Lewis acid ($AlCl_3$ or $FeCl_3$) + halogen (Cl_2 or Br_2) (halogenation, 9.7A)**
- **[C+ I] HNO_3 + H_2SO_4 (nitration, 9.7B)**
- **[C+ I, C+ Rct] RCl + $AlCl_3$ (Friedel-Crafts alkylation, 9.7C)**
- **[C+ I, C+ Rct] Alkene + H_3PO_4 (alkylation using an alkene, 9.7E)**
- **[C+ I, C+ Rct] ROH + H_3PO_4 (alkylation using an alcohol, 9.7E)**
- **[C+ I] RC(=O)Cl + $AlCl_3$ (Friedel-Crafts acylation, 9.7D)**

- Sample problems: 9.17-9.21, see also 9.22-9.33
- Key background:
  - carbocation-forming reactions (from alkenes – ch. 5, RCl – ch. 7, ROH – ch. 8)
  - carbocation stability ($3^o >> 2^o >> 1^o$)
  - inductive effects
  - resonance effects
  - substituent effects (activating & deactivating) (directing: o/p *v.* m) on benzene ring reactions (9.8)

10 Complete a *partial* reaction recipe by filling in a missing reactant, reagent, or product as needed

11 Given a "convert A into B" problem that cannot be accomplished with a single reagent, draw another compound C that can be used as follows: A→ C → B

- Sample problems: 9.22-9.33, 9.39-9.45, 9.46
- Key background:
  - substituent effects (activating & deactivating) (directing: o/p *v.* m) on benzene ring reactions (9.8)
  - phenols (PhOH) are poor nucleophiles, but their conjugate bases (PhO^-) are moderate nucleophiles (S_N2 & S_N1 reactions)