Chapter 13 Benzene and Its Derivatives

alkiphatic hydrocarbons – include alkanes, alkenes, and alkynes

aromatic hydrocarbons – compounds that contain one or more benzene ring – they are also called arenes

An aromatic hydrocarbon group is called an ary1 group (Ar–)

Benzene -
• the simplest aromatic hydrocarbon with the molecular formula, C₆H₆.
• discovered by Faraday
• should be unsaturated, but does not behave like it is (ex. does not react with Br₂ like alkenes do)
• undergoes substitution reactions rather than addition reactions

\[
\text{C}_6\text{H}_6 + \text{Cl}_2 \rightarrow \text{C}_6\text{H}_5\text{Cl} + \text{HCl} \quad \text{(a Chlorine is substituted for a Hydrogen)}
\]

\text{FeCl}_3 \text{ catalyst}

• Kekule proposed the structure for benzene – a 6 membered ring with alternating double bonds

\[
\text{HC} = \text{C} \quad \text{HC} = \text{C} \quad \text{HC} = \text{C}
\]

• The concept of resonance was developed by Linus Pauling – certain molecules or ions are best described by writing more than one Lewis structure.

• The real molecule is a mixture or hybrid of these resonance structures.

• Each of these resonance hybrids is called a contributing structure.

• In the above figure, there is an aromatic sextet – a closed loop of 6 electrons which is characteristic of benzene rings.

• Compounds with resonance are very stable. The benzene ring is stabilized by resonance.

• These structures do not flip-flop – the double bonds are delocalized or spread out over all 6 carbons.
• The 6 carbons share electrons to create a double donut shaped electron cloud.

• When benzene is drawn, it is understood that true benzene has a structure part way between the possible Lewis structures. The individual Lewis structures do not exist on their own. All of the following are equivalent:

• Aromatic compounds contain delocalized rings of electrons which contribute to resonance.

Naming Benzene Derivatives:

monosubstituted benzenes:

chlorobenzene  nitrobenzene  ethylbenzene  bromobenzene

toluene  phenol  aniline  benzoic acid

benzaldehyde  anisole  acetophenone  styrene
disubstituted benzenes:

- When there are 2 groups, then 3 isomers are possible.

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} \\
\end{align*}
\]

- ortho (1,2) 
  \(o\)-dichlorobenzene 
- meta (1,3) 
  \(m\)-dichlorobenzene 
- para (1,4) 
  \(p\)-dichlorobenzene

- The 3 dimethyl benzenes have the common name, \textit{xylene}.

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]

- \(o\)-xylene 
- \(m\)-xylene 
- \(p\)-xylene

- When one of 2 groups produces a compound that has a common name, use the common name as the parent.

\[
\begin{align*}
\text{Br} & \quad \text{CH}_3 \\
\text{NO}_2 & \quad \text{OH} \\
\end{align*}
\]

- \(o\)-bromotoluene 
- \(p\)-nitrophenol

- When neither group produces a common name compound, then put them in alphabetical order.
• When there are 3 or more groups, use numbers like cycloalkanes.

\[ \text{Br} \quad \text{Br} \quad \text{Br} \quad \begin{array}{c}
\text{NO}_2 \\
\text{H}_2\text{N} \\
\text{NO}_2
\end{array} \quad \text{Br} \quad \text{Cl} \quad \text{Cl} \quad \text{Br} \]

1,2,4–tribromobenzene 2,3–dinitroaniline 1,4–dibromo–2,6–dichlorobenzene

(One of the Br’s is given the number 1 because it comes first alphabetically.)

• When a benzene ring is used as a substituent, it is called a phenyl group, abbreviated Ph–

• Do not confuse a phenyl group with a benzyl group.

\[ \begin{array}{c}
\text{phenyl group} \\
\text{benzyl group}
\end{array} \]

Polynuclear Aromatic Hydrocarbons (PAHs) contain 2 or more aromatic rings. The 3 most common are:

\[ \begin{array}{c}
naphthalene \\
anthracene \\
phenanthrene
\end{array} \]
Reactions of Aromatic Compounds – aromatic substitutions

**Halogenation:**

\[
\text{C}_{6}H_{5} + \text{Br}_{2} \xrightarrow{\text{Fe catalyst}} \text{C}_{6}H_{5}\text{Br} + \text{HBr}
\]

**Nitration:**

\[
\text{C}_{6}H_{5} + \text{HNO}_{3} \xrightarrow{\text{H}_{2}\text{SO}_{4}} \text{C}_{6}H_{5}\text{NO}_{2} + \text{H}_{2}\text{O}
\]

**Sulfonation:**

\[
\text{C}_{6}H_{5} + \text{H}_{2}\text{SO}_{4} \xrightarrow{} \text{C}_{6}H_{5}\text{SO}_{3}\text{H} + \text{H}_{2}\text{O}
\]

Sulfonation is used to make synthetic detergents. They make up 90% of the market once held by soap.

**phenols** - compounds containing -OH connected to an aromatic ring –

- phenols are solids which are soluble in water and will dissolve most easily in a basic solution –
- phenol itself is toxic
- The most important property of phenols is that they are weak acids.

Phenol can also refer to a class of compounds with the structure.

Phenols are widely found in nature (ex. capsaicin – the chemical which makes peppers hot)

carbolic acid - an aqueous solution of phenol used as an antiseptic.
tricky naming stuff:

3-methylphenol  
m-cresol

1,3-Benzenediol

**Remember:** Alcohols are neutral, but phenols are acidic.

Phenols will react with strong bases to form salts. Most do not react with weak bases.

**acid–base reaction:**

\[
\text{phenol} + \text{NaOH} \rightarrow \text{phenoxide} + \text{H}_2\text{O}
\]

Triclosan, a phenol compound, is an antiseptic and disinfectant commonly used in deodorant products.