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
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°

Cyclohexane-Chair conformation

Benzene- “flat” unsaturated system
**Benzene – Molecular Orbitals**

The $\pi$ 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

![Diagram of benzene molecular orbitals](image)

**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

![Diagram of benzene resonance model](image)
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.

\[ \text{Cyclohexene} + 3\text{H}_2 \rightarrow \text{Cyclohexatriene (hypothetical)} + 3\text{H}_2 \]

\[ \Delta H = -359.0 \text{ kJ/mol (calculated)} \]

\[ \Delta H = 3(-119.7 \text{ kJ/mol}) \]

\[ \Delta H = -208.4 \text{ kJ/mol} \]

\[ \Delta H = 150.6 \text{ kJ/mol} \]
**Nomenclature-Monosubstituted**

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

![Chemical structures and names](image)

(commit to memory)

---

**Benzyl and phenyl groups:**

![Chemical structures and names](image)
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:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Bromotoluene</td>
<td>4-Bromoanisole (p-Bromotoluene)</td>
</tr>
<tr>
<td>3-Chloroaniline</td>
<td>3-Chloroaniline (m-Chloroaniline)</td>
</tr>
<tr>
<td>2-Nitrobenzoic acid</td>
<td>2-Nitrobenzoic acid (o-Nitrobenzoic acid)</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>m-Xylene</td>
</tr>
</tbody>
</table>

Toluene is the parent name
Aniline is the parent name
Benzoic Acid is the parent name
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)

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)
Acidity of Phenols

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

Phenoxide:

\[
\text{Phenoxide:} \quad \begin{align*}
\text{Phenol} + \text{H}_2\text{O} & \rightleftharpoons \text{Phenoxide}^\text{-} + \text{H}_3\text{O}^+ \\
\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} & \rightleftharpoons \text{CH}_3\text{CH}_2\text{O}^\text{-} + \text{H}_3\text{O}^+ 
\end{align*}
\]

\[pK_a = 9.95 \quad \text{and} \quad pK_a = 15.9\]

Ethoxide

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
**Acidity of Phenols**

Alkyl and halogen substituents effect acidities by inductive effects:

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

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Structure</th>
<th>$pK_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td><img src="image" alt="Phenol" /></td>
<td>9.95</td>
</tr>
<tr>
<td>$m$-Cresol</td>
<td><img src="image" alt="m-Cresol" /></td>
<td>10.01</td>
</tr>
<tr>
<td>$p$-Cresol</td>
<td><img src="image" alt="p-Cresol" /></td>
<td>10.17</td>
</tr>
<tr>
<td>$m$-Chlorophenol</td>
<td><img src="image" alt="m-Chlorophenol" /></td>
<td>8.85</td>
</tr>
<tr>
<td>$p$-Chlorophenol</td>
<td><img src="image" alt="p-Chlorophenol" /></td>
<td>9.18</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Structure</th>
<th>$pK_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td><img src="image" alt="Phenol" /></td>
<td>9.95</td>
</tr>
<tr>
<td>$m$-Nitrophenol</td>
<td><img src="image" alt="m-Nitrophenol" /></td>
<td>8.28</td>
</tr>
<tr>
<td>$p$-Nitrophenol</td>
<td><img src="image" alt="p-Nitrophenol" /></td>
<td>7.15</td>
</tr>
</tbody>
</table>
Acidity of Phenols

- part of the acid-strengthening effect of -NO₂ is due to its electron-withdrawing inductive effect
- in addition, -NO₂ substituents in the ortho and para positions help to delocalize the negative charge

Acidity of Phenols

- Phenols are weak acids and react with strong bases to form water-soluble salts
  - water-insoluble phenols dissolve in NaOH(aq)
Acidity of Phenols

– most phenols do not react with weak bases such as NaHCO₃; they do not dissolve in aqueous NaHCO₃

\[
\text{Phenol} \quad \text{NaHCO}_3 \quad \text{Sodium phenoxide} \quad \text{Carbonic acid}
\]

\[
\begin{align*}
\text{Phenol} &\quad \text{NaHCO}_3 \quad \text{Sodium phenoxide} \\
p K_a &\quad 9.95 &\quad (\text{weaker acid}) \\
\end{align*}
\]

\[
\begin{align*}
\text{Phenol} &\quad \text{NaHCO}_3 \quad \text{Sodium phenoxide} \\
\end{align*}
\]

\[
\begin{align*}
\text{Phenol} &\quad \text{NaHCO}_3 \quad \text{Sodium phenoxide} \\
\end{align*}
\]

\[
\begin{align*}
\text{Phenol} &\quad \text{NaHCO}_3 \quad \text{Sodium phenoxide} \\
\end{align*}
\]

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 \( S_N2 \) reactions

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

\[
\begin{align*}
\text{Phenol} &\quad \text{Alkoxy} \\
\end{align*}
\]
Alkyl-Aryl Ethers

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

\[
\text{Phenol} + \text{3-Chloropropene (Allyl chloride)} \xrightarrow{\text{NaOH, H}_2\text{O, CH}_2\text{Cl}_2, \text{Bu}_4\text{N}^+\text{Br}^-} \text{Phenyl 2-propenyl ether (Allyl phenyl ether)}
\]

\[
\text{Phenol} + \text{Dimethyl sulfate} \xrightarrow{\text{NaOH, H}_2\text{O, CH}_2\text{Cl}_2, \text{Bu}_4\text{N}^+\text{Br}^-} \text{Methyl phenyl ether (Anisole)}
\]

Benzylic Oxidation

- Benzene is unaffected by strong oxidizing agents such as \( \text{H}_2\text{CrO}_4 \) and \( \text{KMnO}_4 \)
  - 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

\[
\text{Benzenoid} \xrightarrow{\text{H}_2\text{CrO}_4 \text{ or } \text{KMnO}_4} \text{Benzoic Acid}
\]
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.

\[
\begin{align*}
\text{Toluene} + \text{Cl}_2 & \xrightarrow{\text{heat or light}} \text{Benzyl chloride} \\
\text{Arene} + \text{X}_2 & \xrightarrow{\text{heat or h}} \text{Benzyl Halides}
\end{align*}
\]
Benzylic Bromination

- Bromination can be conducted with NBS:

  ![Reaction Scheme](image)

  - Ethylbenzene + NBS, (PhCO₂)₂, CCl₄ → 1-Bromo-1-phenylethane (racemic)

Benzoyl Peroxide as a Radical Initiator

- Benzoyl peroxide can act as a radical initiator:
  - Benzoyl peroxide → Phenyl radical
**Benzylic Reactions**

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

  ![Resonance Structures of Benzylic Radical]

**Benzylic Halogenation**

- **Benzylic bromination** is highly regioselective

  ![Benzylic Bromination Reaction]

- **Benzylic chlorination** is less regioselective

  ![Benzylic Chlorination Reaction]
**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

- ![Hydrogenolysis Reaction Equation](image)

**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

- ![Benzyl Ether Reaction Equations](image)