FROM LAST LECTURE:

ELECTROPHILIC ADDITION:

\[ \text{H}_2 / \text{Pd catalyst} \]

\[ \text{Br} \]

\[ \text{dil. H}_2\text{SO}_4 \]

\[ \text{HBr} \]
AROMATIC COMPOUNDS

Benzene $C_6H_6$

Kekule proposed the structure in 1865
Benzene does not behave like cyclohexatriene

<table>
<thead>
<tr>
<th>$\text{Br}_2$</th>
<th></th>
<th></th>
</tr>
</thead>
</table>

H$_2$ with a Pd/C catalyst

The reactions of benzene are not like an alkene at all!

<table>
<thead>
<tr>
<th>carbon-carbon bond</th>
<th>Bond length</th>
<th>Bond strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C (alkane)</td>
<td>154 pm</td>
<td>356 kJ/mol</td>
</tr>
<tr>
<td>C=C (alkene)</td>
<td>133 pm</td>
<td>636 kJ/mol</td>
</tr>
<tr>
<td>benzene</td>
<td>139 pm</td>
<td>518 kJ/mol</td>
</tr>
</tbody>
</table>

Benzene has special properties - it is aromatic.

Benzene’s Unusual Structure
- All its C-C bonds are the same length: 139 pm — between single (154 pm) and double (134 pm) bonds
- Electron density in all six C-C bonds is identical
- Structure is planar, hexagonal
- C–C–C bond angles 120°
• Each of the 6 carbon atoms in benzene is sp\(^2\) hybridised
• Each carbon forms σ-bonds to two neighbouring carbon atoms and a σ-bond to one hydrogen atom
• Each carbon atom has a p-orbital, which can participate in π-bonding giving 3 π-bonds (the p orbitals are perpendicular to the plane of the six-membered ring)

This representation gives alternating single and double bonds, BUT:
There are two possible representations we can draw for benzene with the $\pi$-bonds in different positions. These two structures are related by movement of electron pairs in the $\pi$-bonds:

$$\begin{array}{c}
1 \quad 2 \\
5 \quad 4 \\
\text{ } \\
3 \\
6
\end{array} \quad \leftrightarrow \quad \begin{array}{c}
6 \\
5 \\
\text{ } \\
4 \\
1
\end{array}$$

These structures are called resonance forms of benzene.

Bonding in benzene should be thought of as an average of these two resonance forms or a resonance hybrid.

The resonance hybrid will have:
- half a $\pi$-bond between each adjacent pair of carbons
- a bond strength and bond length between that of a C-C single bond (no $\pi$-bond) and a C=C double (one $\pi$-bond)

*Resonance structures are imaginary, not real:* Benzene has a single unchanging hybrid structure that is the average of the resonance forms.

*Resonance structures differ only in the position of their $\pi$-electrons:* Benzene is a perfect hexagon with all carbon-carbon bond lengths identical (139 pm). Curly arrows denote the movement of electron pairs only, NOT atoms.

i.e. Benzene is NOT:

$$\begin{array}{c}
6 \\
5 \\
\text{ } \\
4 \\
1
\end{array} \quad \leftrightarrow \quad \begin{array}{c}
1 \quad 2 \\
5 \quad 4 \\
\text{ } \\
3 \\
6
\end{array}$$

The more resonance structures there are, the more stable the molecule: Benzene has two identical resonance structures and is 150 kJ mol$^{-1}$ more stable than the energy predicted for 1,3,5-cyclohexatriene.
The benzene ring contains six sp² hybridised carbon atoms, each with a p-orbital which forms part of a delocalised π–bond system characteristic of aromatic compounds. The electron delocalisation results in a stabilisation of 150 kJ/mol compared to the hypothetical cyclohexatriene structure.

**Localised electrons** = constrained to one atom or shared between two atoms

**Delocalised electrons** = shared between three or more atoms = greater stability

### Nomenclature

(i) Prefix + benzene for substituents F, Cl, Br, I, NO₂

![Nitrobenzene](image1)

![Fluorobenzene](image2)

(ii) Common names for some derivatives (must be learnt):

![Phenol](image3)

![Amine](image4)

![Methylbenzene](image5)

![Carboxylic acid](image6)

![Formaldehyde](image7)
(iii) Disubstituted systems

Two substituents in the:
- 1,2- positions referred to as ortho- or o-,
- 1,3- positions referred to as meta- or m-,
- 1,4- positions referred to as para- or p-.

(iv) Three or more substituents: use numbers

NOTE
- phenyl substituent abbreviated as Ph-
- benzyl group
Reactions of Benzene

Like alkenes, the \( \pi \)-electrons are available for reaction and benzene can react with electrophiles.

Aromatic compounds undergo *electrophilic substitution* reactions (NOT *electrophilic addition*).

Electrophilic substitution preserves the special stability associated with the aromatic nature of the compound.

Examples of Electrophilic Substitution

(i) Nitration

\[
\text{HNO}_3 + 2 \text{H}_2\text{SO}_4 \rightleftharpoons \text{NO}_2^+ + \text{H}_3\text{O}^+ + 2 \text{HSO}_4^- \\
\text{nitronium ion}
\]
(ii) Bromination

\[
\text{Br}_2 + \text{FeBr}_3 \rightarrow \text{Br} \text{Br} + \text{FeBr}_4
\]

Bromonium ion

\[
\begin{align*}
\text{nucleophile} & \quad \text{electrophile} \\
\text{Br} + \text{FeBr}_4 & \rightarrow \text{Br} \text{Br} + \text{FeBr}_4
\end{align*}
\]
(iii) Chlorination

\[
\text{C}_6\text{H}_6 + \text{Cl}_2 \xrightarrow{\text{FeCl}_3} \text{C}_6\text{H}_5\text{Cl}
\]

(iv) Friedel-Crafts Acylation

\[
\text{C}_6\text{H}_6 + \text{R}\text{COCl} \xrightarrow{\text{AlCl}_3} \text{C}_6\text{H}_5\text{RCO}
\]

\[
\text{R}\text{COCl} + \text{AlCl}_3 \Rightarrow \text{R}\text{COAlCl}_2
\]

\[
\text{R}\text{COAlCl}_2 \xrightarrow{\text{AlCl}_3} \text{R}\text{CO} + \text{AlCl}_4^-
\]

Step 1: Nucleophile approaches electrophile

Step 2: Aromatic ring substitution

\[
\text{H}_2\text{C}_6\text{H}_4\text{H}_2 + \text{R}\text{CO} \xrightarrow{\text{AlCl}_4} \text{H}_2\text{C}_6\text{H}_3\text{R} = \text{H}_2\text{C}_6\text{H}_3\text{R} \xrightarrow{\text{H}^+} \text{H}_2\text{C}_6\text{H}_2\text{R}
\]
What reagents would you use for this reaction?
Aromaticity

Benzene more stable than a hypothetical cyclohexatiene by 150 kJ/mol

Generally, **for a compound to be aromatic** like benzene, four criteria are necessary:
1) molecule must be cyclic (i.e. ring or **fused** ring structures)
2) all atoms in the ring(s) must be sp² hybridised with a p-orbital perpendicular to the ring(s)
3) the ring(s) must be planar
4) AND there must be **4n + 2** π-electrons
   (n=0, 1, 2, 3 ... ; *i.e.* there must be 2, 6, 10, 14 ....π-electrons)

Are these compounds aromatic?
Aromatic Heterocycles

Some definitions:

**Heterocyclic compounds** contain elements in addition to carbon such as N, S, O, P - together they form a ring.

**Aromatic Heterocycles** are aromatic compounds that have elements in addition to carbon in the ring.

There are many heterocyclic aromatic compounds and many are very common.

Nomenclature is specialized

**Aromatic Heterocycles** contain one or more heteroatoms (usually O, N, or S) in the ring

![Pyridine structure](image)

N is sp² hybridised. There are 6 π-electrons in the aromatic system. The N lone pair is in an sp² orbital perpendicular to the π-system. As a result the N lone pair is available for reaction, e.g. nitrogen is basic:

![Reaction](image)

(product still aromatic)
N is sp$^2$ hybridised. The N lone pair is in a p-orbital and is part of the 6 $\pi$-electrons in the aromatic system. As a result it is not available for reaction, i.e. pyrrole is not basic:

\[
\text{HCl} \quad \xrightarrow{\text{X}} \quad \text{HN}^+ \text{Cl}^- \quad \text{(non-aromatic product)}
\]

O is sp$^2$ hybridised. One O lone pair is in a p-orbital and is part of the 6 $\pi$-electrons in the aromatic system. The other O lone pair is in an sp$^2$ orbital and not part of the aromatic system.

S is sp$^2$ hybridised. One S lone pair is in a p-orbital and is part of the 6 $\pi$-electrons in the aromatic system. The other S lone pair is in an sp$^2$ orbital and not part of the aromatic system.
N1 is analogous to the N of pyrrole (i.e. unreactive), while N3 is analogous to the N of pyridine, i.e. it will be basic:

The imidazole ring is found in the amino acid histidine:

Pyrimidine - 6 $\pi$-electron aromatic structure. Both N's are like the N of pyridine, i.e. they are basic.

Purine - 10 $\pi$-electron aromatic structure. N's 1, 3 and 9 are like the N of pyridine, i.e. they are basic. N 7 is like the N of pyrrole, i.e. non-basic.

Derivatives of purine and pyrimidine form the bases in DNA and RNA.