6.1.1 Aromatic Compounds

There are two major classes of organic chemicals: 

- **aliphatic**: straight or branched chain organic substances 
- **aromatic or arene**: includes one or more ring of six carbon atoms with delocalised bonding.

Benzene’s Structure

The simplest arene is benzene. It has the molecular formula $C_6H_6$. Its basic structure is six C atoms in a hexagonal ring, with one H atom bonded to each C atom. Each C atom is bonded to two other C atoms and one H atom by single covalent $\sigma$-bonds. This leaves one unused electron on each C atom in a p orbital, perpendicular to the plane of the ring. The Six p electrons are delocalised in a ring structure above and below the plane of carbon atoms.

Benzene belongs to the aromatic class.

In 1865 Kekule suggested the following structure for Benzene consisting of alternate single and double covalent bonds between the carbon atoms.

This structure is not correct. Evidence suggests that all the C-C bonds are the same length.

In formulae we draw a circle to show this delocalised system.

The six electrons in the pi bonds are delocalised and spread out over the whole ring. Delocalised means not attached to a particular atom.

Benzene is a planar molecule. The evidence suggests all the C-C bonds are the same and have a length and bond energy between a C-C single and C=C double bond.

The H-C-C bond angle is 120° in Benzene.

Enthalpies of Hydrogenation

Theoretically because there are 3 double bonds one might expect the amount of energy to be 3 times as much.

However, the real amount of energy is less. The 6 pi electrons are delocalised and not arranged in 3 double bonds.

This when represented on an energy level diagram shows that the delocalised benzene is more thermodynamically stable.

The increase in stability connected to delocalisation is called the **delocalisation energy**.

Summary of evidence for why benzene has a delocalised structure.

- Bond length intermediate between short C=C and long C–C
- $\Delta H$ hydrogenation less exothermic than expected when compared to $\Delta H$ hydrogenation for kekule structure
- Only reacts with Br$_2$ at high temp or in presence of a halogen carrier
Naming aromatic molecules

Naming aromatic compounds can be complicated. The simplest molecules are derivatives of benzene and have benzene at the root of the name.

- CH₃Cl
- C₂H₅Br
- NO₂
- CO₂H
- CHO

Methylbenzene, ethylbenzene, chlorobenzene, bromobenzene, nitrobenzene, benzenecarboxylic acid, benzaldehyde

- CH₃CH₃
- CH₃Cl
- COOH
- O₂N

1,3-dimethylbenzene, 1-chloro-4-methylbenzene, 4-hydroxybenzenecarboxylic acid, 2,4,6-trinitromethylbenzene

If two or more substituents are present on the benzene ring, their positions must be indicated by the use of numbers. This should be done to give the lowest possible numbers to the substituents. When two or more different substituents are present, they are listed in alphabetical order and di, tri prefixes should be used.

- NH₂
- CH=CH₂
- CH₃CH=CH₂CH₃
- O

Phenylamine, phenylethene, 2-phenylbutane, phenylethanone, phenylethanoate

Reactions of Benzene

Benzene does not generally undergo addition reactions because these would involve breaking up the delocalised system. Most of Benzene’s reactions involve substituting one H for another atom or group of atoms. Its reactions are usually electrophilic substitutions.

Comparison of Benzene with alkenes: reaction with Bromine

Alkenes react with Bromine easily at room temperature. Benzene does not react with Bromine without additional halogen carrier chemicals.

In benzene, electrons in π-bond(s) are delocalised. In alkenes, π-electrons are localised between two carbons. Benzene therefore has a lower electron density than C=C. Benzene therefore polarises bromine less and induces a weaker dipole in bromine than an alkene would.

Toxicity of Benzene

Benzene is a carcinogen (cancers causing molecule) and is banned for use in schools. Methylbenzene is less toxic and also reacts more readily than benzene as the methyl side group releases electrons into the delocalised system making it more attractive to electrophiles.
Nitration of Benzene

**Change in functional group:** benzene $\rightarrow$ nitrobenzene

**Reagents:** conc nitric acid in the presence of concentrated sulphuric acid (catalyst)

**Mechanism:** Electrophilic Substitution

**Electrophile:** NO$_2^-$

**Overall Equation for reaction**

$$\ce{C6H6 + NO2^+ -> C6H5NO2 + H^+}$$

**Equation for Formation of electrophile: (Learn!)**

$$\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^{2+} + 2\text{HSO}_4^- + \text{H}_3\text{O}^+$$

**Mechanism**

The H$^+$ ion rejoins with the HSO$_4^-$ to reform H$_2$SO$_4$ catalyst.

$$\text{H}^+ + \text{HSO}_4^- \rightarrow \text{H}_2\text{SO}_4$$

**Importance of this reaction**

Nitration of benzene and other arenes is an important step in synthesising useful compounds e.g. explosive manufacture (like TNT, trinitrotoluene/2,4,6-trinitromethylbenzene) and formation of amines from which dyestuffs are manufactured. (The reaction for this is covered in the amines section.)

**Halogenation of Benzene**

**Change in functional group:** benzene $\rightarrow$ Bromobenzene

**Reagents:** Bromine

**Conditions:** iron(III) bromide catalyst FeBr$_3$

**Mechanism:** Electrophillic Substitution

**Overall Equation for reaction**

$$\ce{C6H6 + Br2 -> C6H5Br + HBr}$$

**Equation for Formation of electrophiles: (Learn!)**

$$\text{AlCl}_3 + \text{Cl}_2 \rightarrow \text{AlCl}_4^- + \text{Cl}^+$$

$$\text{FeBr}_3 + \text{Br}_2 \rightarrow \text{FeBr}_4^- + \text{Br}^+$$

**Mechanism**

The H$^+$ ion reacts with the AlCl$_4^-$ to reform AlCl$_3$ catalyst and HCl.

$$\text{H}^+ + \text{AlCl}_4^- \rightarrow \text{AlCl}_3 + \text{HCl}$$

**This reaction can be done with chlorine.**

The catalyst can be AlCl$_3$ or FeCl$_3$

If the benzene ring already has a side group e.g. methyl then the Nitro group can also join on different positions. A-level does not require knowledge of what positions the groups go on.
Friedel Crafts Alkylation

**Change in functional group:** benzene → alkylbenzene  
**Reagents:** chloroalkane in the presence of anhydrous aluminium chloride catalyst  
**Conditions:** heat under reflux  
**Mechanism:** Electrophilic Substitution

Any chloroalkane can be used RCl where R is any alkyl group e.g. \(-\text{CH}_3, -\text{C}_2\text{H}_5\). The electrophile is the R⁺.

### Formation of the electrophile.
\[ \text{AlCl}_3 + \text{CH}_3\text{CH}_2\text{Cl} \rightarrow \text{CH}_3\text{CH}_2^+\text{AlCl}_4^- \]

### Overall Equation for reaction
\[ \text{CH}_3\text{CH}_2^+\text{AlCl}_4^- + \text{benzene} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 + \text{AlCl}_3 + \text{HCl} \]

### Mechanism
The H⁺ ion reacts with the AlCl₄⁻ to reform AlCl₃ catalyst and HCl.

\[ \text{H}^+ + \text{HCl} \]

Friedel Crafts Acylation

**Change in functional group:** benzene → phenyl ketone  
**Reagents:** acyl chloride in the presence of anhydrous aluminium chloride catalyst  
**Conditions:** heat under reflux (50°C)  
**Mechanism:** Electrophilic Substitution

Any acyl chloride can be used RCOCl where R is any alkyl group e.g. –CH₃, -C₂H₅. The electrophile is the RCO⁺.

### Equation for Formation of the electrophile.
\[ \text{AlCl}_3 + \text{CH}_3\text{COCl} \rightarrow \text{CH}_3\text{CO}^+\text{AlCl}_4^- \]

### Overall Equation for reaction
\[ \text{CH}_3\text{CO}^+\text{AlCl}_4^- + \text{benzene} \rightarrow \text{CH}_3\text{C}═\text{O} + \text{AlCl}_3 + \text{HCl} \]

### Mechanism
The H⁺ ion reacts with the AlCl₄⁻ to reform AlCl₃ catalyst and HCl.

\[ \text{H}^+ + \text{HCl} \]
Phenols

In a phenol the OH group is directly attached to the benzene ring.

In a phenol the lone pair of electrons on the oxygen is delocalised with the electron charge cloud of the arene ring. The delocalised bonding changes the reactivity of the OH group and the arene ring.

Phenols are very weakly acidic. They are weaker acids than carboxylic acids. Both phenols and carboxylic acids will react with sodium metal and sodium hydroxide. Only carboxylic acids will react with sodium carbonate as a phenol is not strong enough an acid to react.

\[ \text{Phenol} + \text{Na} \rightarrow \text{Phenoxide} + \frac{1}{2} \text{H}_2 \]

\[ \text{Phenol} + \text{NaOH} \rightarrow \text{Phenoxide} + \text{H}_2\text{O} \]

Reagents: \( \text{Br}_2 \)

Conditions: room temp

Phenol does not need a \( \text{FeBr}_3 \) catalyst like benzene and undergoes multiple substitution whereas benzene will only add one Br.

The product in this reaction is a white solid.

2,4,6-tribromophenol

Phenols are used in the production of plastics, antiseptics, disinfectants and resins for paints.
Reaction of Phenol with Nitric acid

In comparison with benzene, phenol does not need concentrated nitric acid or the concentrated sulphuric acid catalyst

With 4M HNO₃ single substitution occurs (in comparison to the conc HNO₃ needed for benzene)
Reagent 4M HNO₃
Conditions: room temp

Effect of side groups on substitution

Side groups on a benzene ring can affect the position on the ring of substitution reactions.

Electron-donating groups such as OH, NH₂ will force further substitutions to occur on the 2- and 4- positions of the ring

Electron-withdrawing groups (such as NO₂) will have a 3-directing effect of in electrophilic substitution of aromatic compounds