## 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.

All of the organic substances we have looked at so far have been aliphatic

Benzene belongs to the aromatic class.

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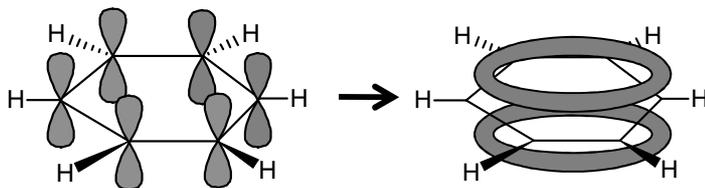
In 1865 Kekule suggested the following structure for Benzene consisting of alternate single and double covalent bonds between the carbon atoms
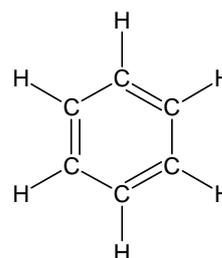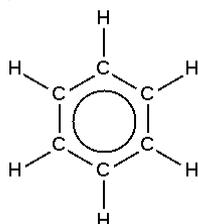

This structure is not correct. Evidence suggests that all the C-C bonds are the same length.

In formulae we draw a circle to show this delocalised system


Abbreviated formula

Displayed formula

The six electrons in the pi bonds are delocalised and spread out over the whole ring. Delocalised means not attached to a particular atom.
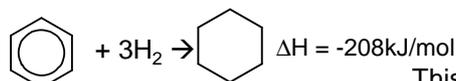
Benzene is a **planar** molecule. The evidence suggests all the C-C bonds are the same and have a length and bond energy between a C-C single and C=C double bond

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

Enthalpies of Hydrogenation

 + H$_2$ → ΔH = -120 kJ/mol

cyclohexene   cyclohexane   ↓ x3

 + 3H$_2$ → ΔH = -360 kJ/mol
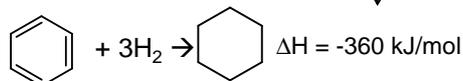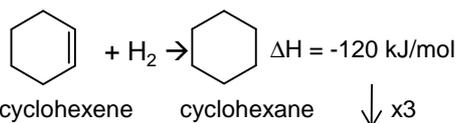
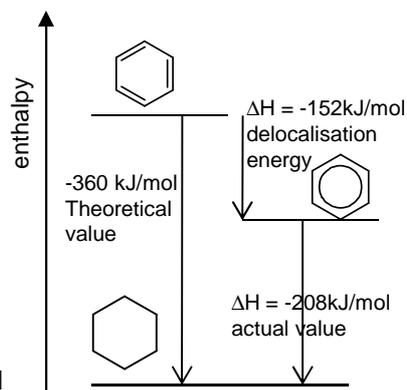Non delocalised structure

 + 3H$_2$ → ΔH = -208kJ/mol

delocalised structure

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.
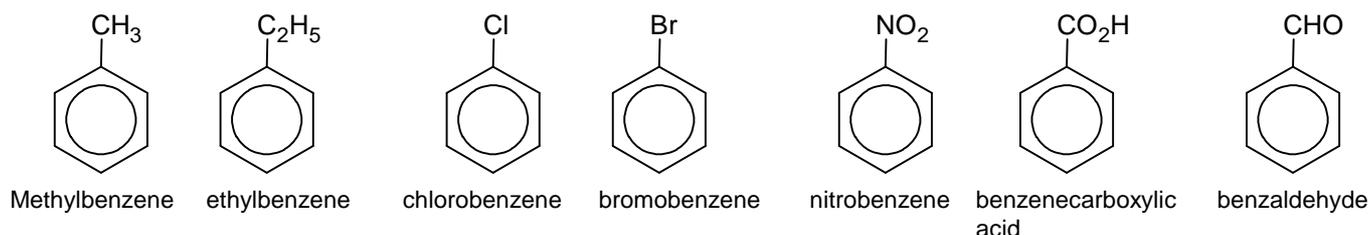

ΔH = -152kJ/mol delocalisation energy

-360 kJ/mol Theoretical value

ΔH = -208kJ/mol actual value

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

Summary of evidence for why benzene has a delocalised structure.
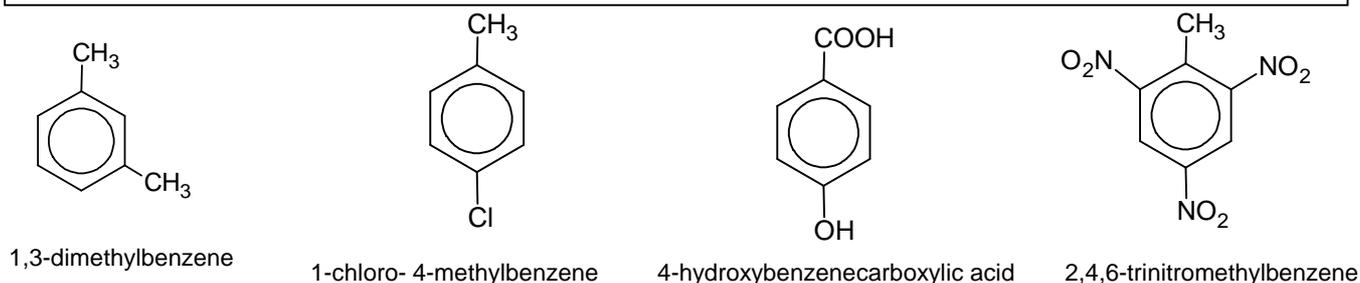* Bond length intermediate between short C=C and long C–C
* ΔH hydrogenation less exothermic than expected when compared to ΔH hydrogenation for kekule structure
* Only reacts with Br$_2$ at high temp or in presence of a halogen carrier

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

CH_3	C_2H_5	Cl	Br	NO_2	CO_2H	CHO
Methylbenzene	ethylbenzene	chlorobenzene	bromobenzene	nitrobenzene	benzenecarboxylic acid	benzaldehyde

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.

1,3-dimethylbenzene

1-chloro- 4-methylbenzene

4-hydroxybenzenecarboxylic acid

2,4,6-trinitromethylbenzene

In other molecules the benzene ring can be regarded as a substituent side group on another molecule, like alkyl groups are. The C_6H_5- group is known as the **phenyl** group.

phenylamine

phenylethene

2-phenylbutane

phenylethanone

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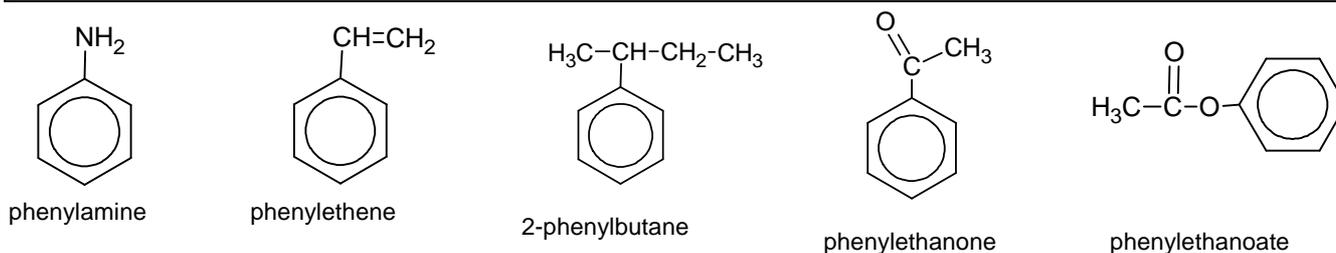
Reactions of Benzene
Benzene does not generally undergo addition reactions because these would involve breaking up the delocalised system. Most of Benzene's reactions involve substituting one H for another atom or group of atoms. It reactions are usually **electrophilic substitutions.**

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.

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.

Nitration of Benzene

Change in functional group: benzene → nitrobenzene
Reagents: conc nitric acid in the presence of concentrated sulphuric acid (catalyst)
Mechanism: Electrophilic Substitution
**Electrophile: NO_2^+**
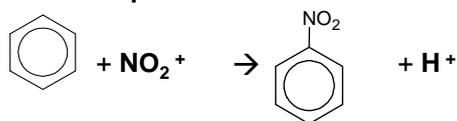
Importance of this reaction
Nitration of benzene and other arenes is an important step in synthesising useful compounds
e.g. explosive manufacture (like TNT, trinitrotoluene/ 2,4,6-trinitromethylbenzene)
and formation of amines from which dyestuffs are manufactured. (The reaction for this is covered in the amines section.)

Overall Equation for reaction

$$+ NO_2^+ \rightarrow \quad + H^+$$

Equation for Formation of electrophile: (Learn!)
$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$

Mechanism

$+ H^+$
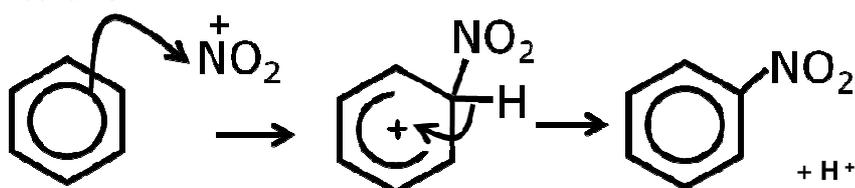
The horseshoe shape of the intermediate must not extend beyond C's 2 to 6

The H^+ ion rejoins with the HSO_4^- to reform H_2SO_4 catalyst.

$$H^+ + HSO_4^- \rightarrow H_2SO_4$$
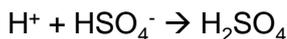
This reaction is done at 60°C. On using higher temperatures a second nitro group can be substituted onto different positions on the ring

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.

Halogenation of Benzene

Change in functional group: benzene → Bromobenzene
Reagents: Bromine
Conditions: iron(III) bromide catalyst $FeBr_3$
Mechanism: Electrophillic Substitution

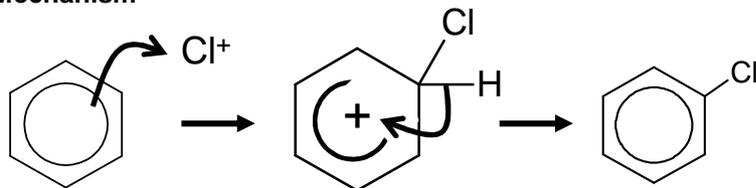This reaction can be done with chlorine. The catalyst can be $AlCl_3$ or $FeCl_3$
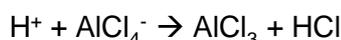
Overall Equation for reaction

$$+ Br_2 \rightarrow \quad + HBr$$
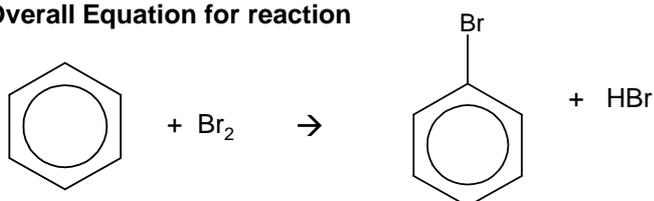
Equation for Formation of electrophiles: (Learn!)
$AlCl_3 + Cl_2 \rightarrow AlCl_4^- + Cl^+$
$FeBr_3 + Br_2 \rightarrow FeBr_4^- + Br^+$
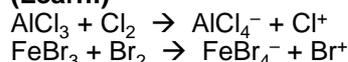
Mechanism

The H^+ ion reacts with the $AlCl_4^-$ to reform $AlCl_3$ catalyst and HCl.
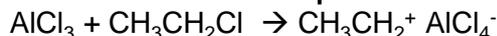
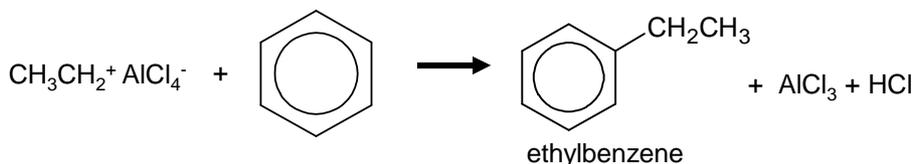$$H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$$

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 Eg –CH_3 , -C_2H_5. The electrophile is the R^+.

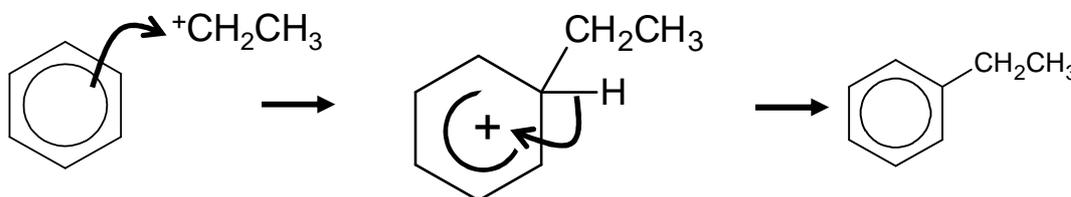**Formation of the electrophile.**
$AlCl_3 + CH_3CH_2Cl \rightarrow CH_3CH_2^+ AlCl_4^-$

Overall Equation for reaction

$CH_3CH_2^+ AlCl_4^-$ + ⬡ → ⬡ CH_2CH_3 + $AlCl_3$ + HCl

ethylbenzene

Mechanism

The H^+ ion reacts with the $AlCl_4^-$ to reform $AlCl_3$ catalyst and HCl.
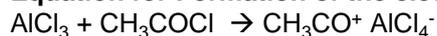
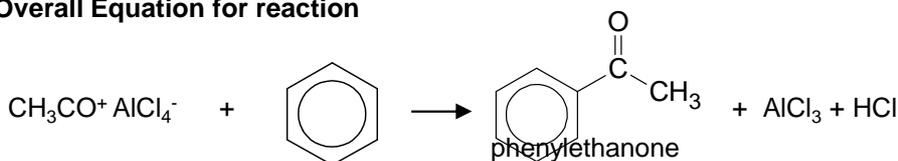$H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$

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^OC)
Mechanism: Electrophilic Substitution

Any acyl chloride can be used RCOCl where R is any alkyl group e.g. –CH_3 , -C_2H_5. The electrophile is the RCO^+.

Equation for Formation of the electrophile.
$AlCl_3 + CH_3COCl \rightarrow CH_3CO^+ AlCl_4^-$

Overall Equation for reaction

$CH_3CO^+ AlCl_4^-$ + ⬡ → phenylethanone + $AlCl_3$ + HCl
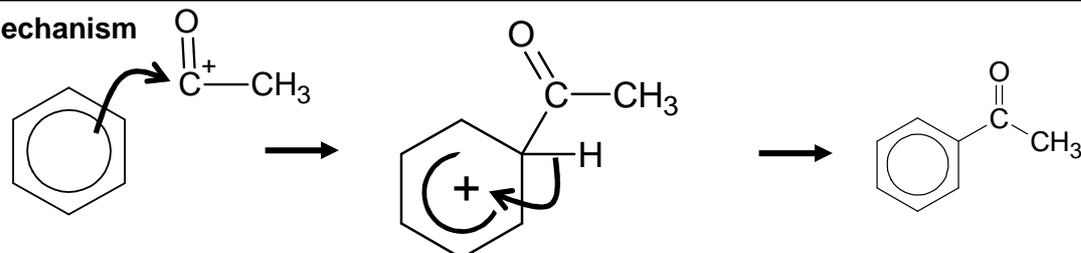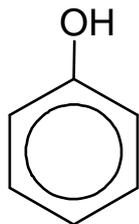
These are important reactions in organic synthesis because they introduce a reactive functional group on to the benzene ring

Mechanism

The H^+ ion reacts with the $AlCl_4^-$ to reform $AlCl_3$ catalyst and HCl.

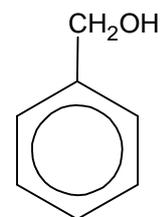$H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$

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.

This is not a phenol, but is an alcohol because the OH group is attached to an alkyl group rather than the benzene 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.
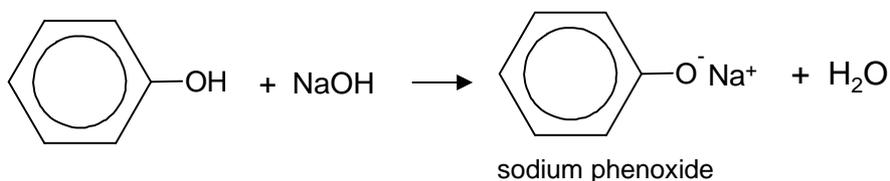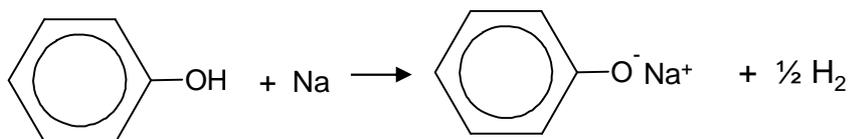
sodium phenoxide

The sodium phenoxide compound is more soluble than the original phenol. So the solid phenol dissolves on addition of NaOH

Reaction with Bromine

Reagents: Br_2
Conditions: room temp

2,4,6 –tribromophenol
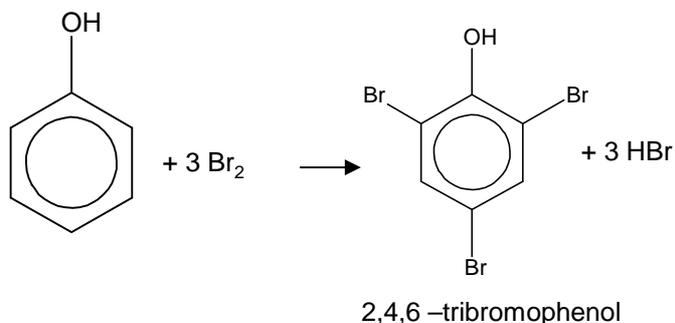
Phenol does not need a $FeBr_3$ catalyst like benzene and undergoes multiple substitution whereas benzene will only add one Br.

The product in this reaction is a white solid

In phenol the lone pair of electrons on the oxygen (p- orbital) is partially **delocalised** into the ring. The electron density increases and the Br_2 is more polarised

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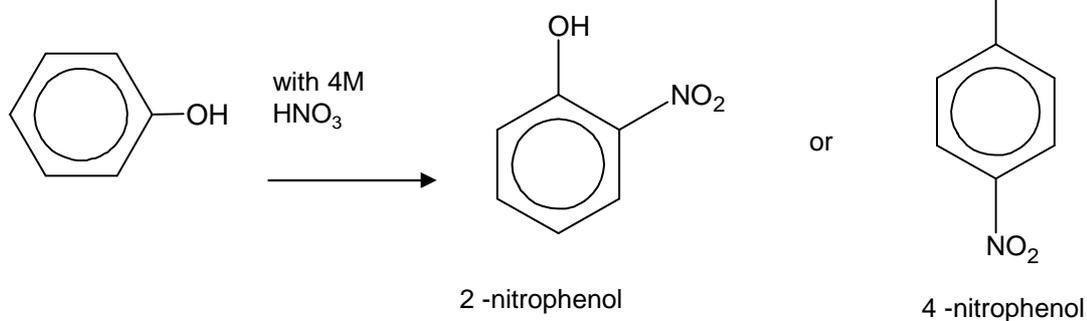
Reaction of Phenol with Nitric acid

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

With 4M HNO_3 single substitution occurs (in comparison to the conc HNO_3 needed for benzene)
Reagent 4M HNO_3
Conditions: room temp

2 -nitrophenol

4 -nitrophenol

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, NH_2 will force further substitutions to occur on the 2- and 4- positions of the ring

2 -nitrophenol

4 -nitrophenol
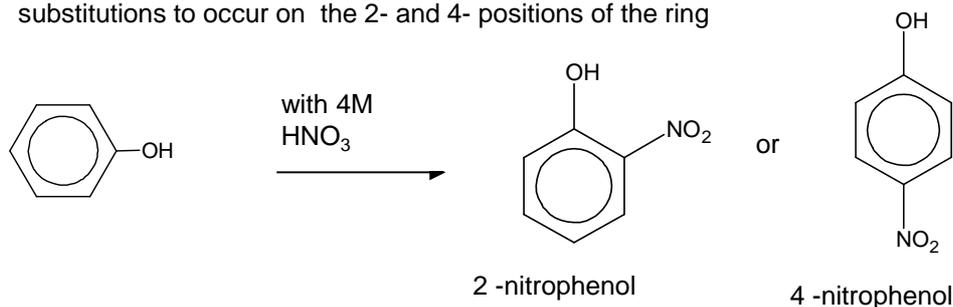
Electron-withdrawing groups (such as NO_2) will have a 3-directing effect of in electrophilic substitution of aromatic compounds

$+ Cl_2$

$AlCl_3$ catalyst