

3. Arenes

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

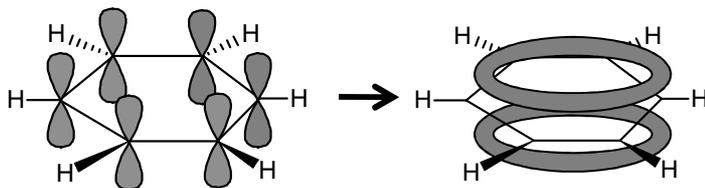
Benzene belongs to the aromatic class.

Benzene's Structure

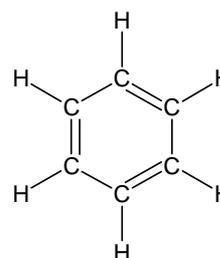
The simplest arene is benzene. It has the molecular formula C_6H_6 . Its basic structure is six C atoms in a hexagonal ring, with one H atom bonded to each C atom.

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.

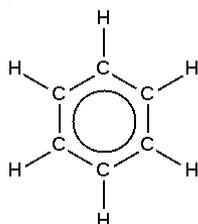


This structure is not correct. Evidence suggests that all the C-C bonds are the same length.

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



Abbreviated formula



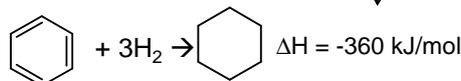
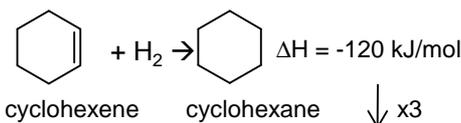
Displayed formula

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

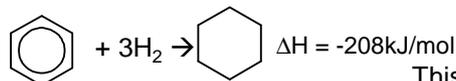
Benzene is a **planar** molecule. The evidence suggests all the C-C bonds are the same and have a length and bond energy between a C-C single and C=C double bond.

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

Enthalpies of Hydrogenation



Non delocalised structure

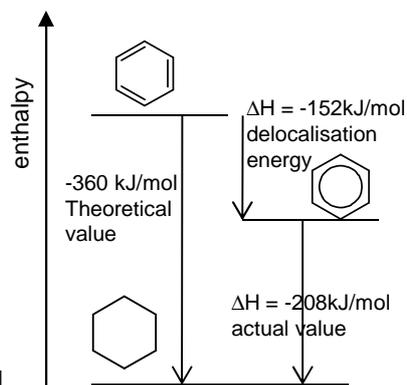


delocalised structure

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.



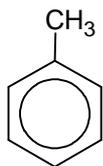
The increase in stability connected to delocalisation is called the **delocalisation energy**.

Reactions of Benzene

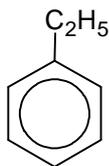
Benzene does not generally undergo addition reactions because these would involve breaking up the delocalised system. Most of Benzene's reactions involve substituting one H for another atom or group of atoms. Benzene has a high electron density and so attracts electrophiles. Its reactions are usually **electrophilic substitutions**.

Naming aromatic molecules

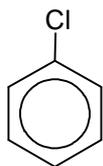
Naming aromatic compounds can be complicated. The simplest molecules are derivatives of benzene and have benzene at the root of the name



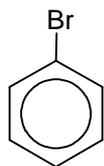
Methylbenzene



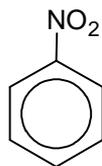
ethylbenzene



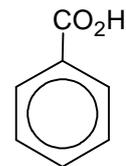
chlorobenzene



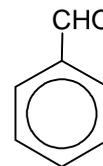
bromobenzene



nitrobenzene

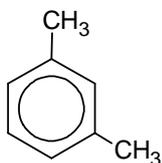


benzenecarboxylic acid



benzaldehyde

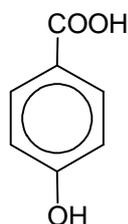
If two or more substituents are present on the benzene ring, their positions must be indicated by the use of numbers. This should be done to give the lowest possible numbers to the substituents. When two or more different substituents are present, they are listed in alphabetical order and di, tri prefixes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



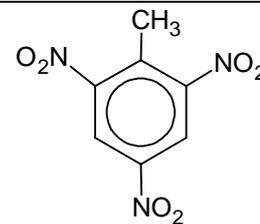
1,3-dimethylbenzene



1-chloro-4-methylbenzene

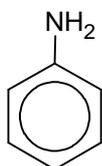


4-hydroxybenzenecarboxylic acid

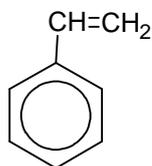


2,4,6-trinitrotoluene

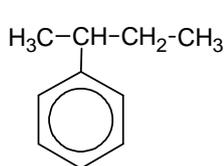
In other molecules the benzene ring can be regarded as a substituent side group on another molecule, like alkyl groups are. The C_6H_5 - group is known as the **phenyl** group.



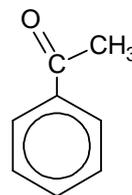
phenylamine



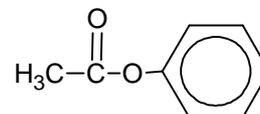
phenylethene



2-phenylbutane



phenylethanone



phenylethanoate

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

Reactions of Benzene

Combustion

Benzene + oxygen → carbon dioxide + water
 $C_6H_6(l) + 7.5 O_2 \rightarrow 6 CO_2 + 3 H_2O$

Benzene will combust with a very sooty flame. The lower the carbon to hydrogen ratio the sootier the flame.

Halogenation of Benzene

Change in functional group: benzene → Bromobenzene

Reagents: Bromine

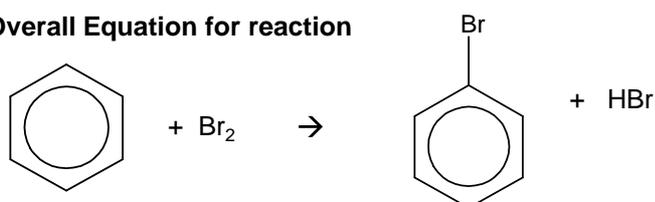
Conditions: iron(III) bromide catalyst $FeBr_3$

Mechanism: Electrophilic Substitution

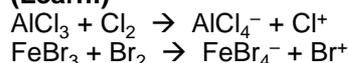
This reaction can be done with chlorine. The catalyst can be $AlCl_3$ or $FeCl_3$

It is possible to create the iron(III) bromide in situ by reacting iron with bromine

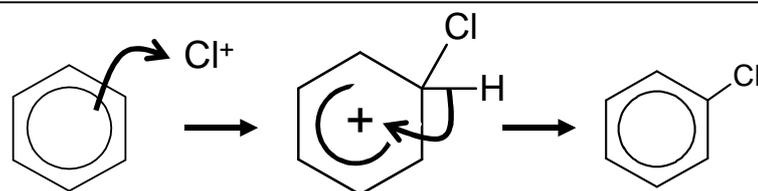
Overall Equation for reaction



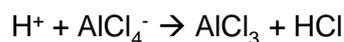
Equation for Formation of electrophiles: (Learn!)



Mechanism



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



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^+

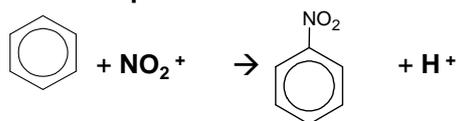
Importance of this reaction

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.)

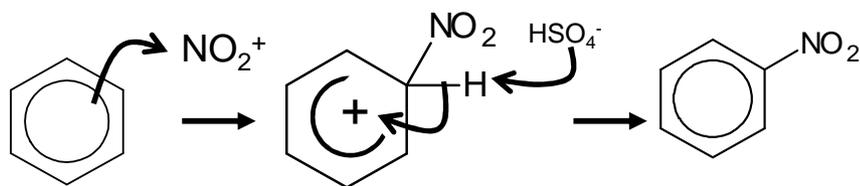
Overall Equation for reaction



Equation for Formation of electrophile: (Learn!)

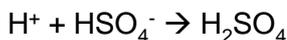


Mechanism



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.



This reaction is done at $60^\circ C$. On using higher temperatures a second nitro group can be substituted onto different positions on the ring

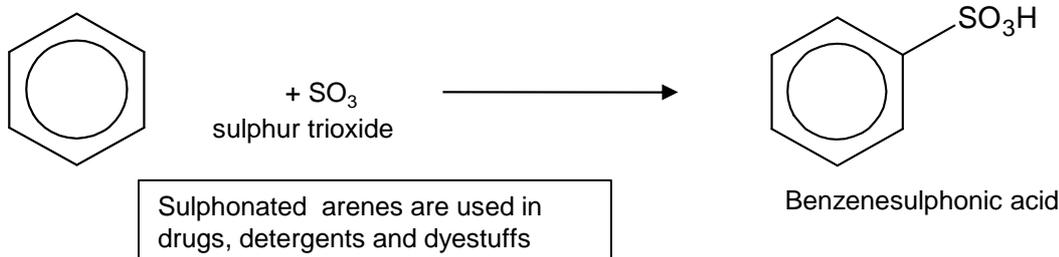
If the benzene ring already has a side group e.g. methyl then the Nitro group can also join on different positions. A-level does not require knowledge of what positions the groups go on.

Sulphonation of Benzene

Change of functional group: benzene → sulphonated benzene
Reagents: Fuming concentrated Sulphuric acid
Conditions: heat under reflux for several hours
Mechanism: Electrophilic Substitution
Electrophile : SO_3 (fuming sulphuric acid is SO_3 dissolved in concentrated sulphuric acid)

The sulfur trioxide can act as an electrophile because it can accept a pair of electrons

The three oxygen atoms on the sulfur give it a large δ^+ charge

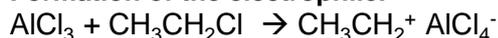


Friedel Crafts Alkylation

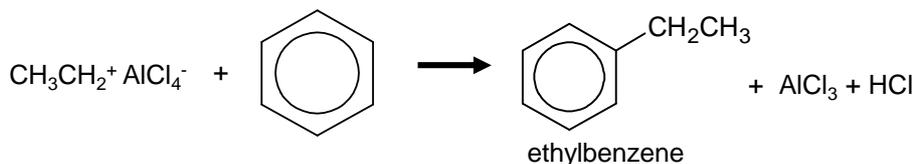
Change in functional group: benzene → alkylbenzene
Reagents: chloroalkane in the presence of anhydrous aluminium chloride catalyst
Conditions: heat under reflux
Mechanism: Electrophilic Substitution

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

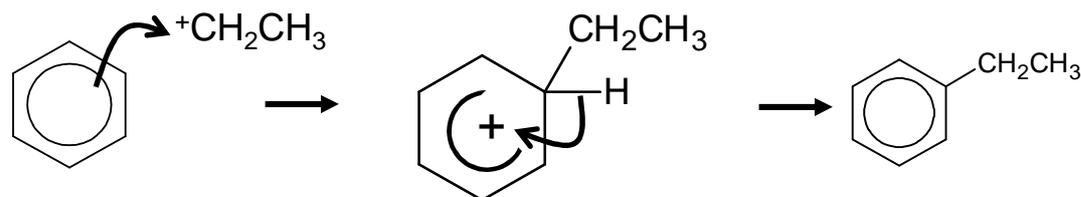
Formation of the electrophile.



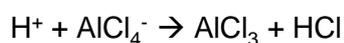
Overall Equation for reaction



Mechanism

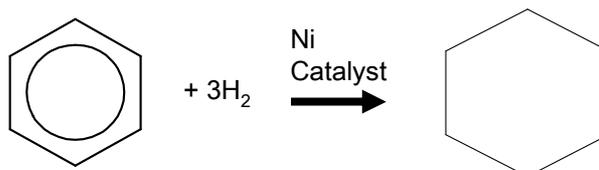


The H^+ ion reacts with the AlCl_4^- to reform AlCl_3 catalyst and HCl .



Hydrogenation of Benzene

Reaction: benzene → cyclohexane
Reagents: Hydrogen
Conditions: Nickel catalyst at 200°C and 30 atm
Type of reaction: Addition and reduction

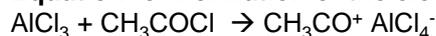


Friedel Crafts Acylation

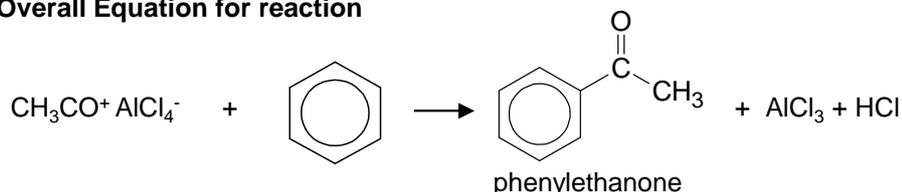
Change in functional group: benzene → phenyl ketone
Reagents: acyl chloride in the presence of anhydrous aluminium chloride catalyst
Conditions: heat under reflux (50°C)
Mechanism: Electrophilic Substitution

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.

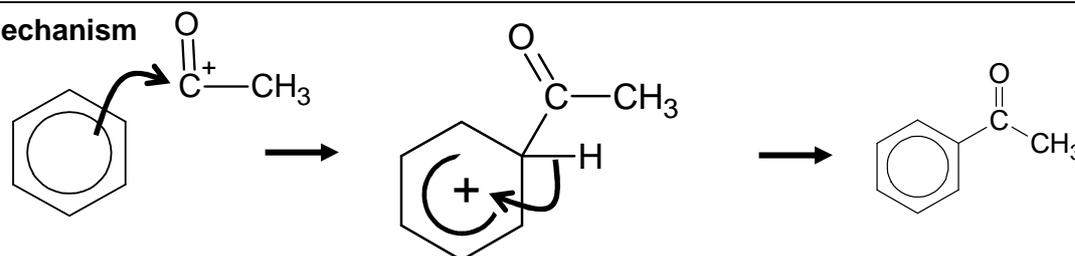


Overall Equation for reaction



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 AlCl₄⁻ to reform AlCl₃ catalyst and HCl.

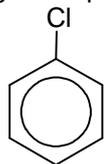


Effect of side groups on benzene ring

Electron releasing side groups such as alkyl groups, phenols and amines releases electrons into the delocalised system making a higher electron density in the ring and it more attractive to electrophiles. They will therefore carry out the substitution reactions more readily with milder conditions

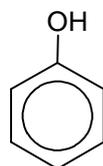
Effect of delocalisation on side groups with lone pairs

If a -OH group, a Cl atom or an NH₂ group is directly attached to a benzene ring the delocalisation in the benzene ring will extend to include the lone pairs on the N, O and Cl. This changes the properties and reactions of the side group



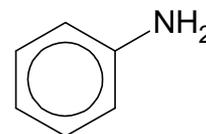
chlorobenzene

The C-Cl bond is made stronger. Typical halogenoalkane substitution and elimination reactions do not occur. Also the electron rich benzene ring will repel nucleophiles



phenol

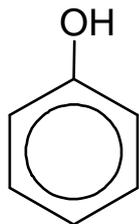
Delocalisation makes the C-O bond stronger and the O-H bond weaker. Phenol does not act like an alcohol- it is more acidic and does not oxidise



phenylamine

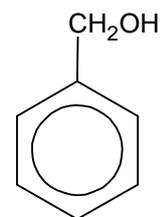
Less basic than aliphatic amines as lone pair is delocalised and less available for accepting a proton

Phenols



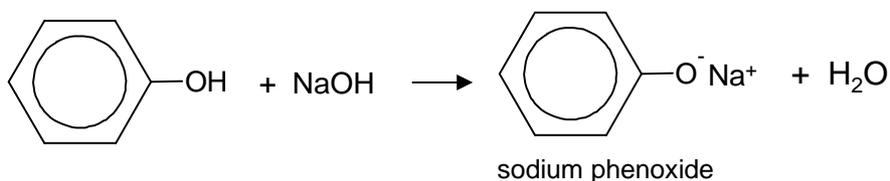
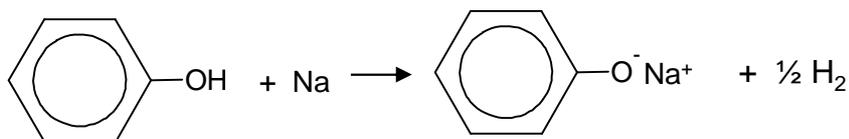
In a phenol the OH group is directly attached to the benzene ring.

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.

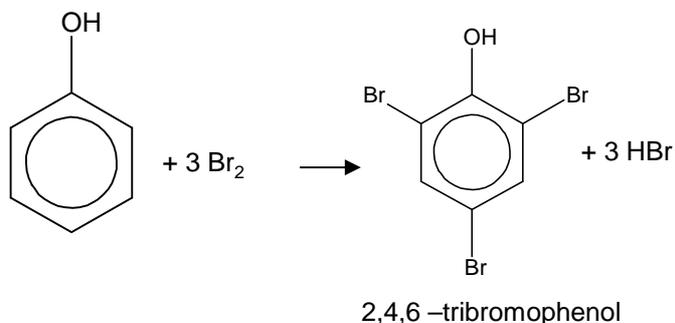


The sodium phenoxide compound is more soluble than the original phenol. So the solid phenol dissolves on addition of NaOH

Reaction of phenol with Bromine

Reagents: Bromine water

Conditions: room temp



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 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

