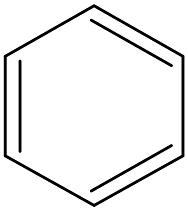
Aromatic Hydrocarbons / Arenes

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.

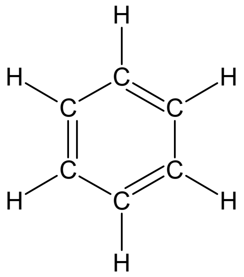
The simplest arene is benzene. Benzene has the molecular formula C_6H_6

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

Skeletal formula showing Kekule structure

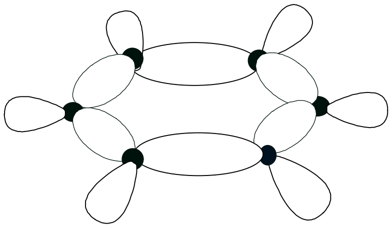


Displayed formula showing Kekule structure

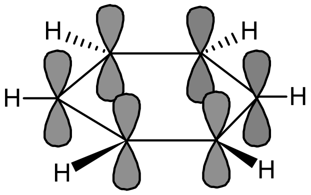


This structure is not correct. Evidence suggests that all the C-C bonds are the same.

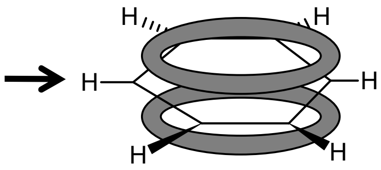
Benzene's Delocalised Structure
Benzene's basic structure is six carbon atoms in a hexagonal ring, with one hydrogen atom bonded to each carbon atom. Each carbon atom is bonded to two other carbon atoms and one hydrogen atom by single covalent σ-bonds.



This leaves one unused electron on each carbon atom in a p orbital, perpendicular to the plane of the ring.



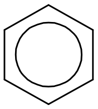
The six p electrons are delocalised in a ring structure above and below the plane of carbon atoms.
The six electrons in the π bonds are delocalised and spread out over the whole ring. Delocalised means not attached to a particular atom.



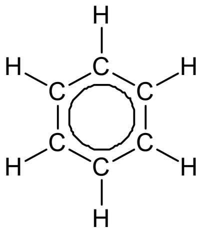
Delocalisation makes the molecule more energetically stable

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 bonds length are all the same at 0.14nm (half way between C-C and C=C).

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



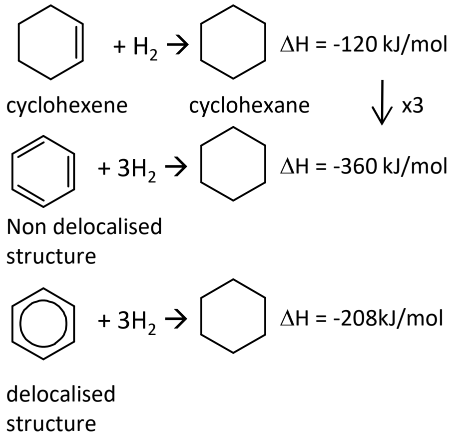
Skeletal formula



Displayed formula

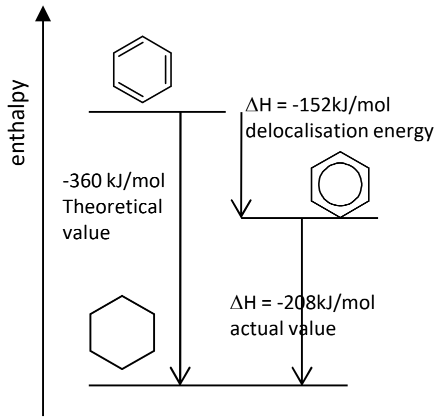
The H-C-C bond angle is 120^{o} in Benzene

Using Enthalpies of Hydrogenation to show Thermodynamic Stability



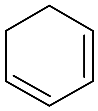
Theoretically because there are 3 double bonds in the theoretical cyclohexa-1,3,5-triene one might expect the amount of energy to be 3 times as much as cyclohexene.

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

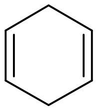


The increase in stability connected to delocalisation is called the **delocalisation energy.**

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



In cyclohexa-1,3-diene, there would be some delocalisation and extra stability as the pi electrons are close together, in the same plane and so overlap . The hydrogenation value would be less negative than -240 kJ/mol (showing more stable)



In cyclohexa-1,4-diene, there would not be delocalisation as the pi electrons are too far apart and so don't overlap. The hydrogenation value would be -240 kJ/mol

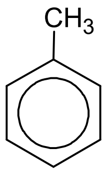
Toxicity of Benzene

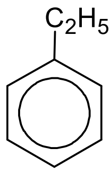
Benzene is a carcinogen (cancers causing molecule) and is banned for use in schools.

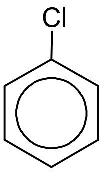
Methylbenzene is less toxic and also reacts more readily than benzene as the methyl side group releases electrons into the delocalised system making it more attractive to electrophiles

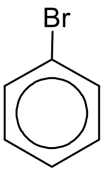
Naming aromatic molecules

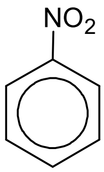
Naming aromatic compounds can be complicated. The simplest molecules are derivatives of benzene and have benzene at the root of the name

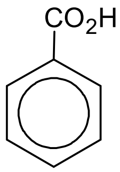

Methylbenzene

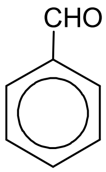

ethylbenzene


chlorobenzene

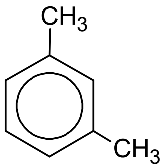

bromobenzene

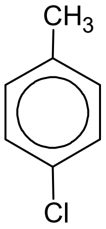

nitrobenzene

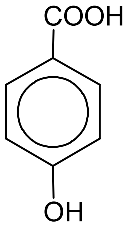

benzenecarboxylic acid

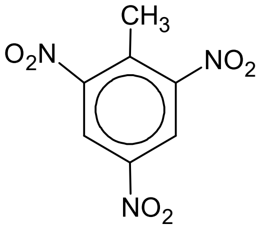

benzaldehyde

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.

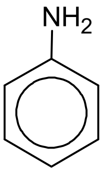

1,3-dimethylbenzene

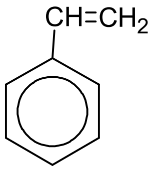

1-chloro- 4-methylbenzene

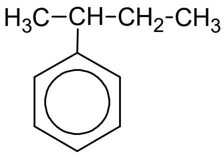

4-hydroxybenzenecarboxylic acid

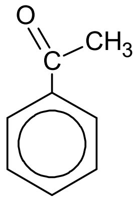

2-methyl-1,3,5-trinitrobenzene

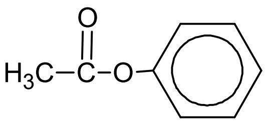
In other molecules the benzene ring can be regarded as a substituent side group on another molecule, like alkyl groups are. The C_6H_5- group is known as the **phenyl** group.

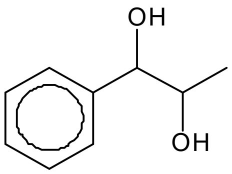

phenylamine

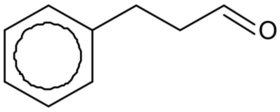

phenylethene

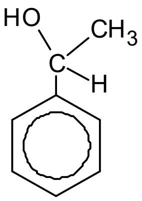

2-phenylbutane


phenylethanone


phenylethanoate


1-phenylpropane-1,2-diol


3-phenylpropanal


1-phenyl ethan-1-ol

Reactions of Benzene

Combustion

Benzene + oxygen → carbon dioxide + water
C_6H_6 (l) + 7.5 O_2 → 6 CO_2 + 3 H_20

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

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

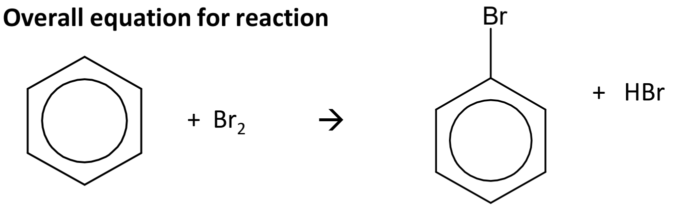
Comparison of Benzene with alkenes: reaction with Bromine
The delocalised electrons above and below the plane of the molecule are attractive for electrophiles to attack. But they do undergo electrophilic reactions more slowly than alkenes
Alkenes react with bromine easily at room temperature. Benzene does not react with bromine without additional halogen carrier chemicals.
In benzene, electrons in π-bond(s) are delocalised around the ring of 6 carbon atoms. In alkenes, π-electrons are localised between two carbons.
Benzene therefore has a lower electron density than a C=C bond in alkenes. Benzene therefore polarises bromine less and induces a weaker dipole in bromine than an alkene would.

The electrophilic substitution mechanisms involve a temporary breaking of the delocalization to form an intermediate. It takes energy to form this intermediate. The activation energies are therefore high, and substitution reactions of arenes tend to be relatively slow.

Halogenation of Benzene

Change in functional group: arene → halogenoarene
Reagents: Bromine or chlorine
Conditions: iron(III) bromide catalyst $FeBr_3$
Mechanism: Electrophillic Substitution

Overall equation for reaction



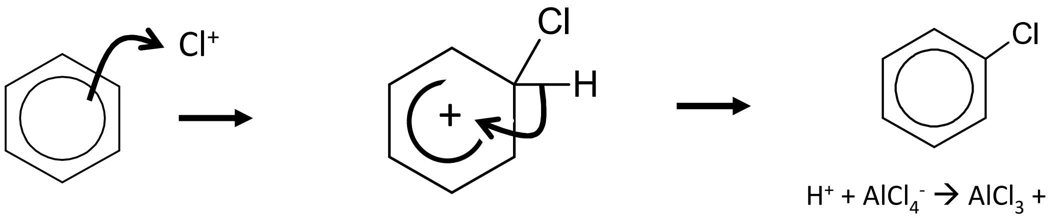
A catalyst called a 'halogen carrier' is needed to produce a strongly electrophilic halogen. Various substances can be used as halogen carriers. Common ones are aluminium chloride $AlCl_3$ or iron (III) chloride $FeCl_3$ for chlorination or arenes. Aluminium bromide $AlBr_3$ or iron (III) bromide $FeBr_3$ can be used for bromination.

It is possible to create the iron(III) bromide in situ by reacting iron with bromine or the analogous reaction or chlorine and iron to produce iron (III) chloride.

The halogen carrier causes the Cl-Cl or Br-Br bond to break heterolytically to produce a positive chlorine or bromine ion

Example equations for formation of electrophiles:
$AlCl_3 + Cl_2 \rightarrow AlCl_4^- + Cl^+$
$FeBr_3 + Br_2 \rightarrow FeBr_4^- + Br^+$

Mechanism



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

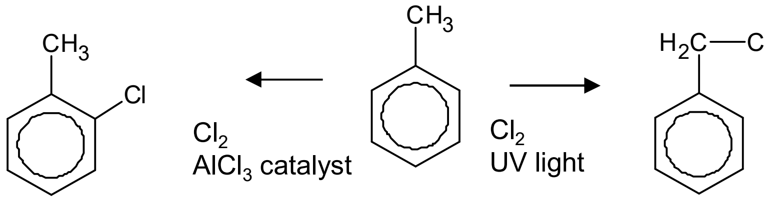
The benzene π cloud attracts the Cl+ electrophile. The Cl^+ ion bonds to the benzene ring to produce an intermediate.

In the intermediate the positive charge is shared between the five other carbon atoms. The C-H bond breaks and the pair of electrons returns to the delocalised orbitals on the benzene ring. The delocalised ring of electrons reforms.

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

Halogenation and conditions

If the arene has an alkyl side chain then using different conditions can cause different halogenation reactions to occur. The use of a halogen carrier catalyst such as aluminium chloride will cause the arene ring to halogenate. If UV light is used then the side group will halogenate by a free radical substitution reaction.



Use the $AlCl_3$ catalyst to substitute directly on the benzene ring

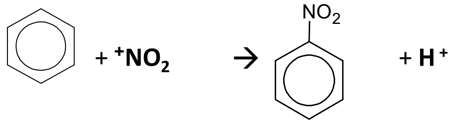
Use UV light to substitute on to the side group

Nitration of Benzene

Nitration of benzene and other arenes is an important step in synthesising useful compounds e.g. explosive manufacture (like TNT, trinitrotoluene/2-methyl-1,3,5-trinitrobenzene) and formation of amines from which dyestuffs are manufactured. (The reaction for this is covered in the amines section 6.10.)

Change in functional group: benzene → nitrobenzene
Reagents: concentrated nitric acid in the presence of concentrated sulfuric acid (catalyst)
Mechanism: Electrophilic Substitution
Electrophile: NO_2^+

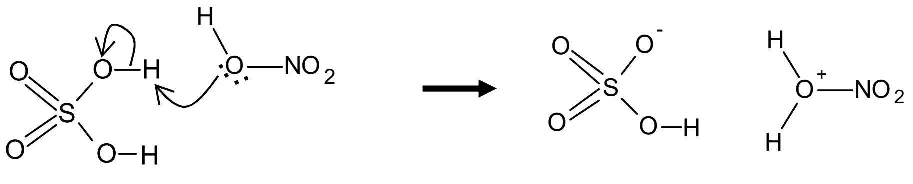
Overall Equation for reaction



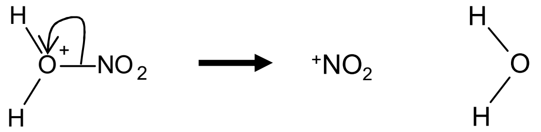
The electrophile called the nitronium ion , $^+NO_2$ is produced by a mixture of concentrated nitric acid and concentrated sulfuric acid. This is called the nitrating mixture. The positive charge is on the nitrogen.

Overall equation for the formation of the electrophile:
$HNO_3 + 2H_2SO_4 \rightarrow {}^+NO_2 + 2HSO_4^- + H_3O^+$

The mechanism for the formation of the electrophile occurs in two steps.

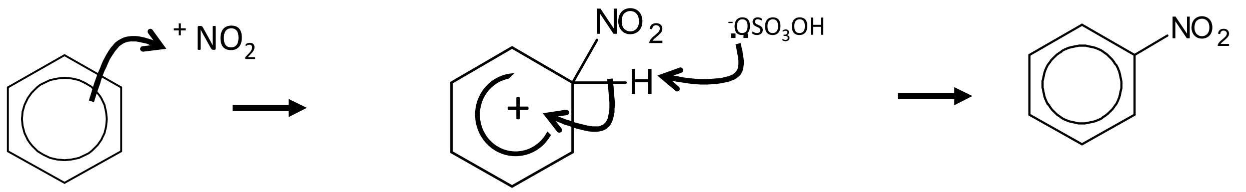


In the first step the HNO_3 acts as a base and accepts a proton (hydrogen ion) from the sulfuric acid



The intermediate then loses a water molecule leaving the electrophile $^+NO_2$

Mechanism



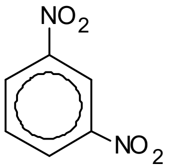
$H^+ + HSO_4^- \rightarrow H_2SO_4$

The benzene π cloud attracts the $^+NO_2$ electrophile. The $^+NO_2$ ion bonds to the benzene ring to produce an intermediate. Both of the electrons in the C-N bond to the electrophile come from the benzene ring. This leaves a positive charge in the intermediate species

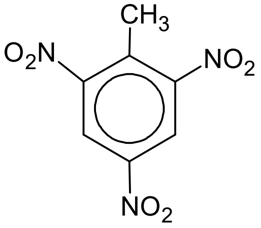
In the intermediate the positive charge is shared between the five other carbon atoms. The C-H bond breaks and the pair of electrons returns to the delocalised orbitals on the benzene ring. The delocalised ring of electrons reforms.

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

The nitration of benzene should be done at 60°C to produce nitrobenzene. If a higher temperature of around 100°C is used a second nitro group can be substituted onto a different position on the ring. It produces 1,3- dinitrobenzene



If the benzene ring already has a electron releasing side group e.g. methyl then the nitro group can also join on different positions. Nitration of substituted arenes can occur more readily and can occur at lower temperatures.
Methylbenzene can undergo multiple substitution to produce 2-methyl-1,3,5-trinitrobenzene. This used to be called 2,4,6-trinitrotoluene (TNT) which was used as an explosive



2,4,6-trinitromethylbenzene

Detailed method for nitration procedure

Measure 2.5 cm^3 of methyl benzoate into a small conical flask and then dissolve it in 5 cm^3 of concentrated sulfuric acid. When the liquid has dissolved, cool the mixture in ice.
Prepare the nitrating mixture by adding **drop by drop** 2 cm^3 of concentrated sulfuric acid to 2 cm^3 of concentrated nitric acid. C**ool this mixture in ice** as well.

Now add the nitrating mixture drop by drop from a dropping pipette to the solution of methyl benzoate. Stir the mixture with a thermometer and keep the temperature **below 10 °C**. When the addition is complete, allow the mixture to stand at room temperature for another 15 minutes.
After this time, pour the reaction mixture on to about 25 g of crushed ice and stir until all the ice has melted and crystalline methyl 3-nitrobenzoate has formed.
Then use the recrystallisation purification method to produce a purer crystal.

Concentrated acids are corrosive- wear gloves
The acids react together to make the NO_2^+ ion
This reaction is exothermic so acids are kept cool and acid is added dropwise

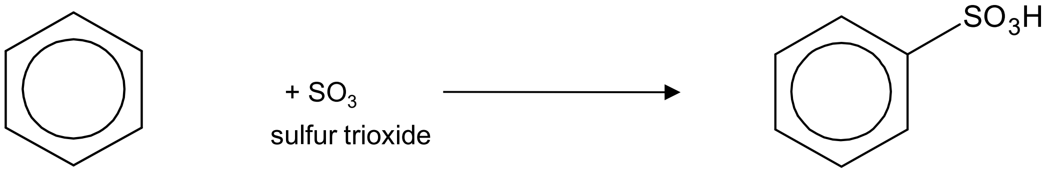
The temperature is kept low at this stage to prevent multiple substitution of nitro groups on the benzene ring

Sulfonation of benzene

Change of functional group: benzene → sulfonated benzene
Reagents: Fuming concentrated sulfuric acid
Conditions: heat under reflux for several hours
Mechanism: Electrophillic Substitution
Electrophile : SO_3 (fuming sulfuric acid is SO_3 dissolved in concentrated sulfuric 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



Benzenesulfonic acid

Sulfonated arenes are used in drugs, detergents and dyestuffs

Friedal Crafts reactions

These reactions add extra carbons to a benzene ring. There are two reactions. Friedal Crafts alkylation adds an alkyl group of various lengths to the benzene ring. Friedal Crafts acylation adds a ketone group to the benzene ring. Both reactions need an aluminium chloride catalyst to produce the electrophile.

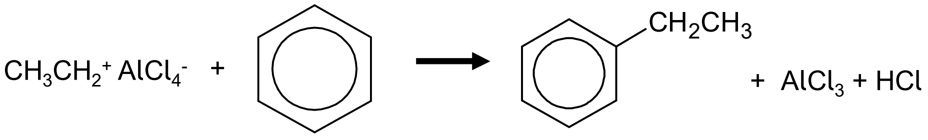
Friedel Crafts Alkylation

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^+.

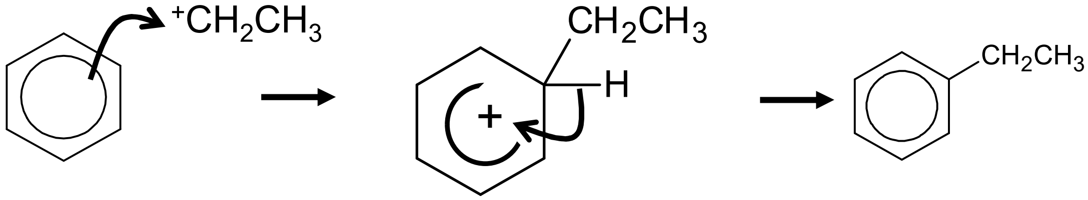
Formation of the electrophile.
$AlCl_3 + CH_3CH_2Cl \rightarrow CH_3CH_2^+ \, AlCl_4^-$

Overall Equation for reaction



ethylbenzene

Mechanism



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

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

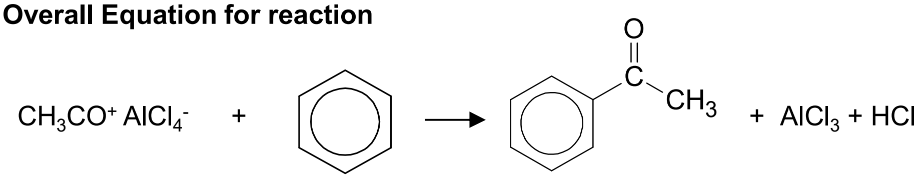
Friedel Crafts Acylation

Change in functional group: benzene → phenyl ketone
Reagents: acyl chloride in the presence of anhydrous aluminium chloride catalyst
Conditions: heat under reflux (50^{O}C)
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.
$AlCl_3 + CH_3COCl \rightarrow [CH_3CO]^+ + [AlCl_4]^-$

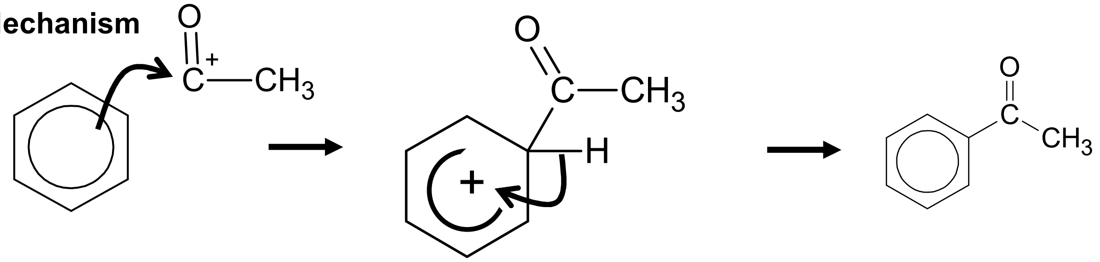
Overall Equation for reaction



phenylethanone

These are important reactions in organic synthesis because they introduce a reactive functional group on to the benzene ring

Mechanism

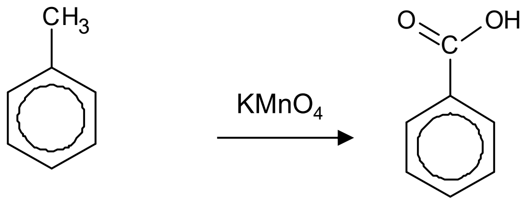


The H^+ ion reacts with the $AlCl_4^-$ to reform $AlCl_3$ catalyst and HCl.

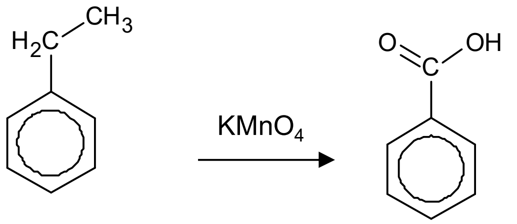
$H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$

Oxidation of side chains

Reaction: alkylbenzene → benzoic acid
Reagents: alkaline $KMnO_4$ (followed by H_2SO_4)
Conditions: heat under reflux
Type of reaction: oxidation

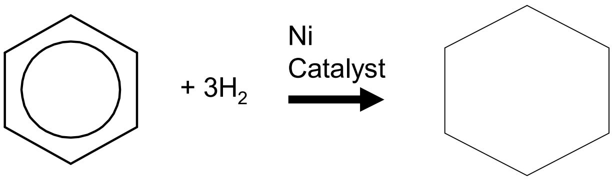


Different lengths of alkyl groups all get oxidised to benzoic acid



Hydrogenation of Benzene

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

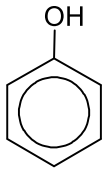


Effect of side groups on benzene ring

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

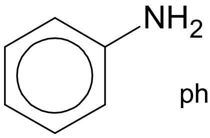
Effect of delocalisation on side groups with lone pairs

If a –OH group, a Cl atom or an NH_2 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



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

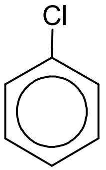


phenylamine

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

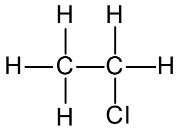
Effect of delocalisation on side groups with lone pairs

If a –Cl atom is directly attached to a benzene ring the delocalisation in the benzene ring will extend to include the lone pairs on the Cl. This changes the properties and reactions of the side group.



chlorobenzene

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

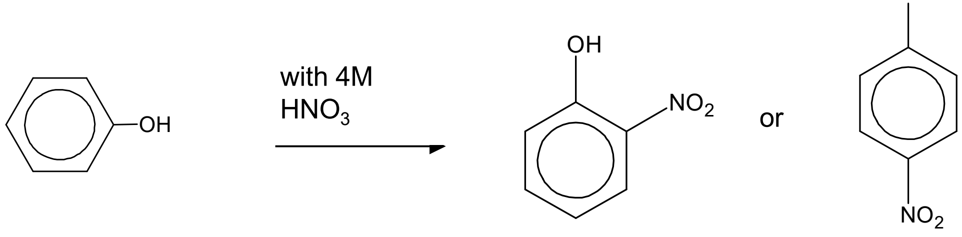


Aliphatic halogenoalkanes will undergo nucleophilic substitution reactions to produce alcohols

Effect of side groups on position of 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 –Cl 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 –CN – CO_2H) will have a 3-directing effect in electrophilic substitution of aromatic compounds