# Aromatic Hydrocarbons / Arenes

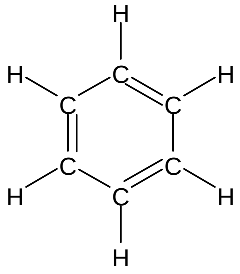
There are two major classes of organic chemicals
**aliphatic** : straight or branched chain organic substances
**aromatic or arene**: includes one or more ring of six carbon atoms with delocalised bonding.

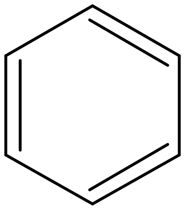
The simplest arene is benzene. Benzene has the molecular formula $C_6H_6$

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

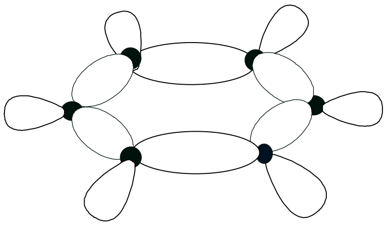
Displayed formula showing kekule structure



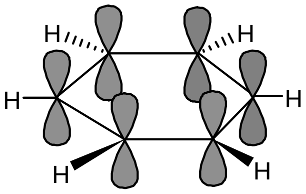


This structure is not correct. Evidence suggests that all the C-C bonds are the same.

**Benzene's Delocalised Structure**
Benzene's basic structure is six 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.

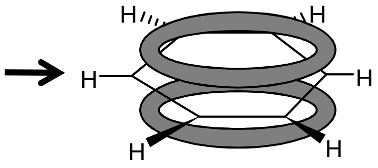


This leaves one unused electron on each C atom in a p orbital, perpendicular to the plane of the ring.



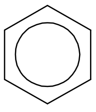
The Six p electrons are delocalised in a ring structure above and below the plane of carbon atoms.
The six electrons in the pi bonds are delocalised and spread out over the whole ring. Delocalised means not attached to a particular atom.

Delocalisation makes the molecule more energetically stable

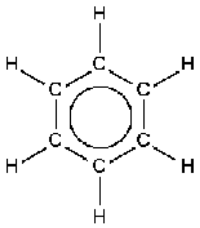


Benzene is a **planar** molecule. The evidence suggests all the C-C bonds are the same and have a length and bond energy between a C-C single and C=C double bond. The bonds length are all the same at 0.14nm (half way between C-C and C=C).

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



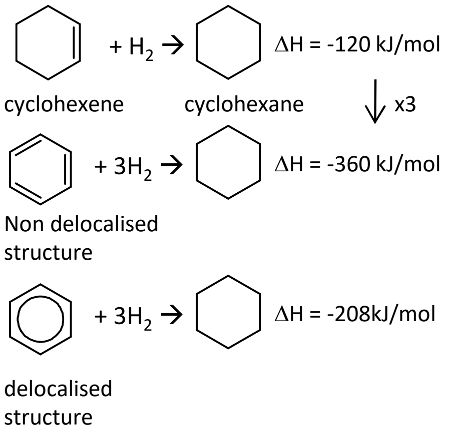
Skeletal formula



Displayed formula

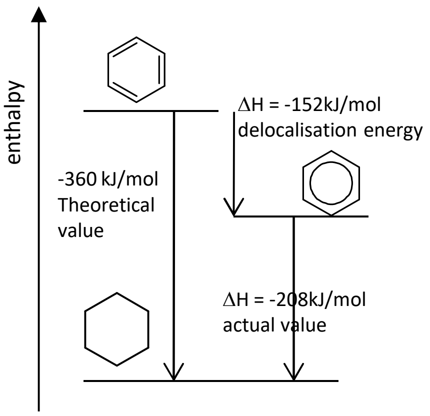
The H-C-C bond angle is 120° in Benzene

### Using Enthalpies of Hydrogenation to show Thermodynamic Stability



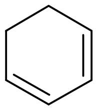
Theoretically because there are 3 double bonds in the theoretical cyclohexa-1,3,5-triene one might expect the amount of energy to be 3 times as much as cyclohexene.

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

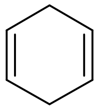


The increase in stability connected to delocalisation is called the **delocalisation energy.**

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

**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 H 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.

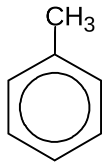
In benzene, electrons in π-bond(s) are delocalised. In alkenes, π-electrons are localised between two carbons.

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.

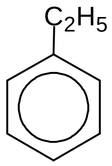
The electrophilic substitution mechanisms involve a temporary breaking of the delocalization to form an intermediate. It takes energy to form this intermediate. The activation energies are therefore high, and substitution reactions of arenes tend to be relatively slow

## Naming aromatic molecules

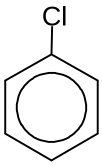
Naming aromatic compounds can be complicated. The simplest molecules are derivatives of benzene and have benzene at the root of the name



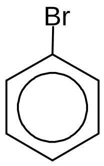
Methylbenzene



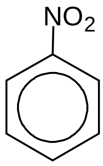
ethylbenzene



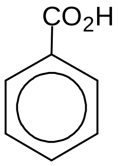
chlorobenzene



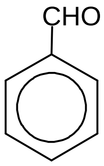
bromobenzene



nitrobenzene

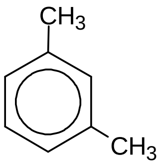


benzenecarboxylic acid

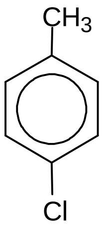


benzaldehyde

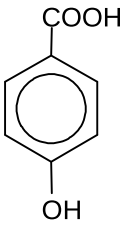
If two or more substituents are present on the benzene ring, their positions must be indicated by the use of numbers. This should be done to give the lowest possible numbers to the substituents. When two or more different substituents are present, they are listed in alphabetical order and di, tri prefixes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



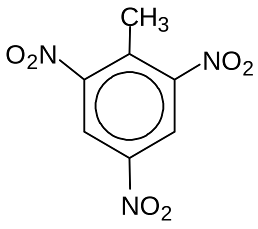
1,3-dimethylbenzene



1-chloro- 4-methylbenzene

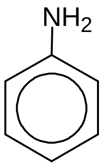


4-hydroxybenzenecarboxylic acid

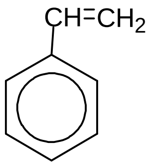


2,4,6-trinitromethylbenzene

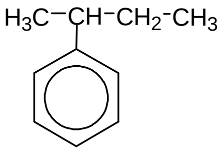
In other molecules the benzene ring can be regarded as a substituent side group on another molecule, like alkyl groups are. The $C_6H_5$- group is known as the **phenyl** group.



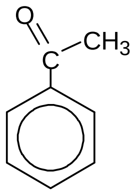
phenylamine



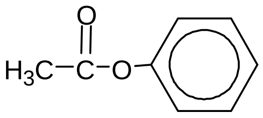
phenylethene



2-phenylbutane



phenylethanone



phenylethanoate

## Reactions of Benzene

### 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 the sootier the flame.

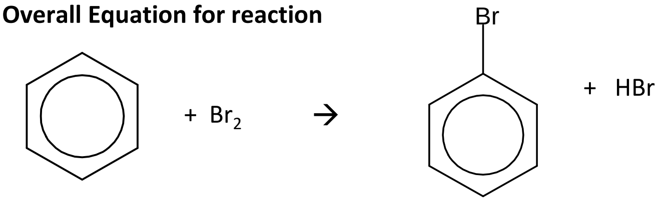
## Halogenation of Benzene

**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 $FeCl_3$

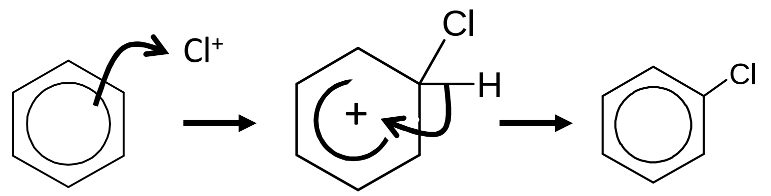
It is possible to create the iron(III) bromide in situ by reacting iron with bromine

**Overall Equation for reaction**



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

**Mechanism**



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

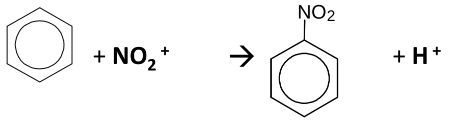
$H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$

## 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:** $NO_2^+$

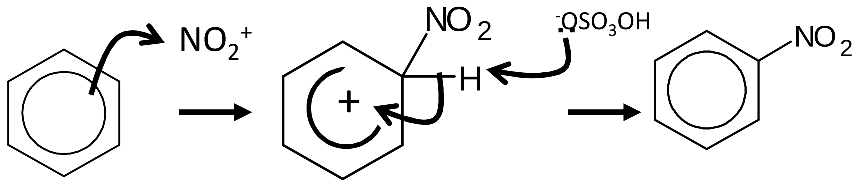
**Importance of this reaction**
Nitration of benzene and other arenes is an important step in synthesising useful compounds
e.g. explosive manufacture (like TNT, trinitrotoluene/ 2,4,6-trinitromethylbenzene) and formation of amines from which dyestuffs are manufactured. (The reaction for this is covered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

**Overall Equation for reaction**



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

**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.

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

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

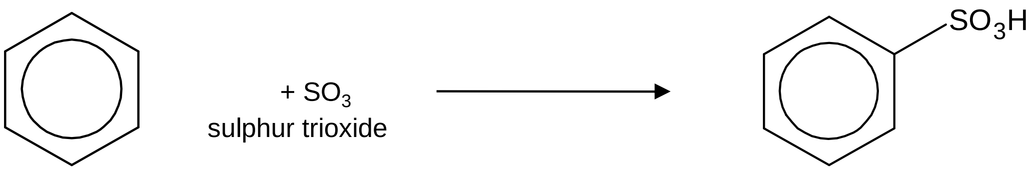
If the benzene ring already has a side group e.g. methyl then the Nitro group can also join on different positions. A-level does not require knowledge of what positions the groups go on.

## Sulphonation of Benzene

**Change of functional group:** benzene → sulphonated benzene
**Reagents:** Fuming concentrated Sulphuric acid
**Conditions:** heat under reflux for several hours
**Mechanism**: Electrophillic 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 $\delta^+$ charge



Sulphonated arenes are used in drugs, detergents and dyestuffs

Benzenesulphonic acid

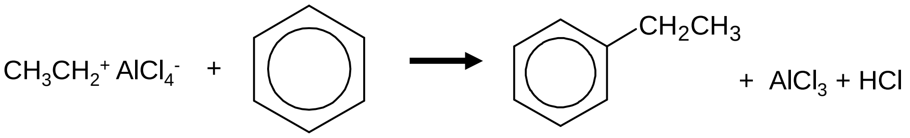
## Friedel Crafts Alkylation

**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 $R^+$.

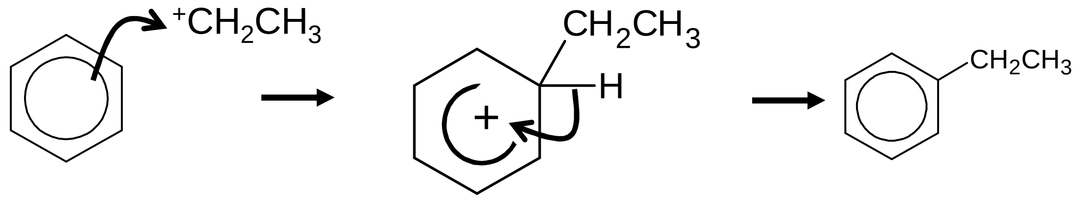
**Formation of the electrophile.**
$AlCl_3 + CH_3CH_2Cl \rightarrow CH_3CH_2^+\ AlCl_4^-$

**Overall Equation for reaction**



ethylbenzene

**Mechanism**



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

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

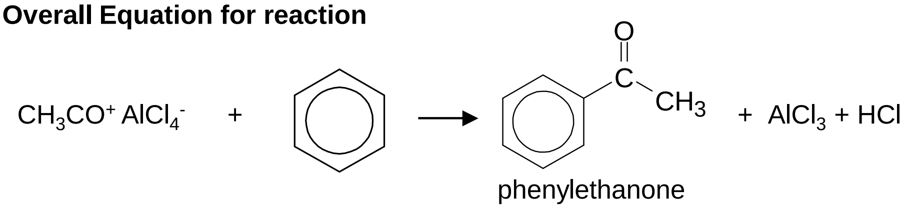
## Friedel Crafts Acylation

**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.**
$AlCl_3 + CH_3COCl \rightarrow CH_3CO^+ \ AlCl_4^-$

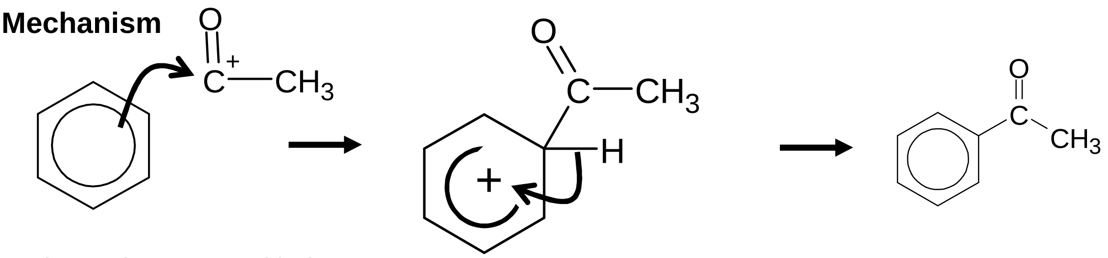
**Overall Equation for reaction**



phenylethanone

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

**Mechanism**

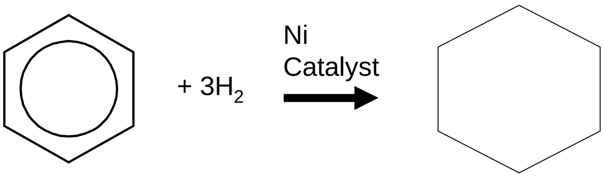


The $H^+$ ion reacts with the $AlCl_4^-$ to reform $AlCl_3$ catalyst and HCl.

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

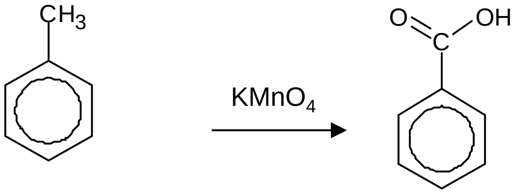
## Hydrogenation of Benzene

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

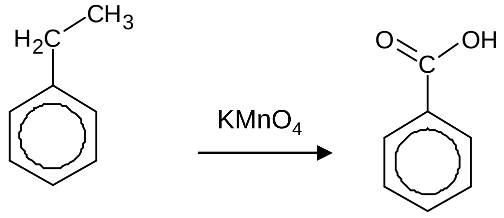


## Oxidation of side chains

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



Different lengths of alkyl groups all get oxidised to benzoic acid

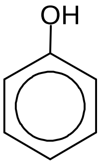


## Effect of side groups on benzene ring

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

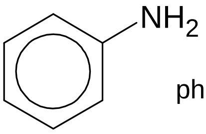
### Effect of delocalisation on side groups with lone pairs

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

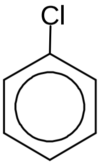


phenylamine

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

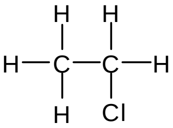
### Effect of delocalisation on side groups with lone pairs

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.



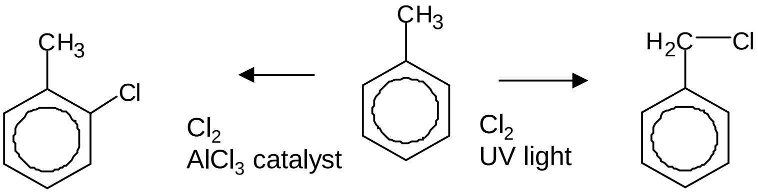
chlorobenzene

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

### Halogenation and conditions



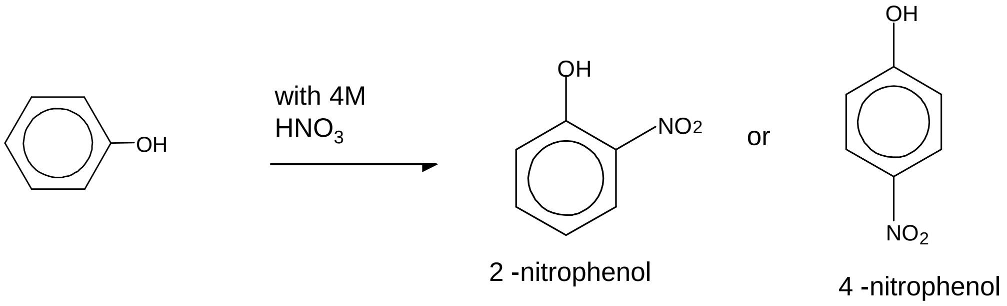
Use the $AlCl_3$ catalyst to substitute directly on the benzene ring

Use UV light to substitute on to the side group

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



Electron-withdrawing groups (such as $NO_2$ –CN – $CO_2H$) will have a 3-directing effect in electrophilic substitution of aromatic compounds