

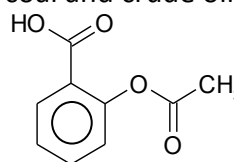
Aromatic Compounds

Naming

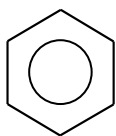
Aromatic compounds contain one or more benzene rings (while **aliphatic** compounds do not contain benzene rings). Another term for a compound containing a benzene ring is **arene**.

The basic benzene ring, C_6H_6 is commonly represented as a hexagon with a ring inside. You should be aware that there is a hydrogen at each corner although this is not normally shown. *N.B. it is OK to use benzene in this form in structural formulae too!*

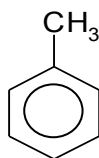
Arenes occur naturally in many substances, and are present in coal and crude oil. Aspirin, for example, is an aromatic compound, an arene:



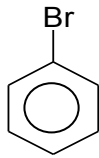
Naming of substances based on benzene follows familiar rules:



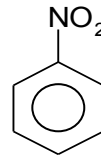
benzene



methylbenzene

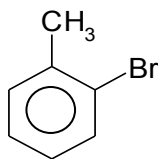


bromobenzene

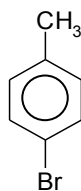


nitrobenzene

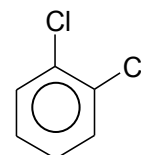
Numbers are needed to identify the positions of substituents. The carbons around the ring are numbered from 1-6 consecutively and the name which gives the lowest number(s) is chosen:



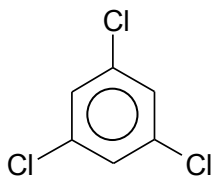
2-bromomethylbenzene



4-bromomethylbenzene



1,2-dichlorobenzene



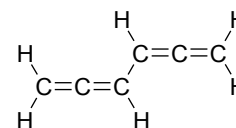
1,3,5-trichlorobenzene

Determining the structure of benzene (historical)

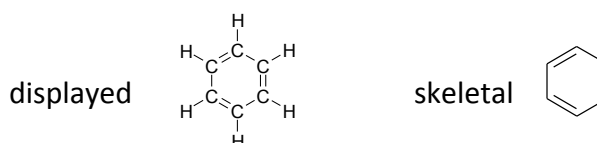
1825 – substance first isolated by Michael Faraday, who also determined its empirical formula as CH

1834 – RFM of 78 and molecular formula of C₆H₆ determined

Much speculation over the structure. Many suggested structures like:

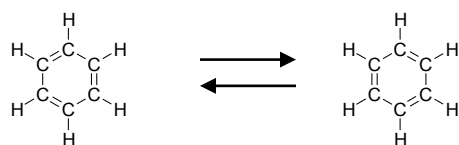


1865 – Kekulé publishes suggestion of a ring with alternating double and single bonds:



This model persisted until 1922, but not all chemists accepted the structure because it failed to explain the chemical and physical properties of benzene fully: if C=C bonds were present as Kekulé proposed, then benzene would react like alkenes. For example benzene would be expected to decolourise bromine water. In fact benzene does not do this, nor does benzene do the other electrophilic addition reactions that alkenes do.

Kekulé's answer was to refine his model to account for this lack of reactivity, suggesting that the double bonds rapidly changed positions round the ring (two forms of benzene in rapid equilibrium) so that approaching electrophiles such as Br₂ could not be attracted to a double bond before it moved when the structure changed.



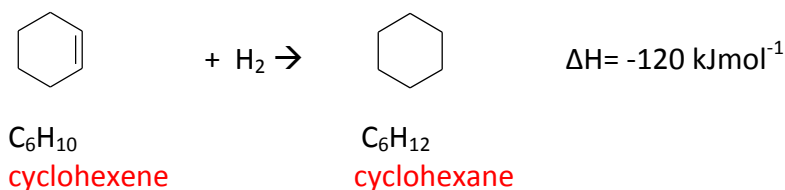
1922 X-ray crystallography used to measure bond lengths in arenes. Kathleen Lonsdale discovers that all the C-C bonds around the ring are the same length:

C-C bonds in alkanes	0.153nm
C=C bonds in alkenes	0.134nm
C to C bonds in benzene	0.139nm (all six carbon-carbon bonds)

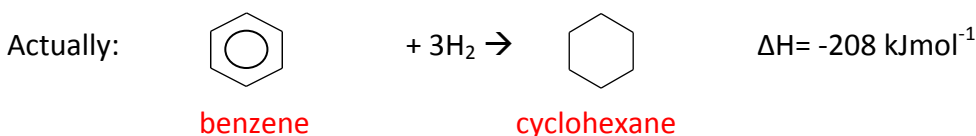
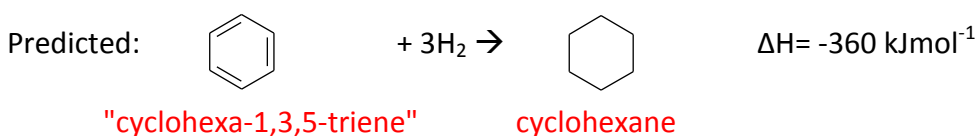
This was important evidence that the Kekulé model was incorrect.

Further modern evidence that Kekulé's model was wrong:

The energy change (enthalpy change) when the double bond in an alkene is hydrogenated can be measured.

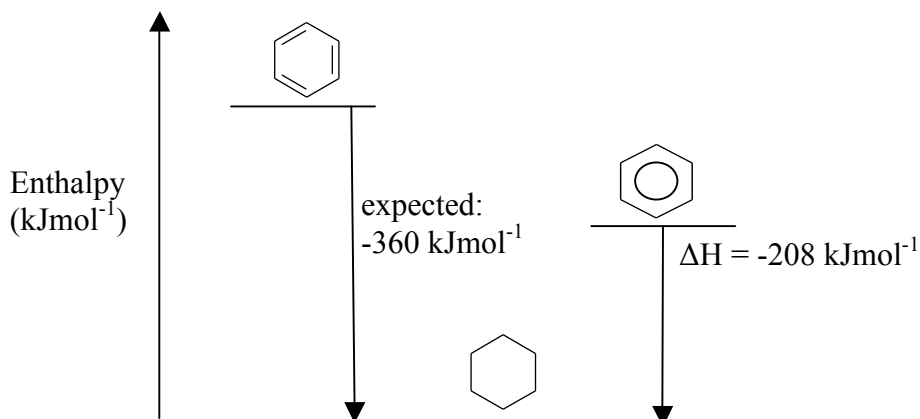


Therefore when the three double bonds in Kekulé's benzene are hydrogenated we should see an enthalpy change of hydrogenation of $3 \times -120 = -360 \text{ kJmol}^{-1}$



When benzene is hydrogenated the enthalpy change is -208 kJmol^{-1} , which is 152 kJmol^{-1} less than predicted. The conclusion has to be that the actual structure of benzene has much less energy than the proposed Kekulé structure – i.e. the real structure is 152 kJmol^{-1} more stable, which helps to explain why benzene is less reactive than alkenes.

We can visualise this on an energy level diagram:



The energy difference between the expected enthalpy of hydrogenation and the actual enthalpy of hydrogenation, which gives rise to the additional stability of benzene

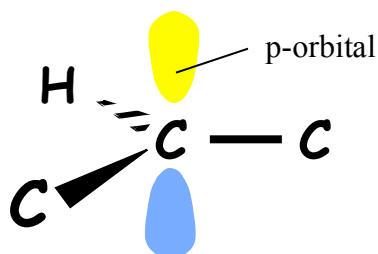
compared to the Kekulé's model, is called the **delocalisation energy**, or **resonance energy** of benzene.

Currently accepted structure of benzene

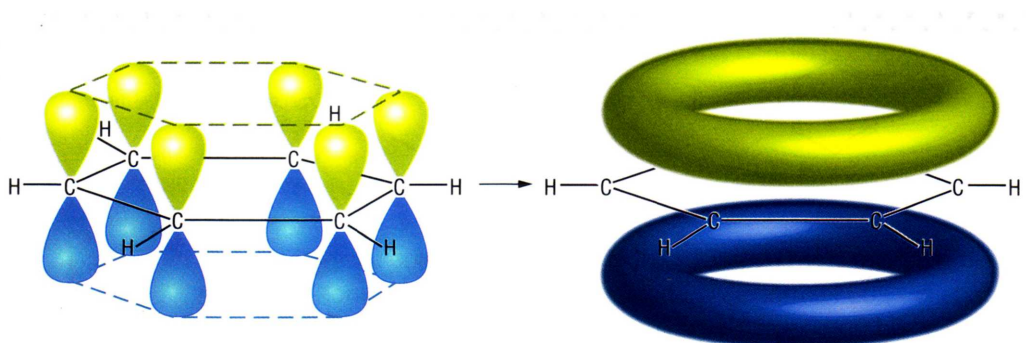
The deficiencies in Kekulé's model led to the currently-accepted **delocalised** model for the structure of benzene.

In this model:

- the six carbon atoms are arranged in a planar hexagonal ring with each carbon sigma-bonded to one hydrogen and two other carbons
- the shape around each carbon is trigonal planar with **120° bond angles** and each carbon to carbon bond is the **same length**
- each carbon has 4 outer shell electrons, three of which are involved in the sigma-bonds to the two other carbons and the one hydrogen. This leaves a fourth outer shell electron in a 2p orbital above and below the plane of the ring.



- Each of these p-orbitals overlaps sideways with the p-orbitals of the carbons on either side. This results in a **system of π -bonds** in the form of a **ring of electron density above and below the plane of the benzene ring**, in which the six electrons are **delocalised**.



(Can you think of where you've come across a similar bonding concept with carbon forming 3 bonds and having one electron able to be delocalised ?)

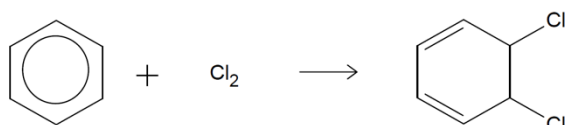
This is what is meant by the circle inside the hexagon when drawing benzene.

How benzene reacts

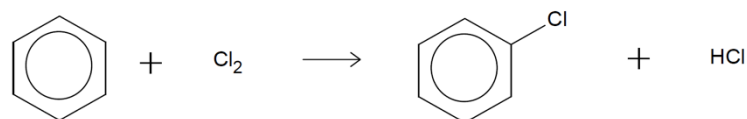
Because it is more stable compared to alkenes, benzene does not (under normal conditions) undergo the addition reactions expected of an alkene:

- it doesn't decolourise bromine water
- it doesn't react with hydrogen halides such as HCl
- react with other halogens (Cl₂, I₂)

Instead, benzene and other arenes undergo **substitution** reactions where one atom/group (often one of the hydrogen atoms) connected to the ring is replaced by a different atom or group. This leaves the delocalised π -system intact (more stable), whereas an **addition** reaction would have broken the π -system by adding to the ring (less stable).



Addition reaction – does not happen as the delocalized π -system gets broken, so organic product less stable than reactant



Substitution reaction – does happen because the delocalized π -system is preserved, so the product is stable, like the reactant.

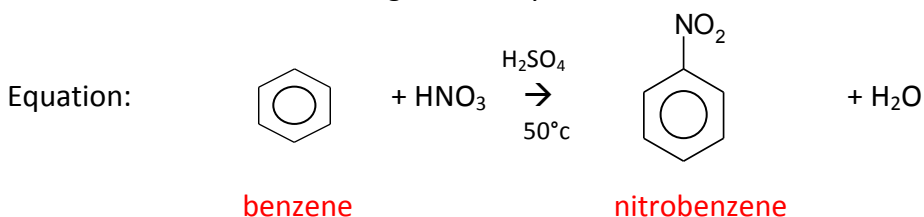
Substitution reactions of benzene

The region of high electron density above and below the plane of the ring attracts **electrophiles**, so these are **electrophilic substitutions**.

1) Nitration of benzene

Effect: One of the hydrogen atoms on the ring is replaced by a nitro (-NO₂) group

Conditions: mixture of conc. HNO₃ and conc. H₂SO₄ at 50°C
H₂SO₄ is acting as a catalyst



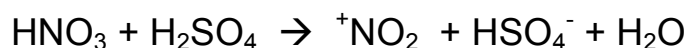
Notes:

If the mixture gets hotter than 50°C then a further nitro- group may be added to the ring (i.e. the product reacts with further nitric acid)

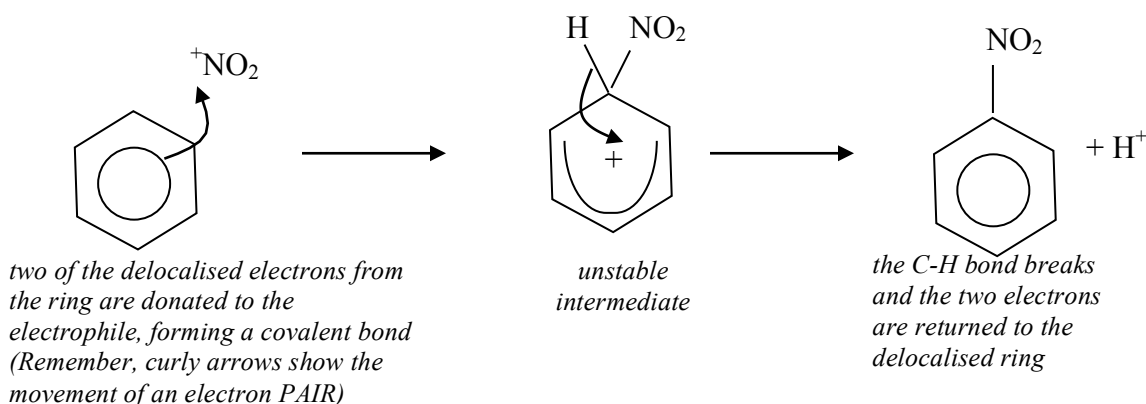
Other aromatic compounds e.g. methylbenzene (toluene) can also be nitrated in this way. This reaction is faster than with benzene and can lead to the formation of 2,4,6-trinitromethylbenzene (TNT) !!

Mechanism (*"Attack of the Nitryl Cations"*)

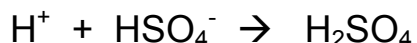
The conc. sulphuric acid is used to generate an electrophile, NO_2^+ from the conc. nitric acid. This ion is called the nitronium ion (or nitryl cation)



The nitryl cation is the electrophile which attacks the benzene ring:



Finally the H^+ which is produced reacts with the HSO_4^- ion, regenerating the H_2SO_4 catalyst:



2) Halogenation of benzene

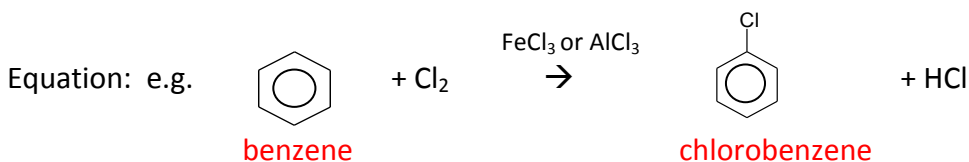
Benzene doesn't react with halogens on their own, but does react with halogens if there is a **halogen-carrier** present as a catalyst.

e.g. when bromine water is added to benzene and a little FeCl_3 is added, the bromine is decolourised and white fumes of HBr are seen.

Common halogen carriers for chlorination are FeCl_3 , AlCl_3 . Fe metal can be used as it reacts with the Cl_2 present to form FeCl_3 in situ. Similarly for bromination, the common halogen carriers would be FeBr_3 or AlBr_3 or Fe .

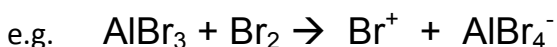
Effect: a hydrogen is replaced on the benzene ring by a halogen atom

Conditions: halogens react with benzene at room temperature and pressure in the presence of a suitable halogen carrier

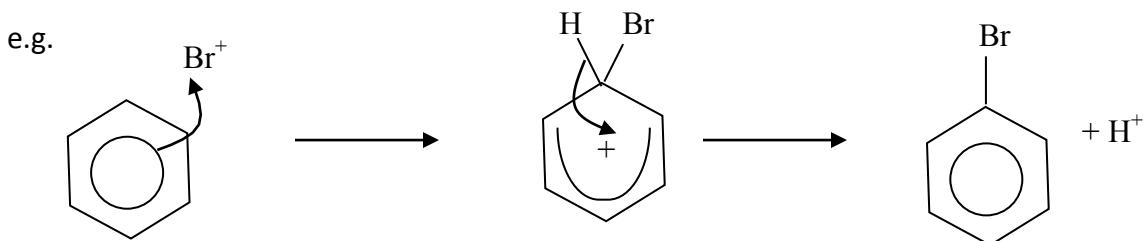


Mechanism:

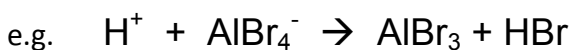
The role of the halogen-carrier is to generate Cl^+ or Br^+ ions, which are more powerful electrophiles than Cl_2 or Br_2 (see later).



The Cl^+ or Br^+ ion is the electrophile which attacks the benzene ring:



Finally the H^+ reacts with the FeBr_4^- or AlBr_4^- regenerating the halogen carrier catalyst:

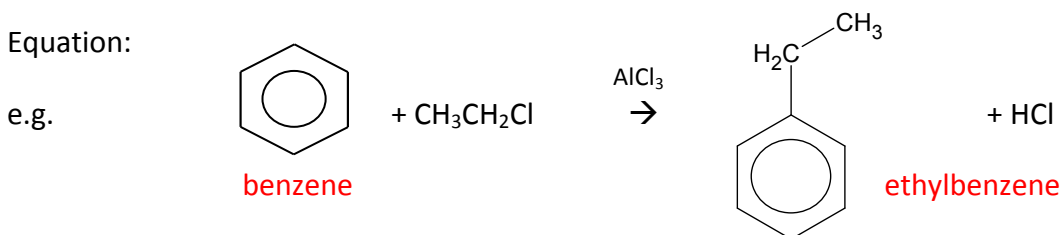


3) Alkylation of benzene (Friedel-Crafts)

This reaction is very important as it results in a bond being formed between a carbon atom and an aromatic ring. This allows the carbon 'skeleton' of a molecule to be modified by extending it during synthesis.

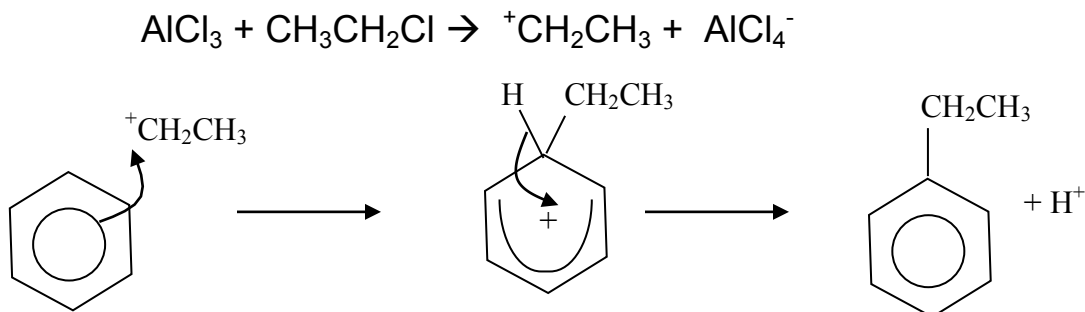
Effect: a hydrogen on the benzene ring is replaced by an alkyl group.

Conditions: a haloalkane, in the presence of a halogen carrier e.g. AlCl_3



Mechanism:

The role of the halogen-carrier is to generate an alkyl cation, e.g. $^+\text{CH}_2\text{CH}_3$, which acts as an electrophile in attacking the aromatic ring.



Finally the H^+ reacts with the AlCl_4^- regenerating the halogen carrier catalyst:

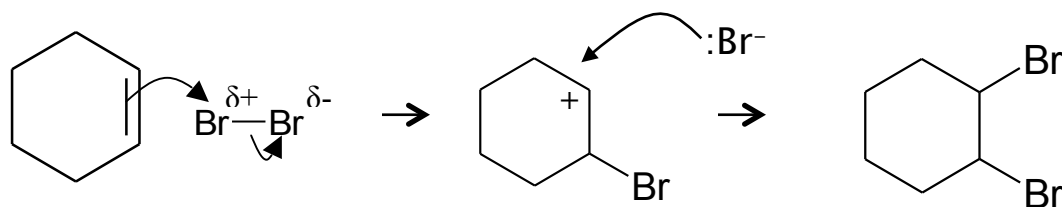


You may be given information about an unfamiliar electrophilic substitution reaction, but the principle will be the same. An electrophile will be generated and all of the rest of the mechanism will be the same as in these examples, with the electrophile being substituted onto the ring.

Comparing and contrasting the reactions of alkenes with those of benzene

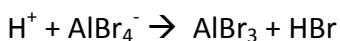
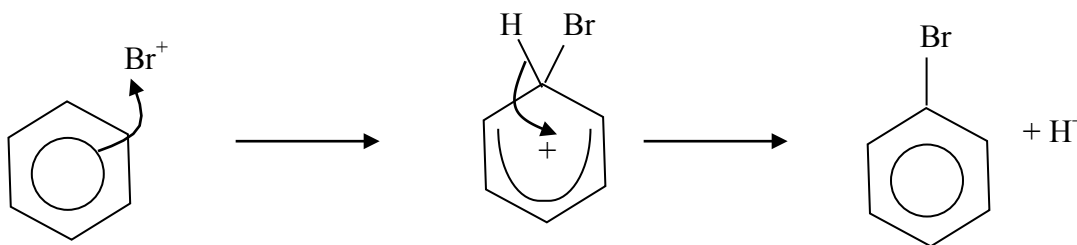
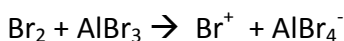
It is important to be able to discuss the differences and similarities in how an alkene (e.g. cyclohexene) react with an electrophile such as Br_2 compared to how benzene reacts.

CYCLOHEXENE reacts by ELECTROPHILIC ADDITION



The two electrons in the π - bond of an alkene are localised between the two carbon atoms. The high electron density here can polarise the bromine, causing the reaction.

Whereas BENZENE reacts by ELECTROPHILIC SUBSTITUTION



The six electrons in the π -system above and below the plane of the benzene ring are delocalised over the six carbon atoms, so the electron density is lower. The bromine cannot be polarised sufficiently to react, and the lower electron density does not attract the electrophile so strongly.

Key differences:

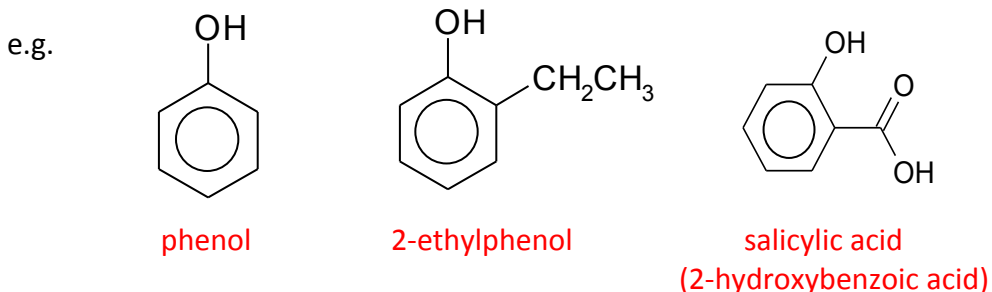
Benzene has delocalised π -electrons spread over all six carbon atoms in the ring (6 electrons spread over 6 bonds). Alkenes have π -electrons localised in the double bond (2 electrons localised in 1 bond), so benzene has a lower π -electron density than alkenes.

When a non-polar molecule such as bromine approaches the benzene ring there is insufficient π -electron density above and below any two carbon atoms cause the necessary polarisation of the bromine molecule, so a halogen carrier is needed to generate Br^+ to attack the ring

The π -electron density in an alkene's double bond is sufficient to polarise the bromine molecule so that it can act as an electrophile without needing a halogen carrier.

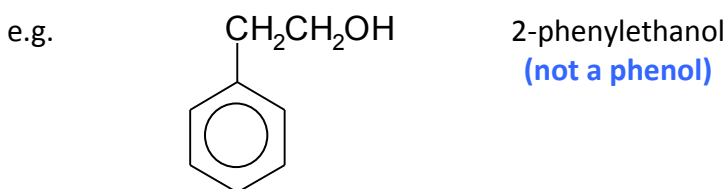
Phenols

In a phenol there is an –OH group directly attached to the benzene ring. The –OH group is taken as being in position 1 for the purposes of naming a phenol, although in some aromatic compounds the –OH can be a substituent group and is indicated by ‘hydroxy-’ in the name.



Salicylic acid is a phenol used in the preparation of aspirin and other pharmaceuticals.

Note that an aromatic compound where the –OH group is not attached to the benzene ring would be an aromatic alcohol, not a phenol.

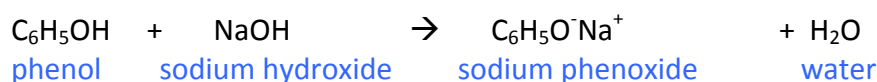


Properties of phenols

- Slightly soluble in water because the –OH group forms hydrogen bonds with water, but the presence of the benzene rings makes phenols less soluble than alcohols.
- Weakly acidic in aqueous solution:



The acidic nature of phenols means that they can be neutralised by alkalis such as sodium hydroxide, to form a salt and water:



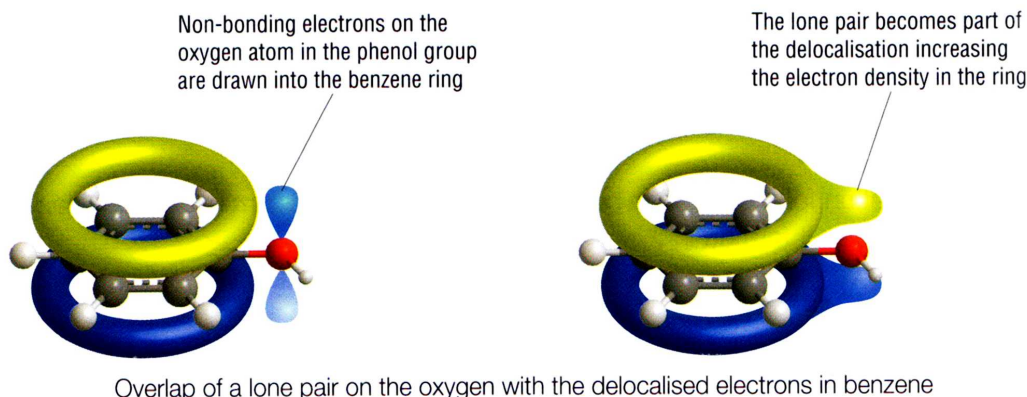
However, phenols are such weak acids that unlike other acids they do not react with carbonates such as sodium carbonate.

Reactions with electrophiles

Like benzene, phenol undergoes electrophilic substitutions. Unlike benzene the reactions take place at room temperature and without the need for a halogen carrier catalyst.

Why are electrophilic substitutions of phenol easier than with benzene?

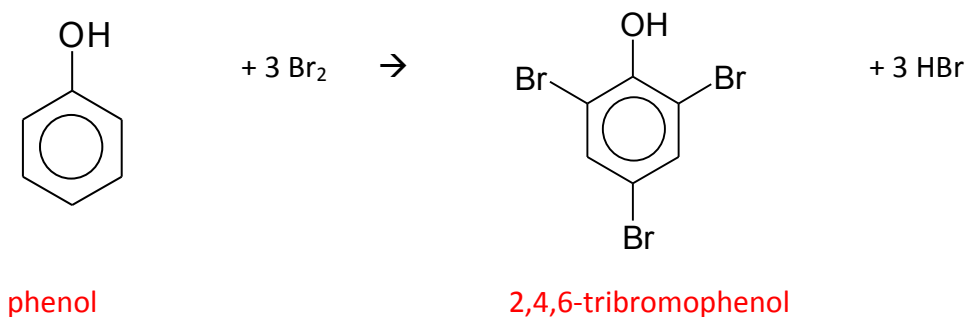
- A lone pair occupying a p-orbital **on the oxygen atom** of the –OH group is **delocalised into** the benzene ring (adding two more electrons to the π -system).
- This creates a **higher electron density in the ring structure** – the ring is **activated**.
- The increased electron density makes the ring more susceptible to attack by electrophiles.

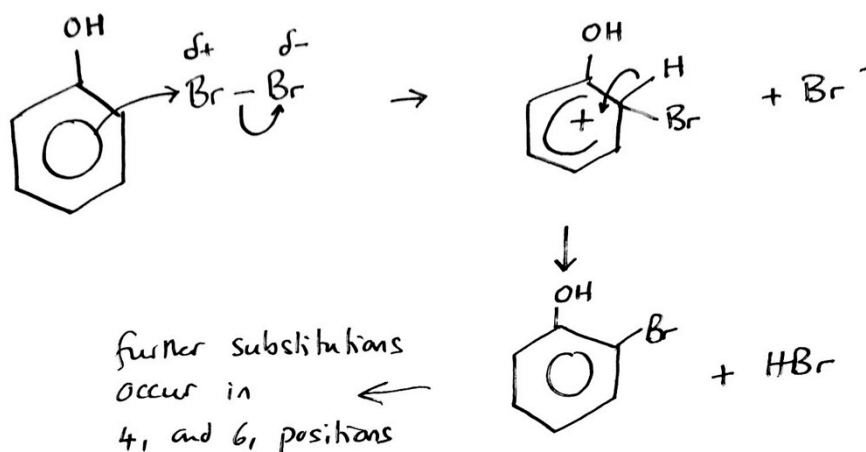


1) With bromine

When bromine water is added to an aqueous solution of phenol, the **bromine is decolourised** and a **white precipitate** of 2,4,6-tribromophenol is formed (steamy fumes of HBr may also be seen). No halogen carrier is required because the increased electron density in the ring **increases the polarisation** of Br_2 molecules, which are thus **attracted more strongly** towards the ring than in benzene, and able to attack as electrophiles.

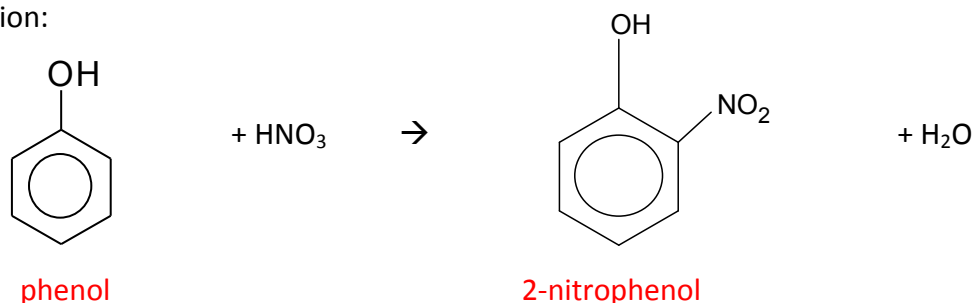
Equation:



Mechanism**2) With nitric acid**

Phenol readily undergoes nitration to form a mixture containing mainly 2-nitrophenol, and some 4-nitrophenol. Nitration of phenols does not require conc. nitric acid or a conc. sulphuric acid catalyst, and can be carried out using dilute nitric acid alone.

Equation:

**Directing effects**

The presence of groups bonded to the aromatic ring does not only affect how reactive the ring is towards electrophiles, but also influences where around the ring substitution takes place. We refer to these as directing effects.

Groups such as $-\text{OH}$ and $-\text{NH}_2$ are electron-donating towards the ring, and have a 2- and 4- directing effect when electrophilic substitution takes place (as well as activating the ring, increasing its reactivity).

Electron-withdrawing groups such as $-\text{NO}_2$ have the opposite effect. They are 3-directing (as well as decreasing the reactivity of the ring).

You may be given information in exams about the electron-donating or electron-withdrawing properties of other groups, and should be able to predict their directing

properties accordingly in electrophilic substitution reactions of substituted aromatic compounds.

Worked examples:

Q1) Phenylamine, $C_6H_5NH_2$ can react with bromine in an electrophilic substitution reaction. Predict the product formed, and the relative ease of bromination compared to the bromination of benzene.

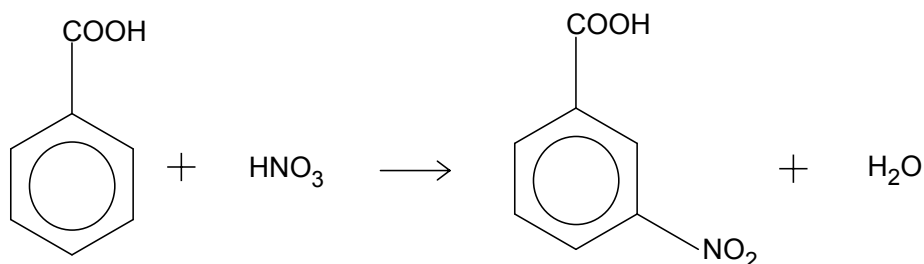
Ans: The $-NH_2$ group, like the $-OH$ group, is electron-donating. It is therefore 2- and 4- directing. We can predict that the ring will be activated like in phenol and therefore the reaction will take place readily without need for a halogen carrier. Like with phenol we might expect multiple substitutions to form 2,4,6-tribromophenylamine.

Q2) Nitrobenzene, $C_6H_5NO_2$ can react with bromine in an electrophilic substitution reaction. Predict the product formed, and comment on the relative ease of bromination compared to that of benzene.

Ans: The NO_2 - group is electron-withdrawing. It is therefore 3-directing and the product we expect would be 3-bromonitrobenzene. The reaction will be slower than with benzene, requiring both a halogen carrier catalyst and a high temperature.

Q3) Benzoic acid comprises a carboxylic acid group bonded to a benzene ring. The $-COOH$ group is electron-withdrawing. Benzoic acid can be nitrated using a mixture of nitric and sulphuric acids. Identify the mono-substituted product that would be formed, and write an equation for the reaction that takes place.

Ans: Electron-withdrawing groups are 3-directing, so the product would be predicted to be 3-nitrobenzoic acid.



Q4) Methylbenzene is brominated more readily than benzene because the alkyl group is electron-donating. Predict the mono-substituted products that will be formed, and the relative proportions of each.

Ans: Electron-donating groups are 2- and 4- directing, so the products would be expected to be 2-bromomethylbenzene and 4-bromomethylbenzene. The 6- position is equivalent to the 2- position, so there are effectively twice as many 2- positions as 4- positions. There will therefore be twice as much 2-bromomethylbenzene as 4-bromomethylbenzene.