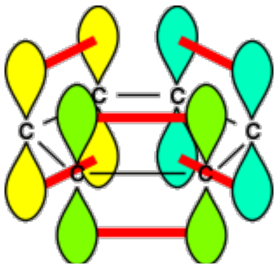
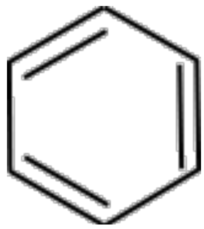
Aromatic compounds

Structure of benzene

Benzene has the molecular formula C_6H_6. Kekule suggested a planar, cyclic ring with alternating double and single bonds.

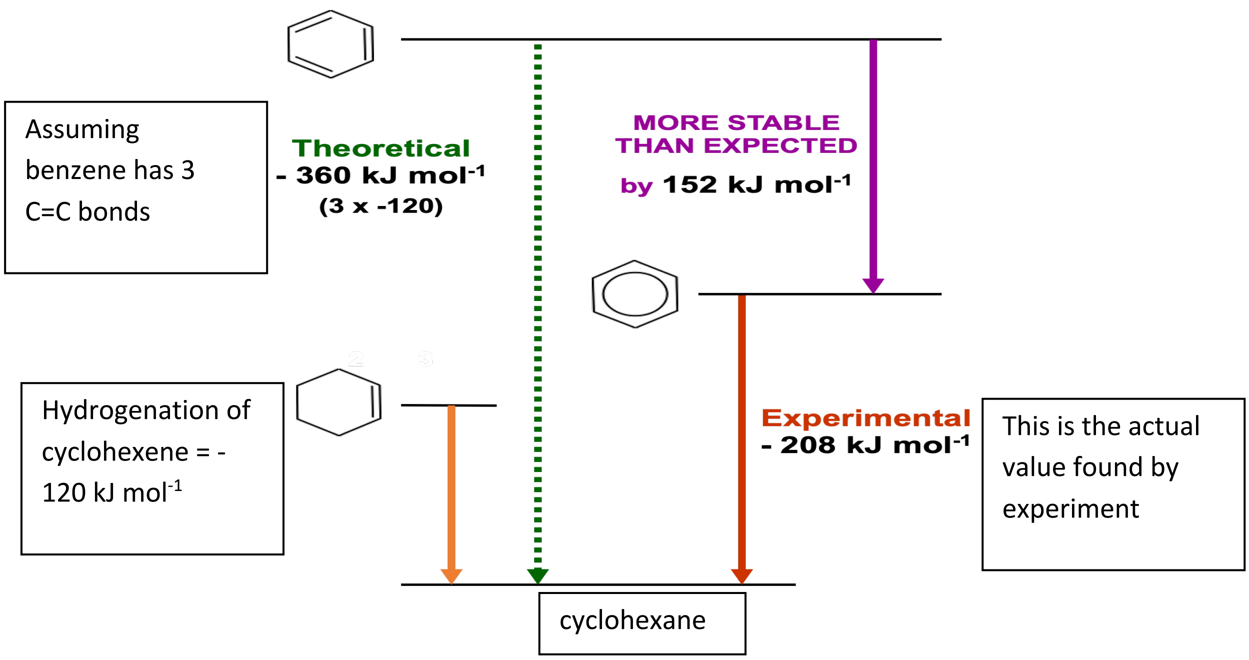




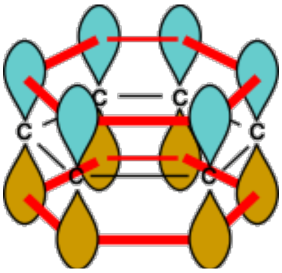
However,

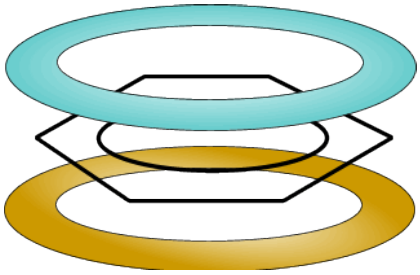
1. The Kekule formula shows single and double bonds, but benzene does not decolourise Br_2. Its most common reaction is substitution not addition.
2. Double bonds are shorter than single bonds. Kekule implies a distorted structure. In fact benzene is a regular planar hexagon with angles 120°, and all C-C bonds the same length, intermediate between double and single bonds.
3. Energetics calculations and experiments indicate that benzene is more stable than expected. Enthalpy of hydrogenation of ethene:

$$H_2C{=}CH_2 \quad + \quad H_2 \quad \rightarrow \quad CH_3CH_3 \qquad \Delta H = -120\ kJ\ mol^{-1}$$



We now know the hexagonal molecule is **planar**, with six C-C bonds of equal length. Overlap of **p-orbitals** leads to formation of **pi-bonds** that are spread over all six C atoms. The electrons are said to be '**delocalised**', forming a ring of electrons above and below the C nuclei.





Electrophilic Substitution of arenes

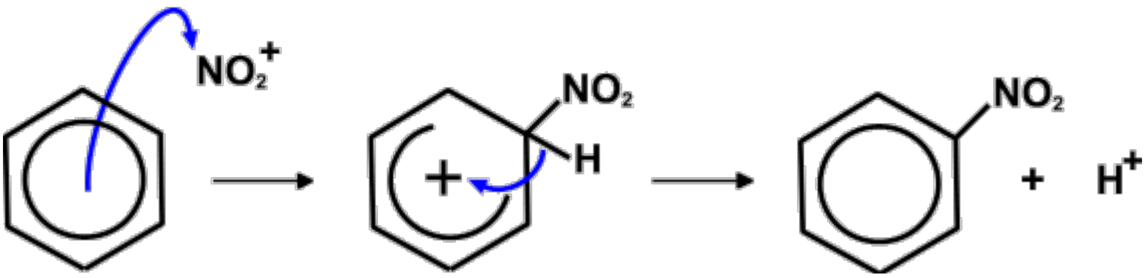
1. **Nitration** uses a mixture of conc nitric acid and conc sulphuric acid at 50 - 60 degrees Celsius.

Benzene + nitric acid → nitrobenzene + water

Mechanism: the electrophile is the nitryl cation, $\mathbf{NO_2^+}$, produced in the nitrating mixture:

$$H_2SO_4 + HNO_3 \rightarrow NO_2^+ + HSO_4^- + H_2O$$

The NO_2^+ is attracted to the delocalised pi-electrons in benzene.
An unstable intermediate is formed without full delocalisation.
Delocalisation is restored when a proton is lost.



Finally the sulphuric acid catalyst is reformed : $H^+ + HSO_4^- \rightarrow H_2SO_4$

2. **Electrophilic substitution with a halogen in the presence of a halogen carrier (**Halogen carriers include iron, iron halides and aluminium halides).

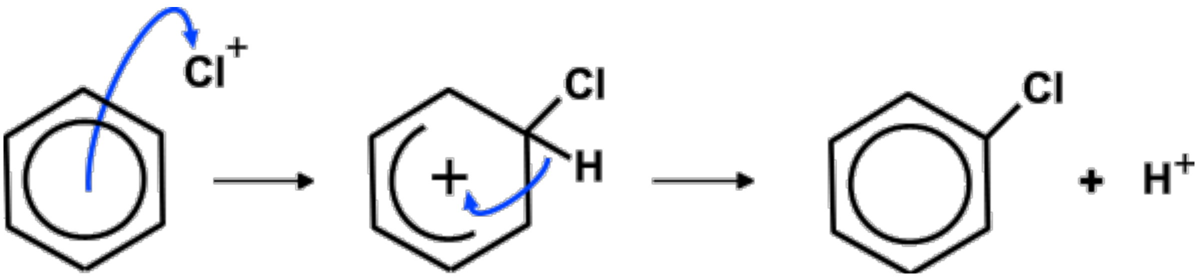
$FeCl_3$ catalyst
benzene + chlorine → chlorobenzene + hydrogen chloride

$$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$$

Mechanism:

When chlorine is bubbled through benzene in the presence of iron, iron (III) chloride is generated, which then reacts with more Cl_2 to form the electrophile Cl^+.

$$Cl_2 + FeCl_3 \rightarrow FeCl_4^- + Cl^+$$

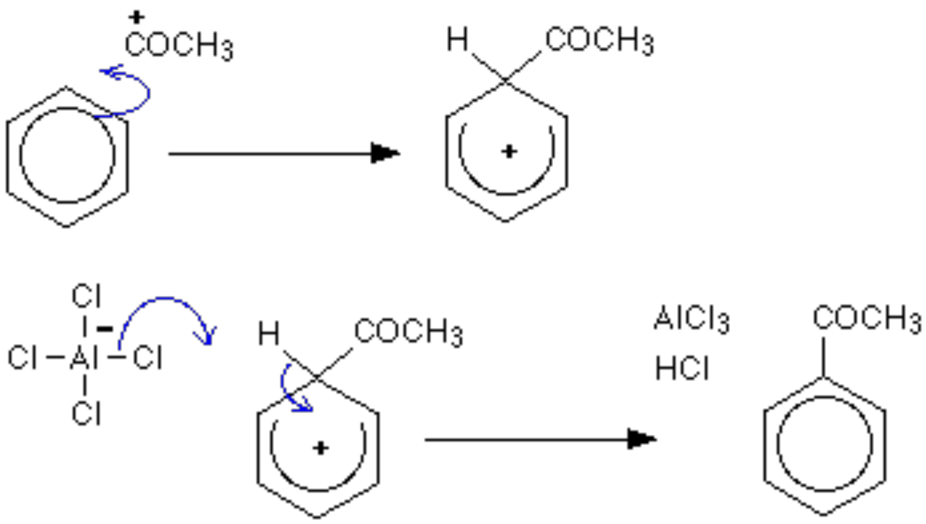


3. **Friedel-Crafts acylation reactions**

a) Benzene + ethanoyl chloride → methyl phenyl ketone + hydrogen chloride

Aluminium chloride, $AlCl_3$, is an electron deficient molecule. It is covalently bonded, but because the aluminium is only forming 3 bonds, and has no lone pairs, there are only 6 electrons around the aluminium atom rather than 8. It takes a chlorine (as a chloride ion) from the ethanoyl chloride, and forms a co-ordinate (dative covalent) bond with it

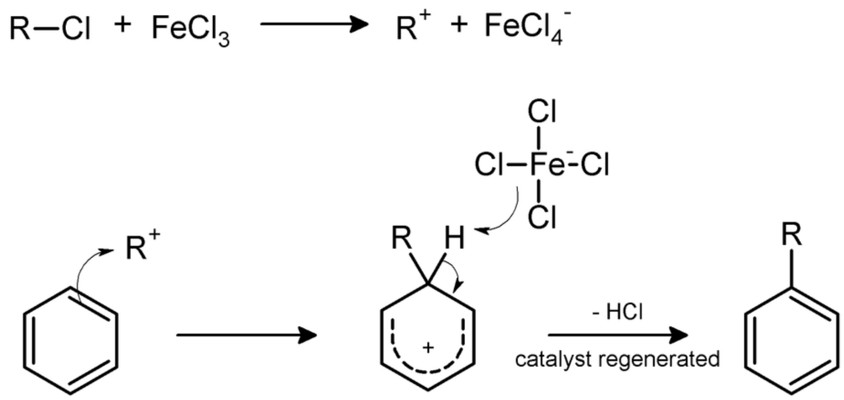
$$CH_3COCl + AlCl_3 \longrightarrow CH_3CO^+ + AlCl_4^-$$



NOTE: $AlCl_3$ is a catalyst.

4. Benzene +chloromethane → methyl benzene+ hydrogen chloride

$AlCl_3$ is a catalyst.



Reactivity of benzene:

Benzene reacts less readily than cyclohexene with electrophiles like bromine. The six delocalised electrons in benzene are delocalised over six bonds. However, alkenes have a higher π electron density to attract electrophiles more readily because the two π electrons are localised over one bond.

Phenols

Phenol is a weak acid, forming salts with bases and with sodium:

phenol + sodium hydroxide → sodium phenoxide + water

C_6H_5OH + NaOH → $C_6H_5O^-Na^+$ + H_2O

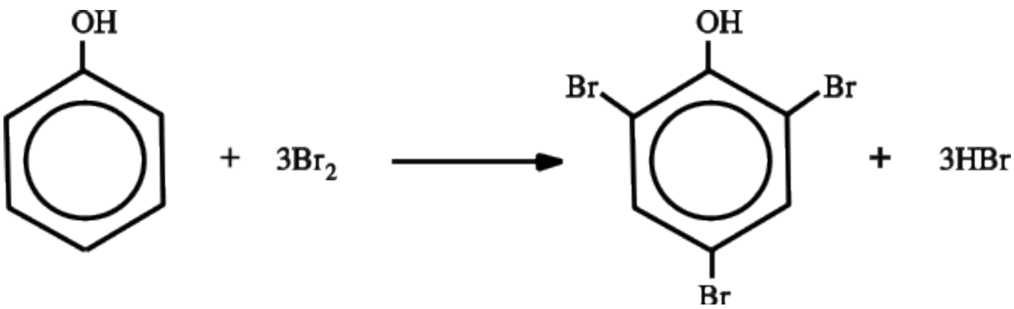
phenol + sodium → sodium phenoxide + hydrogen (vigorous) **FIZZING OBSERVED**

C_6H_5OH + Na → $C_6H_5O^-Na^+$ + ½ H_2

Sodium phenoxide is ionic and water soluble

Phenol does NOT react with metal carbonates.

1. **Electrophilic Substitution with bromine water** A white ppt of 2,4,6-tribromophenol is produced and the bromine is decolourised. This is a test for phenols.



This reaction occurs more readily than with benzene as the OH group "activates" the benzene ring. A lone pair in a p orbital on the oxygen atom overlaps with the delocalised π electrons, increasing the electron density in the ring so it is more susceptible to electrophilic attack. **No catalyst is needed**.

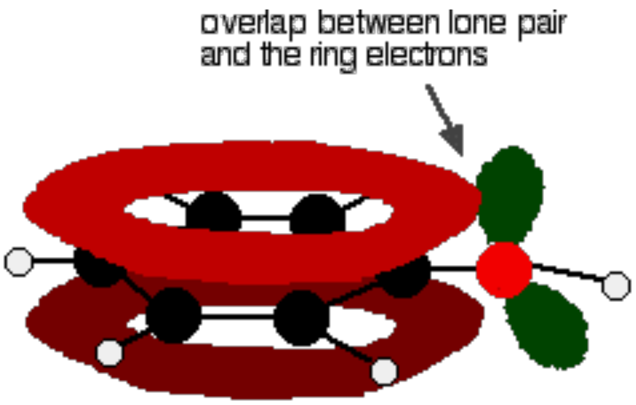
2. Phenol will also react with **dilute nitric acid** to form 2-nitrophenol.

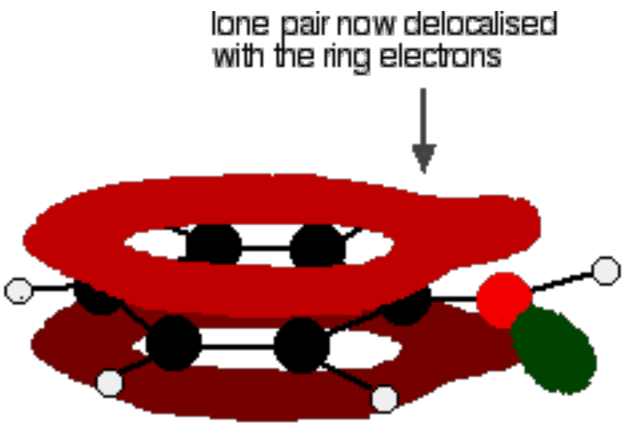
Phenols are used in the production of plastics, antiseptics, disinfectants and resins for paints.

Directing Groups

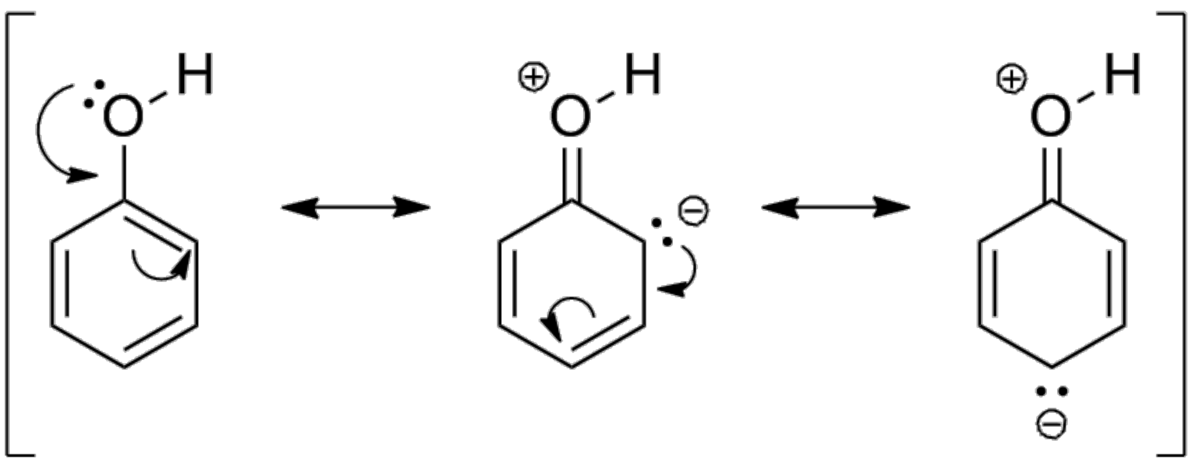
Groups such as OH and NH_2 when attached to a benzene ring are known as 2, 4 directing groups. This is because they donate the lone pair on the O or N atom into the benzene ring. This increases the electron density in the 2 and 4 positions, hence electrophiles will attack these carbons.

In phenol:

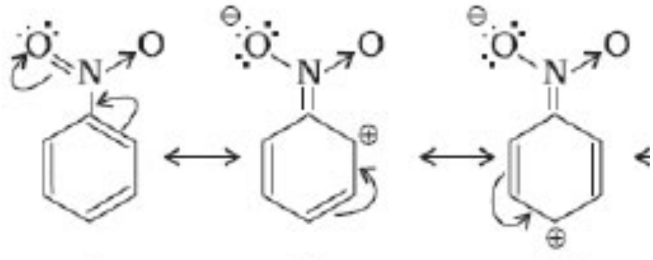




<u>The diagrams below are resonance structures and show why electron density is concentrated on the 2 and 4 positions.</u>



Conversely, electron withdrawing groups such as NO_2 direct incoming electrophiles to the 3 position.



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This is because the three position is less affected by the electron-withdrawing group.