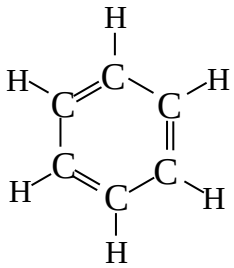
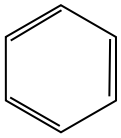
Organic Chemistry – Arenes and Phenols

Arenes - Structure of benzene

The term ***arene*** includes all compounds with a delocalised π-system: these are also called ***aromatic*** compounds. e.g. benzene, C_6H_6.

Kekulé suggested the following structure for this compound.



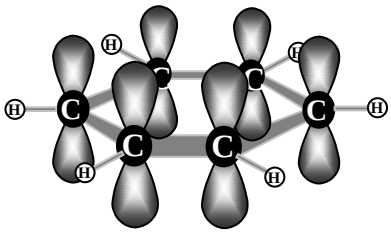


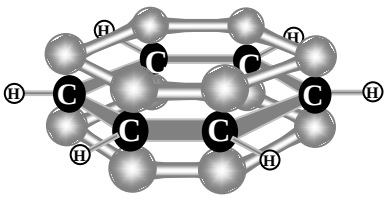
X-ray diffraction studies provide information about bond lengths.

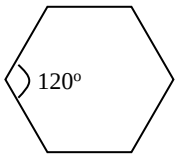
Bond lengths	C-C	in cyclohexane	0.154 nm
	C=C	in cyclohexene	0.133 nm

This would give benzene a distorted hexagon. However, X-ray diffraction studies show that the C-C bond lengths in benzene are all 0.139 nm. This means that the Kekule structure is incorrect.

The benzene ring is a flat, regular hexagon, with six electrons in the delocalised π–"sandwich" above and below the ring.
The σ-bonds are built up in a similar way to ethene, leaving an unused 2p orbital on each of the six carbons. These can overlap sideways in both directions, resulting in a delocalised π-electron cloud, containing six π-electrons and stretching over all six atoms, in a "sandwich" which lies above and below the plane of the ring:







Thus the C–C bonds in benzene are all equal, each of length between a single and a double bond.

The delocalised structure is much more stable (lower in enthalpy content) than one with three double bonds - probably by more than 150 kJ/mol $^{-1}$ and so benzene is much less reactive than ethene, since reaction involves loss of at least part of this extra stabilisation. Ethene also has two π-electrons between the C atoms, while benzene has only one.

Thermochemical evidence

Evidence for this extra stable structure for benzene is provided by thermochemical evidence.

In the presence of a nickel catalyst hydrogen can be added to a double bond. When this is carried out with cyclohexene the following reaction takes place.

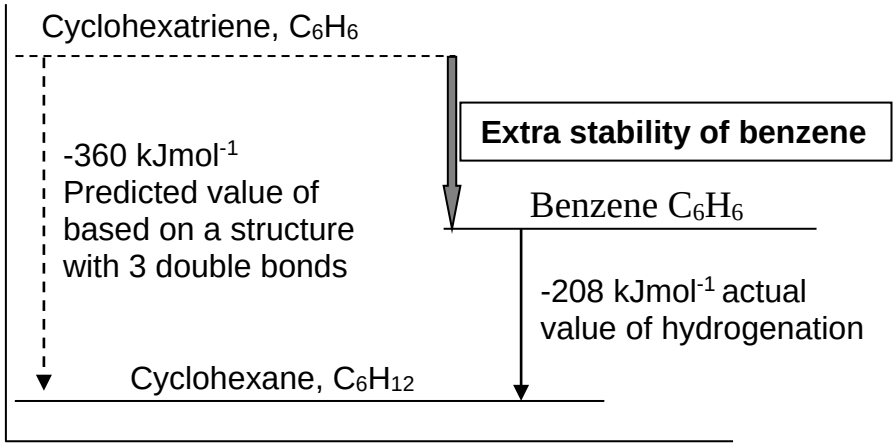
$$C_6H_{10} + H_2 \rightarrow C_6H_{12} \qquad \Delta H = -120\ kJmol^{-1}$$

This would suggest that a similar reaction using benzene would give us the following reaction

$$C_6H_6 + 3H_2 \rightarrow C_6H_{12} \qquad \Delta H = -360\ kJmol^{-1}$$

The measured value for the hydrogenation of benzene is actually -208 kJmol^{-1}.

This indicates that benzene is more stable than would be expected from a structure with three C=C.



Spectroscopic evidence

The infra-red spectrum of a compound containing a double bond shows an absorption between 1610 and 1680 cm^{-1}. This absorption however is absent in benzene compounds.

Reactions of Benzene

Benzene requires much more forcing conditions to make it react than does ethene:

- benzene does not decolorise bromine water.
- benzene will not react with hydrogen at an appreciable rate under conditions at which ethene reacts (e.g. 150°C and normal pressures, over a nickel catalyst).
- benzene will not react with oxidising agents like alkaline $KMnO_4$.

Reactions of Arenes

The main reactions which benzene does undergo are with electrophiles, but since it has a lower electron density between carbon atoms than ethene, benzene requires stronger electrophiles and more forcing conditions.

Once an electrophile has added on to the ring, the subsequent step is likely to be loss of a proton, leading to **electrophilic substitution** rather than addition, since the stable delocalised π-system is regained.

Combustion

Arenes have the equivalent of three double bonds per molecule and so tends to produce incomplete combustion, so when it burns it produces a smoky flame.

Nitration of Arenes

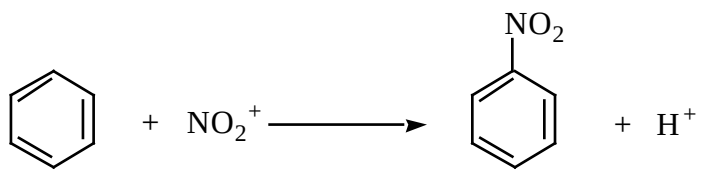
Arenes can be nitrated if they are mixed with conc nitric and sulphuric acids at temps below 50°C.

$$C_6H_6\ (l) + HNO_3\ (l) \rightarrow C_6H_5NO_2\ (l) + H_2O\ (l)$$

Nitrobenzene

The sulphuric acid protonates the nitric acid, which ionises, forming the *nitronium ion*, NO_2^+

$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^-$$

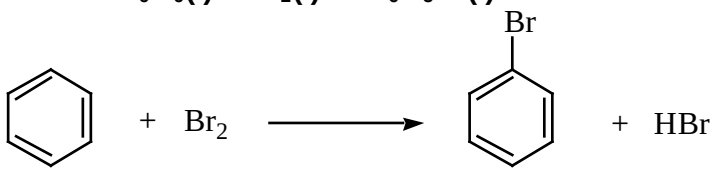


If the temperature is raised above 50°C there is a chance of multiple nitrations occurring.

Bromination of Arenes

Arenes will react with halogens in the presence of a halogen carrier catalyst, Fe, $FeBr_3$, Al or $AlCl_3$.

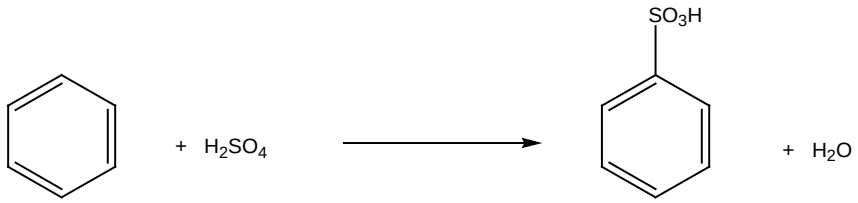
$$C_6H_6(l) + Br_2(l) \rightarrow C_6H_5Br(l) + HBr$$



Sulphonation of Arenes

Arenes will react with concentrated (fuming) sulphuric acid to form sulphonic acids
The reaction is carried out at room temperature.

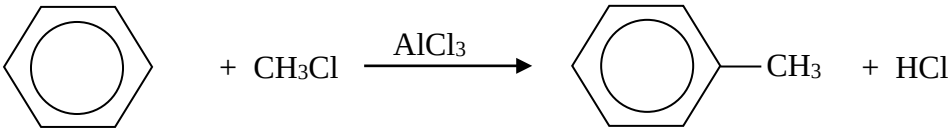
$$C_6H_6 + H_2SO_4 \rightarrow C_6H_5SO_3H + H_2O$$



Sulphonic acid groups are often used in organic synthesis to increase the water solubility of large organic drug molecules.

Feidel-Craft Alkylation

Alkylation: Reaction with a halogenoalkane in the presence of the catalyst $AlCl_3$.



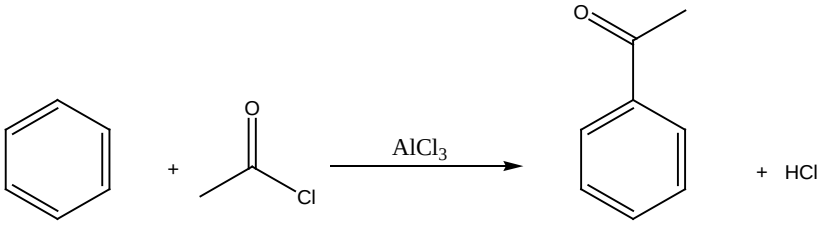
This is an important reaction in organic synthesis as it is a C-C bond forming reaction.

Feidel-Craft Acylation

Acylation: Reaction with an acyl chloride in the presence of the catalyst $AlCl_3$.
Conditions: Anhydrous $AlCl_3$ as a catalyst.

$$C_6H_6(l) + CH_3COCl\ (l) \rightarrow C_6H_5COCH_3(l) + HCl(g)$$

acid chloride



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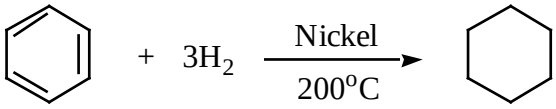
Addition reaction with hydrogen

This reaction is unlike all those above in that whereas most reactions of benzene are substitution this is an **addition process**. In the presence of a nickel catalyst hydrogen can add on to a benzene ring across the double bonds.

This reaction requires Raney nickel, which is a particularly finely divided form of the metal, and the temperature of 200°C is higher than that used for addition to an alkene.

The more extreme conditions for this reaction compared with those needed for addition of hydrogen to an alkene because of the extra stability of the delocalized electron ring structure.



Mechanisms - Electrophilic substitution.

Arenes commonly undergo **electrophilic substitution** reactions.

In this type of substitution two of the delocalised [π] electrons on the benzene ring are donated to the electrophile.

An unstable π-complex containing both an electrophile and a leaving group is formed as an intermediate.

Nitration

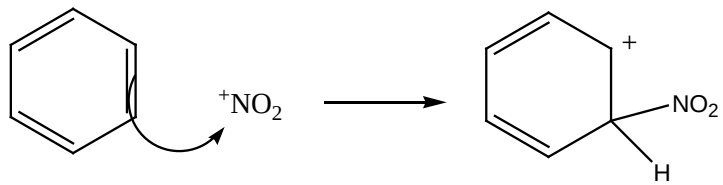
Nitration is carried out under reflux at 55-60°C using a nitrating mixture.

This contains equal amounts of concentrated nitric acid and sulphuric acid.

The sulphuric acid protonates the nitric acid, which ionises, forming the *nitronium ion*, NO_2^+ (sometimes called the nitryl cation):

$$\mathbf{HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^-}$$

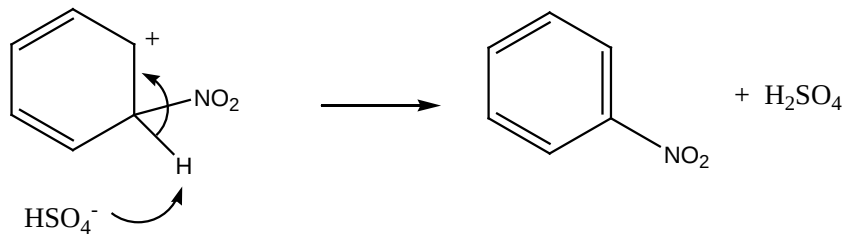
The nitronium ion is a powerful electrophile, and this pulls out an electron pair from the π–system, adding on to the ring:



Note a carbocationic intermediate is formed. This first step, addition of an electrophile, is similar to the attack of bromine on ethene.

However, the positive benzene intermediate can lose much more energy by giving up a proton to a base than it could by adding on a nucleophile.

The loss of a proton (to an HSO_4^-) ion restores the full delocalisation energy, and sulphuric acid is reformed, as a catalyst.



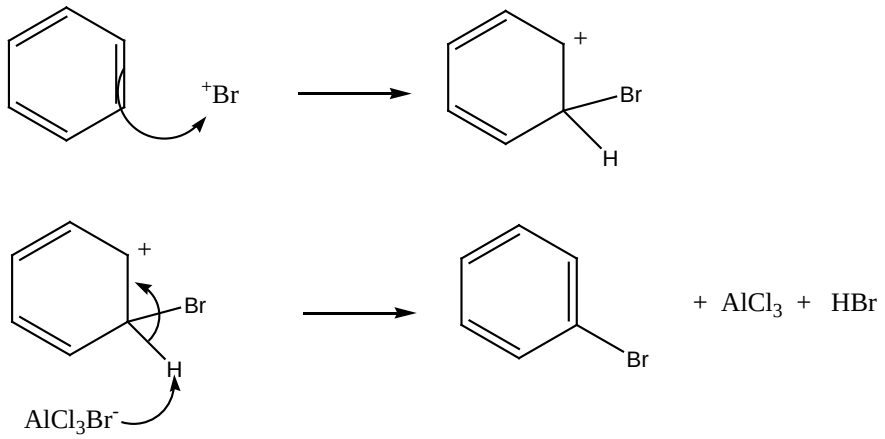
Bromination

The reaction with bromine also follows the same mechanism.

Aluminium chloride is used as a **halogen carrier catalyst** which helps form the electrophile.

$$\mathbf{Br\text{-}Br + AlCl_3 \rightarrow Br^{d+}\text{---}Br\text{---}AlCl_3^{d-}}$$

The mechanism is then the same as for nitration.



The delocalised π-system requires a large activation energy to disrupt (hence the need for a catalyst). The positive benzene intermediate once again restores the full delocalisation energy by losing H^+ (hence substitution rather than addition).

Chlorine reacts in a similar way, giving C_6H_5Cl and HCl, and also needing Al or Fe to be present (forming $AlCl_3$ or $FeCl_3$).

Alkylation

Alkylation follows the same mechanism.

Halogenoalkanes are weak electrophiles because their polar bond. e.g.$CH_3^{d+}\text{-}Br^{d-}$.

The catalyst $AlCl_3$ makes the halogenoalkane a better electrophile.

$$\mathbf{CH_3\text{-}Br + AlCl_3 \rightarrow {}^{d+}CH_3\text{---}Br\text{---}AlCl_3^{d-}}$$

Acylation

Acylation also follows the same mechanism.

The electrophile is again improved by $AlCl_3$. $\mathbf{CH_3COCl + AlCl_3 \rightarrow CH_3C^+{=}O + Cl\text{-}AlCl_3^-}$

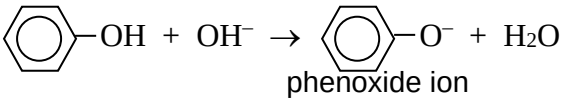
Phenols

Phenols are compounds in which the -OH group is directly attached to the benzene ring.
Phenol itself is a white crystalline solid which is sparingly soluble in water at room temperature.
The benzene ring helps to stabilise a negative charge on the phenoxide ion, $C_6H_5O^-$, and this makes phenol appreciably acidic (unlike ethanol, which is neutral, a solution of phenol in water has a pH of about 5).

Reactions of phenol

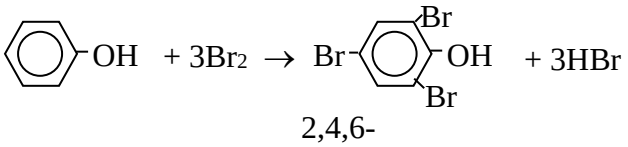
Phenol with sodium hydroxide

Phenol dissolves in aqueous sodium hydroxide because phenol behaves as an acid and gives up its proton to the hydroxide ion which is a base. A soluble ionic product is formed.



Phenol with bromine - electrophilic substitution.

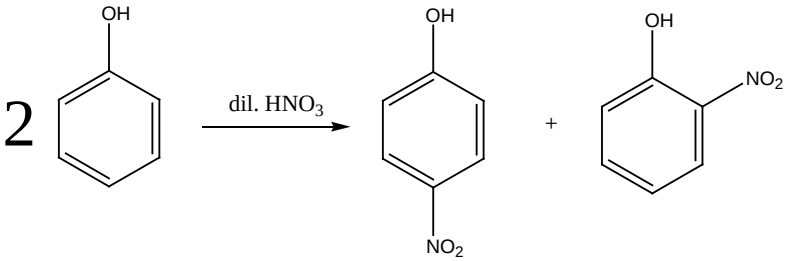
The hydroxyl group in phenol can donate electrons back to the delocalised π-system, helping to stabilise the intermediates of electrophilic substitution and so making phenol much more reactive than benzene. It will react **immediately** with bromine water, **decolorising** it and forming a **white precipitate** of 2,4,6-tribromophenol.



[reaction with chlorine gives 2,4,6-trichlorophenol, or TCP, used as an antiseptic]

Nitration of Phenol.

Phenol can be nitrated with **dilute nitric acid**. This once again shows that the delocalised π-system, makes phenol much more reactive than benzene.



Uses of phenols

Phenol, in dilute solution, was the first successful antiseptic used by Lister (called *carbolic acid*). Now substituted phenols are used both as **antiseptics** (to keep surfaces free of pathogens) and as **disinfectants** (to kill pathogens already present).