Organic crib notes – Benzene and phenol

General

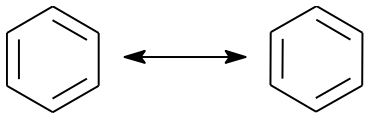
Benzene and products made from benzene (such as phenol) are known as “aromatic” compounds. Benzene itself is highly toxic yet as part of a compound is found in a large number of products such as pain killers, food additives and fuels.

Benzene comes under a number of names other than benzene (such as cyclohexa-1,3,5-triene)

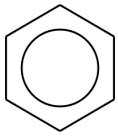
Structure and bonding – a historical view

The benzene molecule shows sp^2 hybridisation which would give rise to double bonds. However, physical data conflicts with this and shows something else

Traditionally, benzene had been thought of having two structures of equal energy (known as *resonant structures*). This was proposed by a chemist called Kekule who suggested that benzene looks like this



This structure was accepted for many years until in the 1950s a new structure (*right*) was proposed and quickly accepted as it fitted the evidence of the structure much better than the Kekule model.



While the Kekule model helped explain the chemistry of benzene, it had a number of problems.

1. The bond length : a C=C bond is much shorter than a C-C bond, yet the bond length in benzene is somewhere between the two.
2. Enthalpy of formation : When a C=C bond is broken, it releases a certain amount of energy (which is not quite the same as 2 C-C bonds being broken). Again, the bond energy released when the benzene molecule was tested showed a value between the C=C and C-C bonds
3. Reactivity. C=C bonds are reactive on specific carbons and the groups attached do not usually alter the position of where the next group adds on. Depending on the groups added depends on where the next group is added.

For a while, it was supposed that benzene had half a double bond between each carbon, but this did not have popular support amongst organic chemists and so was dropped.

Structure and bonding – a chemists view

As benzene has sp^2 hybridised orbits, it will have both σ and π bonds with a single electron from the free p orbital. It was established using a technique called “X-Ray Diffraction” (or XRD) that this single p electron is free to move around the π orbits and is not just restricted to the host carbon. This gives an effect of electrons occupying all of the orbits in a circular motion.

As the electrons are not on any one specific carbon but spread across all of the carbons, this is known as a delocalised π system. This π system has a negative charge which makes benzene prone to electrophilic attack.

General chemical description

Benzene is a very stable compound and smells of pears (though it is unwise to smell benzene as it is both cancer forming [*carcinogenic*] and is thought to cause fertility and sperm motility problems [*mutagenic*]).

Benzene is soluble in the fat of the human body, so can remain there for a long time – it is also possible for it to pass through the skin directly into the blood as well (without any cuts being present)

It is a colourless liquid commonly used as a fuel additive (in the likes of unleaded petrol) and drugs (such as aspirin, opiates and analgesics).

Naming benzene compounds

Benzene is an odd molecule as there are a number of ways compounds containing it can be named, so there is no hard and fast rules that can be applied.

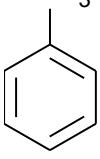
As benzene is also one of the oldest organic compounds known to man (it was originally thought to be elemental which dates it to the 1200s), chemists have grown up with the "trivial" names given to benzene and benzene compounds. A trivial name is a short name which does not describe the components of the compound but which chemists know it by (for example toluene is actually methyl benzene but toluene is the common name used as it has been around for so long) – diagram 1

The position of groups on skeleton also have different naming conventions. For example, on a cyclohexane or cyclohexene, the first substitution is always known as the one position. With benzene this too is the case, however the next group can be also called "ortho", "meta" or "para" to the substituted group - diagram 2

Unfortunately there is no way around this and it is something that just has to be learned.

There is a third level to the confusion on naming benzene compounds. Benzene itself can be a group (called "phenyl") and have two different skeletal names : benzene and phen – diagram 3

In short, naming benzene compounds is not easy!



Dia 1

Diagram 1 (*left*) shows the compound methyl-benzene. Here benzene is being used as the skeletal name with methyl as the group. As this is a mono-substituted benzene (only 1 H has been replaced), the methyl group does not need to be numbered.

This compound has the trivial name "toluene"

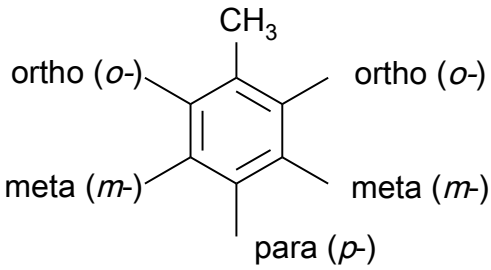
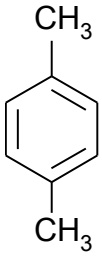


Diagram 2

Diagram 2 (*left*) shows the positional names for the other non-substituted carbons. If a group is added to one of these carbons, it can be described as being (say) meta to the 1st substitution.

With benzene, using the *o*-, *m*-, *p*- style is much preferred to the usual 1,2,3 style due to different carbons being electronically equivalent to each other.

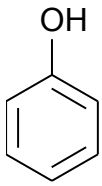
For example



The compound (*left*) has a number of different names :

1,4-dimethyl benzene
xylene (trivial)
p-xylene (positional trivial)

The 1,4 name has been covered plenty of times. Xylene is the trivial name. However, the CH_3 group can also be at the *o*- position. The name is still xylene, however, it is now *o*-xylene.



Dia 3

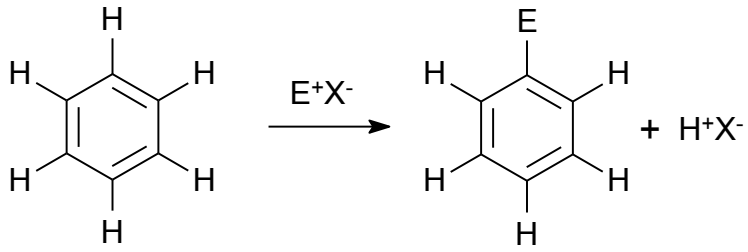
Diagram 3 (*left*) again has 3 names

Benzenol (the skeletal name is taken, alcohol ending added)
Phenol (the skeletal name phen is used, alcohol ending added)
Hydroxybenzene (benzene is being used as a terminal group here and changes the name of the OH group to hydroxy)

<u>Reactions of benzene</u>

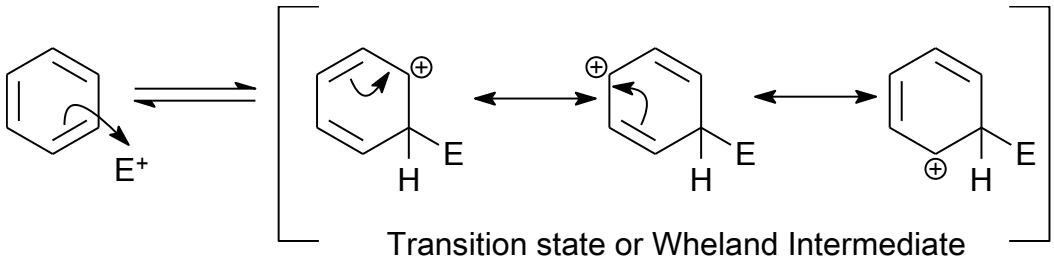
Thankfully, the way benzene reacts is essentially the same whether the electrophile is being used or not. To get the benzene molecule to react though requires quite strong conditions.

The generalised mechanism looks like this

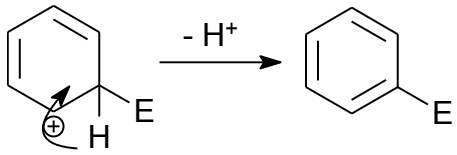


As long as the electrophile can be identified, the above mechanism is always true.

The detailed mechanism shows a two step process. The first is the electrophilic attack on the delocalised π system. This is the slow step; disrupting the π system is not easy! The result is also known as a delocalised cyclohexadienyl cation



The second step is the much quicker removal of the H from the intermediate to reform the aromatic compound.



Electrophilic substitution reactions

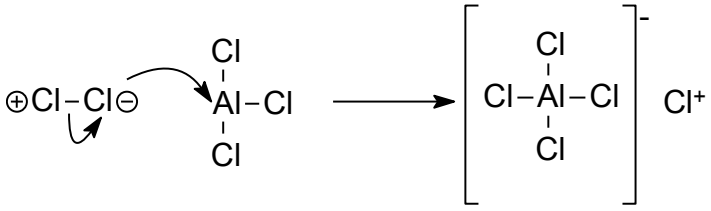
Halogenation of benzene.

Halides are group VII elements. These elements exist as diatomic molecules, filling their empty p_z shell by sharing with another halide. While this will give no overall charge, the shared electron causes a temporary dipole to form giving a slight positive charge to one halide and a slight negative charge to the other.

In alkene and alkyne chemistry this slight charge is enough for a reaction to occur.

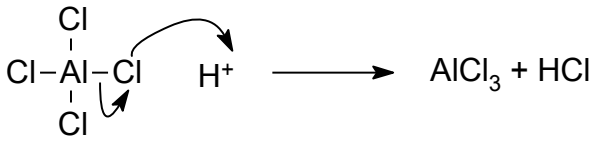
The delocalised π ring on the benzene is too stable and does not react with the slightly charged halide.

For the halide molecule to react, one "end" of the molecule has to be made very positive. This is achieved by using a strong electron withdrawing compound such as $AlCl_3$ or $FeBr_3$ as catalysts. Both of these compounds act as electron acceptors.



The chlorocation (above) can now act as the electrophile which can then attack the phenyl ring using the general mechanism previously shown.

At the end of the reaction, H^+ is removed. This has a strong enough pull to remove the additional Cl^- on the $AlCl_3$ to form HCl with the catalyst being restored.

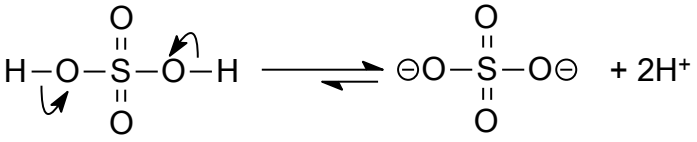


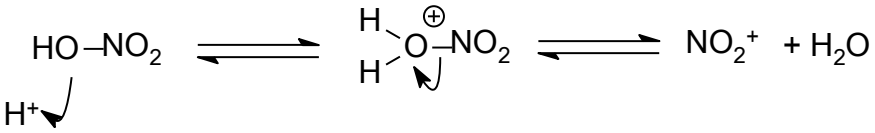
Nitration of benzene

Nitric acid is a strong mineral acid. When the hydrogen dissociates it forms H^+ and NO_3^-. No reaction will occur at this point as all that would happen is the H^+ from the acid would replace the H^+ from the benzene.

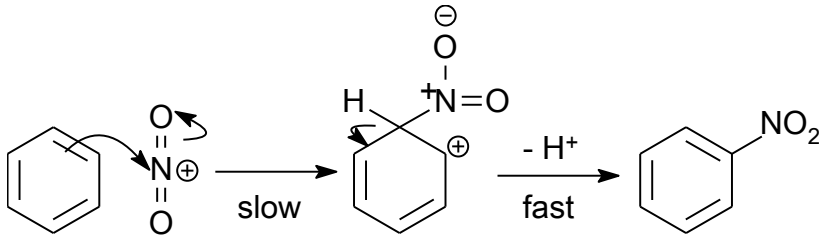
In order for a reaction to occur, a nitronium ion (NO_2^+) needs to be generated. This is achieved by reacting the nitric acid with concentrated sulfuric acid.

When sulfuric acid dissociates, it forms SO_4^{2-} and $2H^+$. In order to understand the full reaction, HNO_3 needs to be thought of as $HO\text{-}NO_2$. The O will still have a lone pair on and will attract the newly formed H^+ from the sulfuric acid to form a hydroxonium ion which is still attached to the NO_2. The bond between the hydroxonium ion and NO_2 breaks to give NO_2^+ and H_2O (this part is a reversible reaction).





The nitronium ion is then free to react as an electrophile.



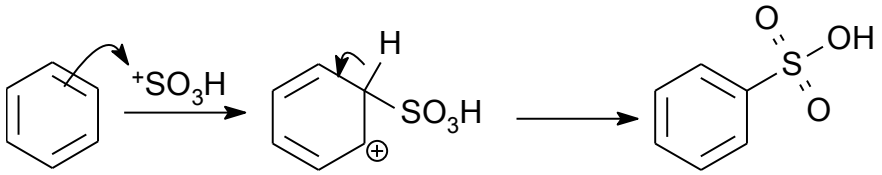
Sulfonation of benzene

This is very similar to the nitration of benzene. As with nitric acid, when sulfuric acid dissociates it gives $2H^+$ and SO_4^{2-}. The same as with nitric acid here also occurs in that all that would happen is a H^+ swaps for a H^+.

In order for sulfonation to occur, “fuming” sulfuric acid (concentrated sulfuric acid mixed with additional SO_3) has to be used. This is an extremely hazardous reaction - “fuming” sulfuric acid can be thought of as concentrated concentrated sulfuric acid.

With “fuming” sulfuric acid, the HSO_3^+ ion is formed and acts as the electrophile which reacts in the same way as other electrophiles do with benzene.

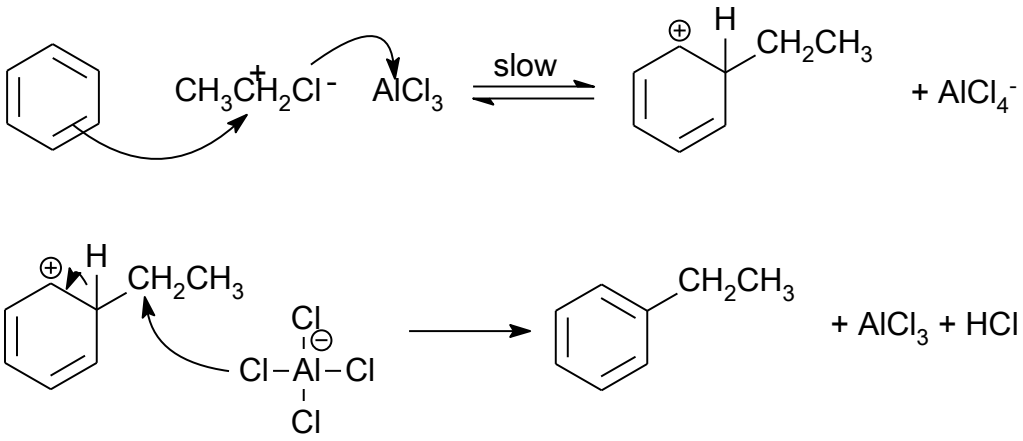
As with the sulfonation of an alkene, a further reaction can take place by adding OH^-, this removes the sulfate group and replaces it with OH.



Friedel Crafts Alkylation

This is the addition of an alkyl halide to benzene using an $AlCl_3$ catalyst. It is a similar type of reaction as for halide addition to benzene. The carbocation does not have enough charge to react with the delocalised π system on the benzene.

As with halide addition, $AlCl_3$ is used as a catalyst and it acts in the same way as before, accepting the halide and releasing the much highly charged carbocation.

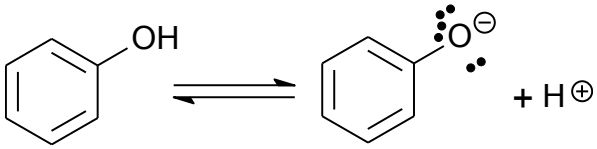


<u>Phenol</u>

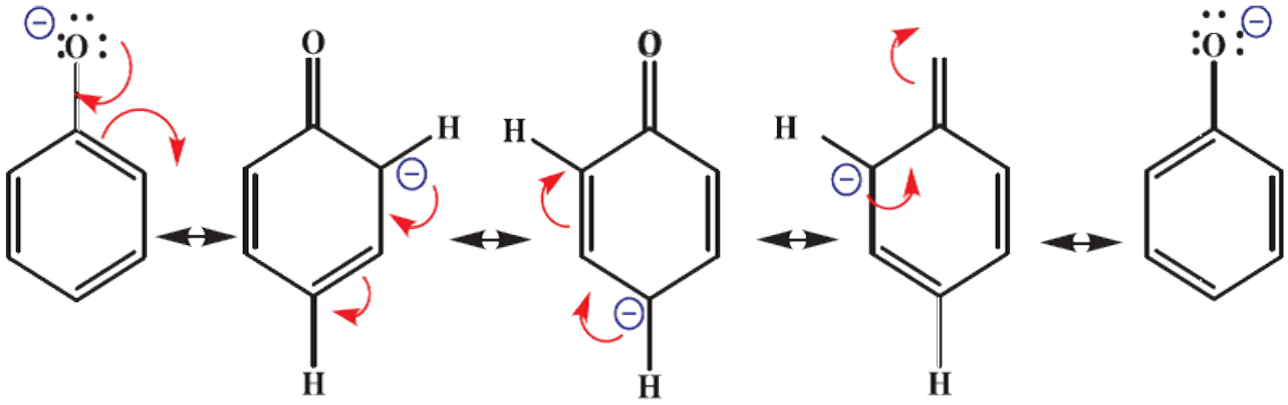
Phenol is a derivative compound from benzene. At room temperature, it is a white/pink crystalline solid. It is a weak acid (pKa 9.9) and for many years was used as an antiseptic and soap until it was deemed to be too dangerous (phenol can cause skin burns and when tested was thought to be a contributor to various cancers in rats). Phenol is now classed as a schedule 1 poison.

Acid dissociation

When the hydrogen is lost from the phenol, a phenoxide ion is formed



While this has a negatively charged oxygen, it is not that reactive as the charge is able to be spread around the delocalised π system.



Solubility

Phenol is soluble in water due to the OH bond forming hydrogen bonds. In weak solutions, it can be used as a soap or disinfectant. At higher concentrations, burning of the skin occurs and if ingested is fatal.

Phenol production

Phenol is produced by reacting benzene with “fuming” sulfuric acid (sulfonation) followed by reacting with NaOH