Chem Factsheet

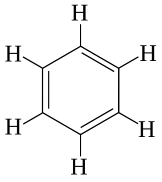
September 2002 Number 39

Reactions of Benzene and its Compounds

To succeed in this topic you need to:
- Have a good understanding of AS-level Organic Chemistry (Factsheets 15, 16,17, and 27);
- Be confident in using organic nomenclature and structural formulae.

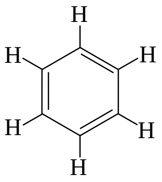
After working through this Factsheet you will:
- Be able to explain the structure of benzene;
- Know the names and structures of common substituent products of benzene;
- Know the necessary reactions of benzene and its compounds.

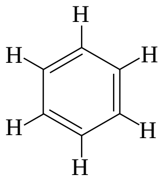
Benzene, C_6H_6, is an aromatic hydrocarbon, or an **arene**. When the formula was first found, the structure proposed initially was:



This structure would have resulted in bonds having different lengths; double bonds are shorter than single bonds, due to the greater attractive forces.

If this had been the correct structure, two equivalent forms would have existed:

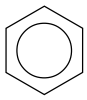




However, where equivalent bond structures can be written for a compound neither exist. Instead, all bond lengths will be equal as the available electrons are shared equally amongst the atoms involved.

The benzene ring consists of 6 C-C single bonds and the remaining electrons exist in a **delocalised system**.

The structure of benzene is often written:



In this representation the H atoms need not be shown. The C-C bonds are somewhere between single and double bonds, as illustrated by the following bond length data:

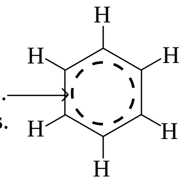
C-C single bond length in cyclohexene	= 0.15 nm
C=C double bond length in cyclohexene	= 0.13 nm
But	
C-C bond length in benzene	= 0.14 nm

Benzene is a clear colourless liquid at room temperature and pressure. It is relatively unreactive due to the strong bonding within its structure

Benzene used to be used as a non-polar organic solvent, but this is no longer the case due to its carcenogenic (cancer causing) properties.

Derivatives of benzene

Derivatives of benzene are formed by substitution reactions which will be electrophilic in nature due to the high concentration of electrons in the delocalised system of benzene.



High concentration of electrons.
Benzene attracts **electrophiles**.

The group C_6H_5-, derived from benzene with one H atom having been substituted, is known as the **phenyl** group.

Listed below are some common substituent products.

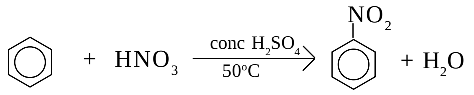
Substituent group		Systematic name
Methyl	$-CH_3$	Methylbenzene
Chloro	-Cl	Chlorobenzene
Nitro	$-NO_2$	Nitrobenzene
Hydroxyl	-OH	Phenol
Amino	$-NH_2$	Phenylamine
Carboxylic acid	-COOH	Benzenecarboxylic acid

Reactions of benzene

Candidates are expected to be able to recall the following reactions, in terms of reagents and reaction conditions.

1. Nitration of benzene.

Benzene reacts with a mixture of concentrated nitric acid and concentrated sulphuric acid (called a nitrating mixture) at 50°C to form nitrobenzene.

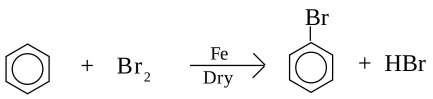


Reaction type: Substitution
Conditions: Conc. H_2SO_4, 50°C
Mechanism: Electrophilic

> ***Exam Hint: -*** *This is a commonly examined reaction. Candidates should pay careful attention to the mechanism of this reaction – see Factsheet 40.*

2. Bromination of benzene.

Bromine reacts with benzene in the presence of an iron wire catalyst in dry conditions at room temperature and pressure.

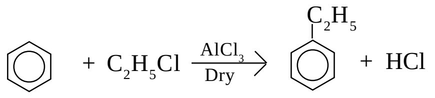


Reaction type: Substitution
Conditions: Fe catalyst, dry, room temp.
Mechanism: Electrophilic

See Factsheet 40 for the reaction mechanism.

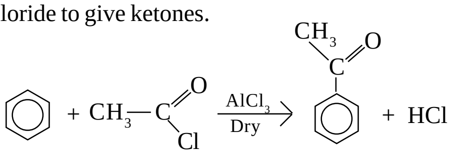
3. Alkylation of benzene (Freidel-Krafts Reactions).

Benzene reacts with chloroalkanes in the presence of anhydrous aluminium chloride to give an alkyl benzene.



Reaction type: Substitution
Conditions: Anhydrous $AlCl_3$, dry, possible heat under reflux.
Mechanism: Electrophilic

A similar reaction takes place with acid chlorides, benzene and aluminium chloride to give ketones.

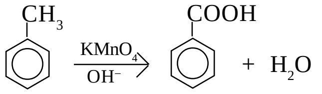


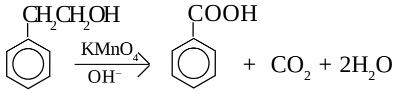
Reaction type: Substitution
Conditions: Anhydrous $AlCl_3$, dry, possible heat under reflux.
Mechanism: Electrophilic

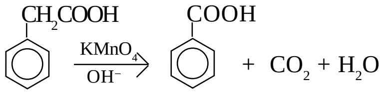
Again, see Factsheet 40 for the reaction mechanism.

4. Oxidation of side chains on arenes.

If an arene (i.e. benzene) with a carbon-containing side chain (with the C atom bonded directly to the ring structure) is heated under reflux with alkaline potassium manganate (VII) solution, benzenecarboxylic acid is formed.





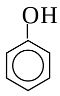


The carbon-containing side chain (whatever it is) is oxidised to –COOH.

Reaction type: Oxidation
Conditions: $KMNO_4$ in alkali, heat under reflux

Reactions of phenol.

Phenol, C_6H_5OH is a common derivative of benzene.

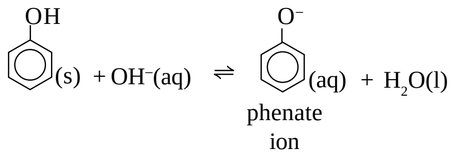


Phenol is an alcohol, but whereas straight chain alcohols have just the -OH functional group, phenol has the -OH group and the electron- rich benzene ring.

Care must be taken when using phenol, a white crystalline solid, as it is both corrosive and an anaesthetic.

1. Reaction of phenol with sodium hydroxide.

The -OH group in phenol is more acidic (proton donating) than in straight chain alcohols. Phenol is not very soluble in water, but forms a colourless solution with aqueous sodium hydroxide.

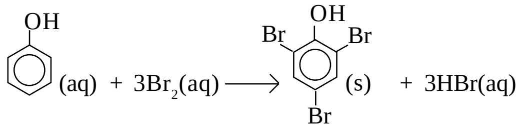


Conditions: Aqueous NaOH at room temp.

Note how phenol has acted as an acid, donating a proton to neutralise the hydroxide ion.

2. Reaction of phenol with bromine water.

Substitution of the hydrogen atoms on the benzene ring is made easier by the presence of the -OH group.

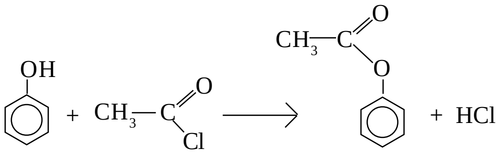


Reaction type: Substitution
Conditions: Bromine water added - no catalyst required.
Mechanism: Electrophilic

This reaction is easily observed as the red/brown bromine water decolourises and a white precipitate is formed.

3. Reaction of phenol with acid chlorides.

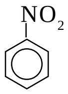
Phenol reacts with acid chlorides to form esters, but alkaline conditions are necessary as phenol does not react as readily as straight chain alcohols.



Conditions: Aqueous NaOH

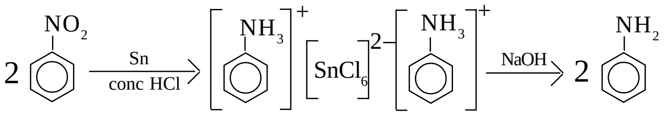
Nitrobenzene

Nitrobenzene $C_6H_5NO_2$ is another common benzene derivative.



The reduction of nitrobenzene to an amine using tin and concentrated hydrochloric acid.

Tin and concentrated hydrochloric acid are used as reagents to form an intermediate tin complex, then large quantities of alkali are required to release the amine after the initial reaction.

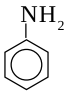


Reaction type: Reduction
Conditions: Tin, conc. HCl, then large quantities of NaOH.

Note: This reaction will work for other aromatic nitro-compounds. Other reducing agents (e.g. $LiAlH_4$) can work.

Phenylamine

Phenylamine $C_6H_5NH_2$ is produced from nitrobenzene, as described above.



Amines, being basic, usually react with acids to form salts. The following reaction, however, is different.

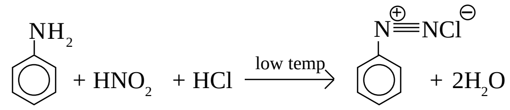
(i) The reaction between phenylamine and nitrous acid

First the unstable nitrous acid (HNO_2) is produced *in situ* by reacting sodium nitrite with hydrochloric acid.

$$NaNO_2(aq) + HCl(conc.) \rightarrow HNO_2(aq) + NaCl(aq)$$

(ii) The diazotisation reaction

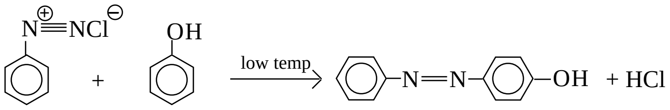
Phenylamine then reacts with the nitrous acid and HCl to form benzenediazonium chloride.



Diazonium ions are important intermediates.

(iii) The coupling reaction of benzenediazonium ions with phenol.

Azo-dyes are formed as diazonium salts react with phenol.

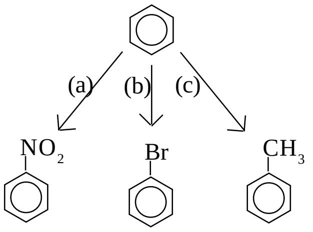


yellow precipitate
(diazo compound)

There are many diazo compounds with different colours, and they can be used in textile dyes.

Questions

1. Explain the stability of the benzene ring structure.
2. State what sort of species will attack the benzene ring, and why.
3. State why care should be taken when handling benzene.
4. Give reagents and conditions for the following conversions:



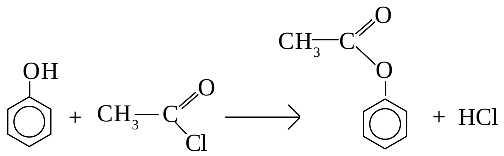
5. State why phenol reacts more readily with sodium hydroxide than ethanol.
6. Show how phenol can be used to form an ester.

Answers.

1. Strong carbon-carbon bonds due to delocalised system of electrons througfhout the ring structure.
2. Electrophiles. They are attracted to the electron rich delocalised system.
3. Benzene is carcenogenic.
4. (a) reagents: conc. HNO_3
   conditions: conc. H_2SO_4, 50^0C

   (b) reagents: $Br_{2\,(l)}$
   conditions: Fe catalyst, dry

   (c) reagents: CH_3Cl
   conditions: anhydrous $AlCl_3$, dry, heat under reflux
5. Phenol is more acidic than ethanol, it donates protons more readily.
6.



Acknowledgements:
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