3.10 Arenes

Introduction to arenes:

- These are structures that contain benzene.

The structure of benzene:

- The discovery of the structure of benzene has not been straight forward:

1825:

- Michael Faraday isolated benzene and found its composition to be:

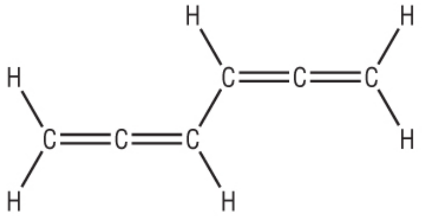
92.3% carbon	7.7% hydrogen	Mr = 78

Empirical formula =

Molecular formula =

1858:

- This molecular formula was a conundrum to try and determine its structure.
- The lack of hydrogens in its structure suggested that there must be double (or even triple) bonds within the structure.
- The first structure suggested was:



- If this was the case it would readily react with:

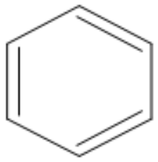
  Reagent:

  Expected observation:

  Actual observation:

1865

- Friedrich **Kekulé** suggested a ring type structure after having a dream of snakes eating their tales:



- It is known as **Kekulé's** structure.
- It is a plausible explanation of its structure.
    - It did not however explain why it **did not react** with **bromine.**

1928

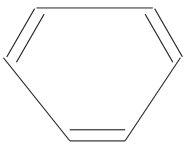
- Kathleen Lonsdale used X – Ray diffraction to confirm the ring type structure.
- It did however throw up new problems:
    - The structure was shown to be planar
    - It was found that all the C-C bond lengths were equal in length and in between C – C and C = C bond lengths

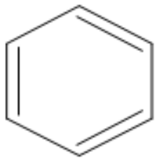
C – C 0.153nm cyclohexane

C = C 0.134nm cyclohexene

C – C 0.139nm benzene

- **Kekulé's** structure would look like this: It actually looks like this:



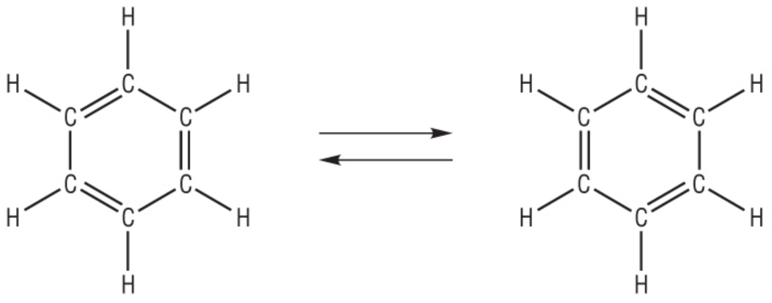


This suggests that the C - C bond is somewhere between a single and double bond

Hydrogenation of benzene

Kekulé defends his model:

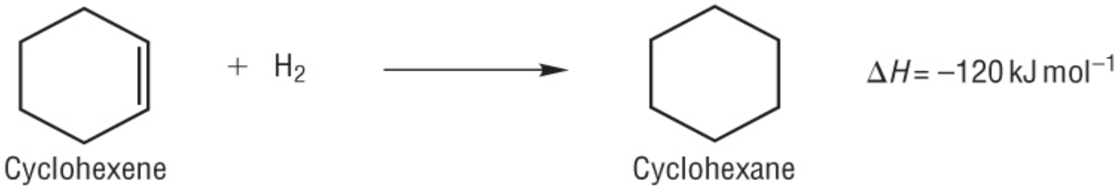
- Kekulé suggested that this was due to an equilibrium which involved the double bonds switching positions.
- He explained that the C=C changed position before any reactions could occur:



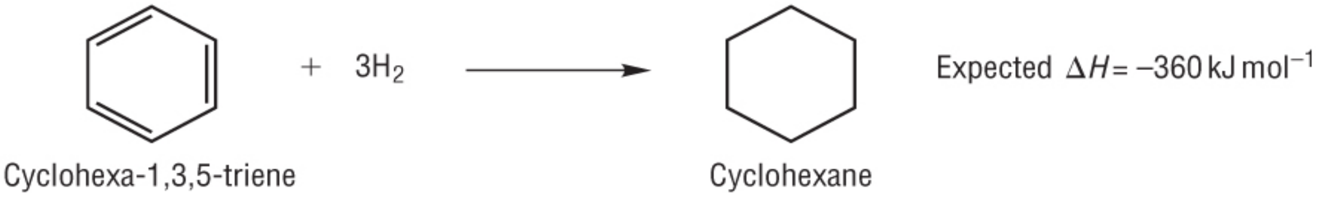
Thermochemical evidence:

- Benzene is in fact quite unreactive compared to alkenes.

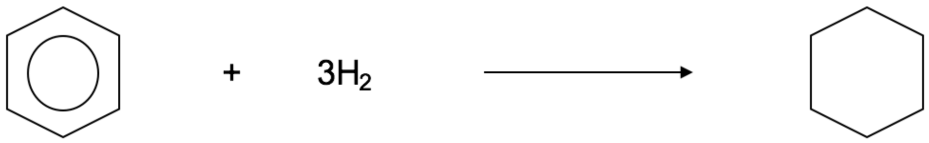
Hydrogenation of cyclohexene – one double bond



Hydrogenation of Kekulé's benzene: cyclohexa-1,3,5-triene – three double bonds

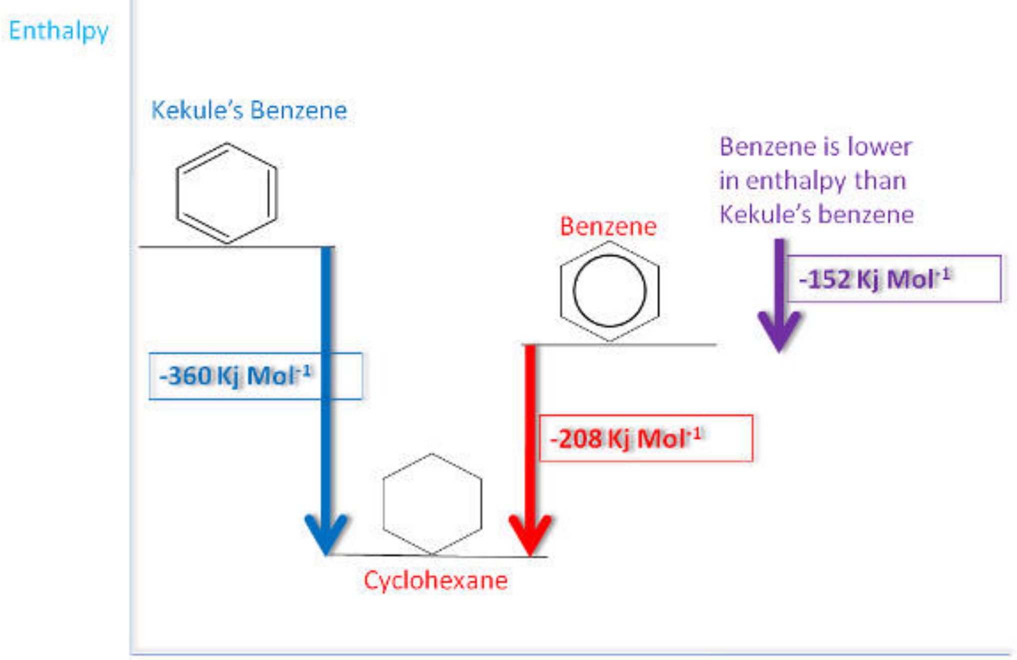


- Compare the results with the known value for Benzene:



Actual ΔH = -208 kJ Mol^{-1}

- This tells us that benzene is more stable than the Kekulé model as less energy is given out:



Summary: The problems with Kekulé's model:

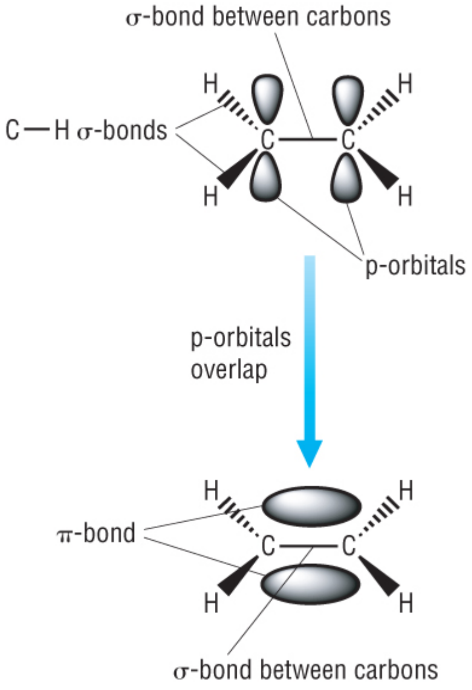
1) Benzene is a planar molecule, bond angle of 120°
2) Benzene's C – C bonds are equal in length (between C – C and C = C bond lengths)
3) It is more stable / less exothermic / unreactive than corresponding alkenes

A new model: The delocalised structure of benzene

- Benzene has the following properties which need explaining:

  1) **6 carbon's and 6 hydrogen's.**
  2) **Arranged in a planar hexagonal ring.**
  3) **Around each carbon – Trigonal planar with a bond angle of 120°.**
  4) **C – C bonds have the same bond length.**
  5) **Each carbon has 3 bonds**

- This can only be explained if we look at the bonding in benzene around the carbon atoms:

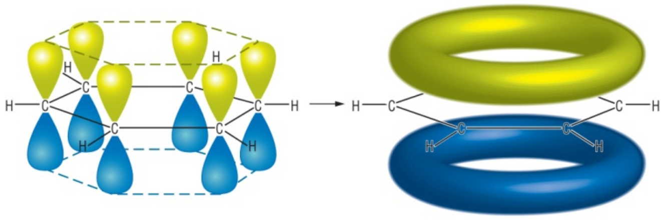


P orbital

σ bond with p orbitals overlapping to form a π bond in alkenes

- The clue comes from the alkenes:
- The second covalent bond is due to 2 adjacent **p orbitals overlapping to form a π bond.**
- The alkenes have 4 electrons between the carbon carbon double bond making it **electron rich** enough to **attract an electrophile.**
- These electrons are **localised** - only between the 2 C's in the C=C.

- Imagine 6 of these p orbitals on every carbon in benzene:



6 x p orbitals

π delocalised orbital

- Each C has 3 bonds
- Each C has a spare e in a p orbital
- 6 of these p orbitals can **overlap forming a π orbital** where 6e's spread over all 6 carbons.
- The 6 electrons can be anywhere in the π orbital formed.
- These is **delocalisation.**

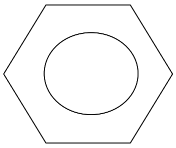
The unreactivity of benzene:

- This means that each C - C has 2e in the σ bond and 1e from the delocalised π system.
- This makes benzene **less electron rich** than alkenes.
- This means they are not as good at attracting electrophiles.
- The bonding but must be considered as a delocalised electron charge cloud spread out over the whole ring.
- This gives rise to certain difficulties when drawing the structure of benzene:

– Represents 2e's in a bond

= Represents 4e's in a double bond

- As neither of these is appropriate to show the distribution of electrons in benzene, the following structure is often used:



The delocalised model of benzene and chemical reactivity:

- Benzene is more stable than expected, less so than alkenes.
- This is because the electron density between the carbon atoms is less than in alkenes.
- This makes them attract electrophiles less well than alkenes:

Reaction with	**Alkenes**	**Benzene**
Decolorise bromine water	✓	✗
Strong acids, HCl	✓	✗
Halogens, Cl_2	✓	✗

Questions:

1) Draw the Kekulé structure of benzene and give its IUPAC name

2) Outline 3 problems with Kekulé's structure:

3) Draw a labelled diagram showing the more modern structure of benzene

4) Use your diagram drawn in (3) to explain the following:
    i) Bond lengths in benzene

    ii) Relative unreactive nature of benzene with bromine

    iii) It is a planar molecule, give the bond angle

5) Write chemical reactions and draw an enthalpy profile showing how benzene is more stable than the Kekulé structure

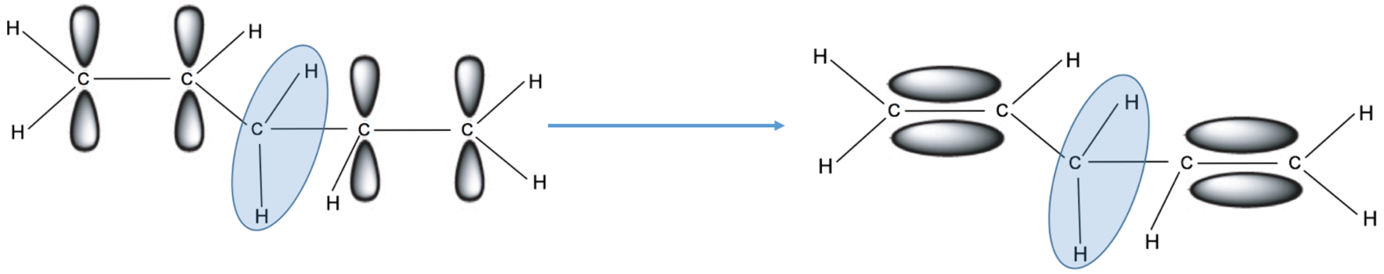
Delocalisation of electrons:

A delocalised electron is an electron in an atom, ion or molecule that is not associated with any single atom or single covalent bond.

1) Consider ethene – $H_2C{=}CH_2$:
   One double bond.

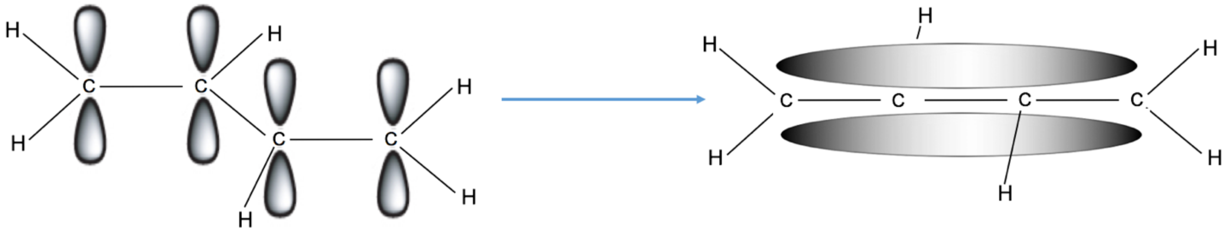
- Although 2 p orbitals overlap creating a π orbital, the electrons are still localised in a covalent (double) bond – ie between 2 carbon atoms
- **Not delocalised**

2) Consider Pent – 1,4 – diene – $H_2C{=}CH – CH_2 – CH{=}CH_2$:
   2 double bonds with 2 single bonds between:



- Although there are 4 p orbitals, they cannot all overlap as they are not all next to each other. The carbon in blue has no p orbital so they cannot overlap with each other.
- They only overlap between 2 carbon atoms creating 2 separated π orbitals.
- The electrons are still localised in a covalent (double) bond – ie between 2 carbon atoms.
- **Not delocalised**

3) Consider But – 1,3 – diene – $H_2C{=}CH – CH{=}CH_2$
   Alternating double / single bonds ie double bond separated by one single bond:



- There are 4 p orbitals, they can now all overlap as they are all next to each other.
- They all overlap across 4 carbon atoms / 3 bonds creating one delocalised π orbitals.
- **Delocalised – therefore more stable than a standard alkene**

Summary: For delocalisation of electrons:

- **p orbitals** must be **adjacent** to each other for them to overlap
- Look for double **bonds separated by single bonds** – ie they must alternate
- This makes them **more stable / less reactive / less exothermic**
- As they are **less electron rich**

Questions

1) Draw the following molecules. Which of them would have delocalised electrons:

a) Propene

b) Pent – 1,4 – diene

c) Hex – 1,3 - diene

d) Pent – 1,3 – diene

e) Hex – 1,3 – diene

f) Hex – 2,4 – diene

g) Cyclohex – 1,3 – diene

h) Cyclohex – 1,4 – diene

h) Prop – 2 – enal

h) But – 3 - enal

2) The chlorination of cyclohexene has an enthalpy change, $\Delta H = -80.0\ \text{kJ mol}^{-1}$
   a. Write a balanced chemical reaction for the chlorination of cyclohexene:

   b. Write a balanced chemical reaction for the chlorination of cyclohex – 1,4 – diene and predict its enthalpy change?

   c. Write a balanced chemical reaction for the chlorination of cyclohex – 1,3 – diene and predict its enthalpy change?

   d. Your answers to (c) and (d) should be different, explain why they have different enthalpy changes?

Extension:

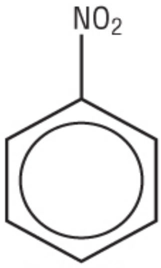
3) Ethanoic acid is acidic because the OH bond can dissociate. Alcohols are not acidic as their OH bond cannot dissociate.
   a. Write a chemical equation for the dissociation of ethanoic acid

   b. Look at the ethanoate ion in the reaction above. Draw the ethanoate ion displayed and include the p orbitals in the carbonyl (carbon and oxygen) and one of the p orbitals containing the lone pair electrons on the O^-

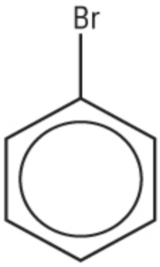
   c. Your diagram in (b) to explain why carboxylic acids dissociate whereas alcohols do not?

Naming basic aromatic compounds:

- For a group to be attached to a benzene ring, a hydrogen must be replaced.
- Common groups are - Cl chloro, - Br Bromo, - NO_2 Nitro, and alkyl groups, - CH_3 Methyl:

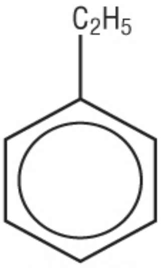


$C_2H_5NO_2$
Nitrobenzene



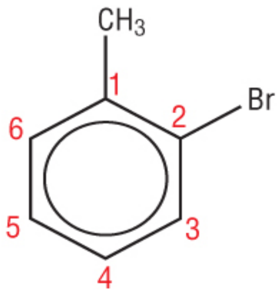
C_6H_5Br
Bromobenzene

C_6H_5Cl
Chlorobenzene

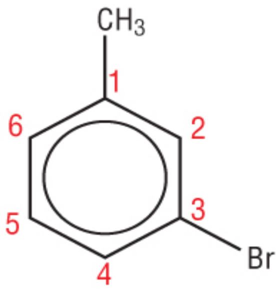


$C_6H_5C_2H_5$
Ethylbenzene

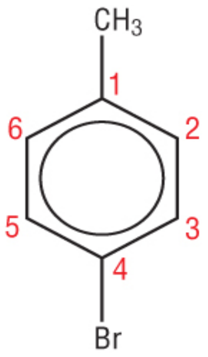
- If there is more than 1 group attached, then we number to give the lowest value around the ring.
- We start numbering at the alkyl group / major functional group:



2-bromomethylbenzene



3-bromomethylbenzene

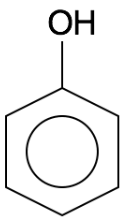


4-bromomethylbenzene

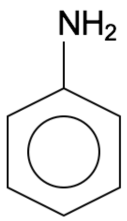
- We use the name 'benzene' when it is the highest priority group.

Naming aromatic compounds where another functional group takes priority:

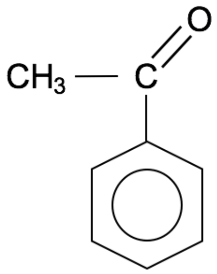
- Just as hydroxy is used for the alcohols, OH when a higher priority group is present.
- Benzene becomes **phenyl**
- Common higher priority groups are - NH_2 Amine, - OH Alcohols, - C=O aldehydes and ketones, and C=C alkenes:



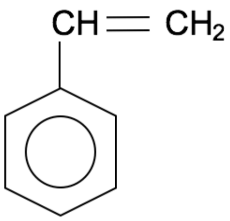
Phenol



Phenylamine



Phenylethanone



Phenylethene

Reactions of benzene:

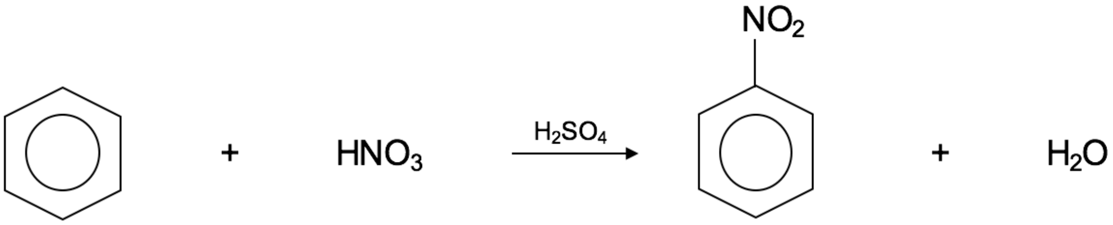
- If it was an addition reaction like the alkenes, then the delocalised ring structure would be disrupted as the electrons would be needed to form bonds with the electrophile.
- This would make the product less stable than benzene meaning the reaction would be energetically unfavorable.
- For this reasons, benzene undergoes **substitution** instead of **addition** in order to maintain the delocalised electron system and its stability.
- They all react with **electrophiles**, and these are always **positive** as benzene is not as electron rich as alkenes.

1) Nitration:

Reagents and conditions:

Concentrated nitric acid and concentrated sulphuric acid (catalyst) / Reflux at 55°C

Overall Equation:



Reaction Type:

Electrophilic substitution

Reaction:

a) Generation of the electrophile:

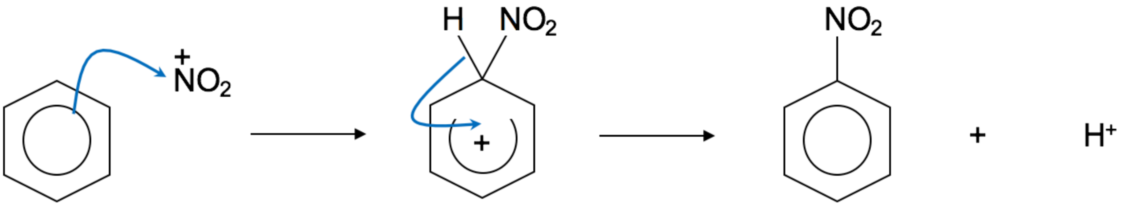
Nitration of benzene requires the production of a the more reactive nitronium ion:

HNO_3 + H_2SO_4 → NO_2^+ + HSO_4^- + H_2O

Nitronium ion is the electrophile

Note: The **Nitric acid** has become NO_2^+, in effect losing an OH^- ion, making it a **base!!**

b) Electrophilic Substitution Steps



c) Regeneration of the catalyst

H^+ + HSO_4^- → H_2SO_4

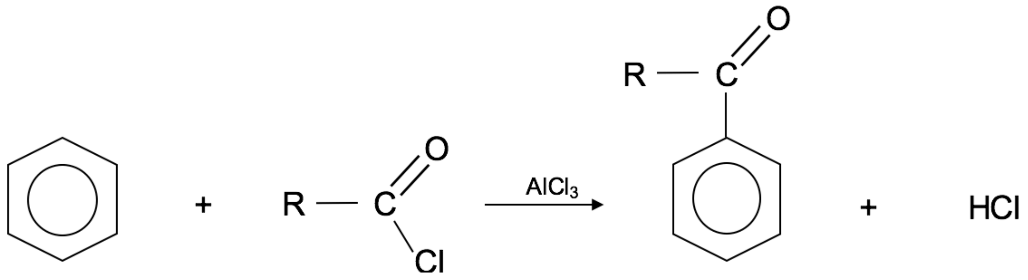
- The H^+ generated will react with HSO_4^- forming sulphuric acid, H_2SO_4. This means sulphuric acid is a catalyst.

2) Friedel – Crafts - Acylation:

Reagents and conditions:

Acyl chloride and $AlCl_3$ (**Halogen carrier** / catalyst) / Heat under reflux

Overall Equation:



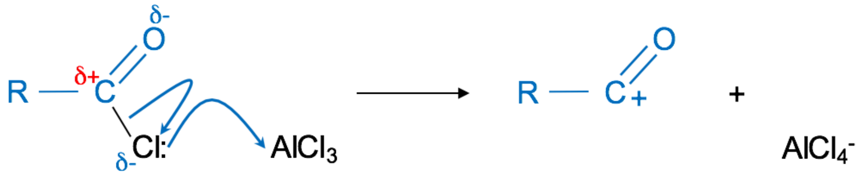
Reaction Type:

Electrophilic substitution

Reaction:

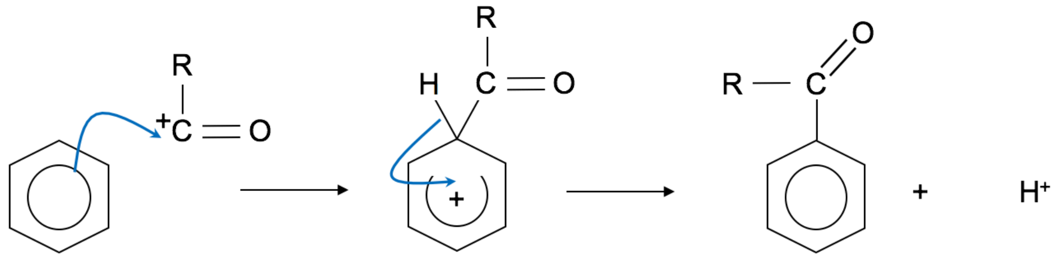
a) Generation of the electrophile:

Acyl chlorides are not polar enough to react with benzene, a (+) charge is required:



Carbocation is the electrophile

b) Electrophilic Substitution Steps



c) Regeneration of the catalyst

$$H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$$

- The H^+ generated will react with $AlCl_4^-$ forming $AlCl_3$. This means $AlCl_3$ is a catalyst.
- $AlCl_3$ is often referred to as a halogen carrier

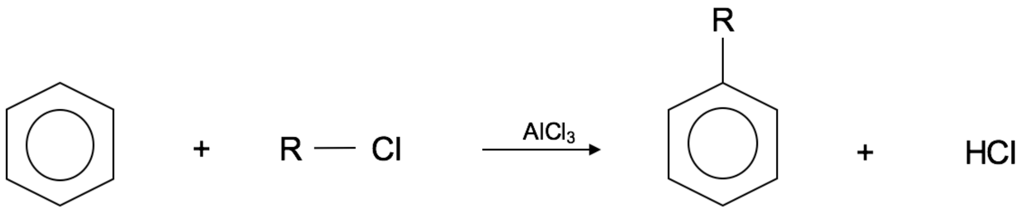
Extension –reactions and mechanisms 3 and 4 are not in the specification.

3) Friedel – Crafts - Alkylation:

Reagents and conditions:

Halogenoalkane, RCl and $AlCl_3$ (**Halogen carrier** / catalyst) / Heat under reflux

Overall Equation:



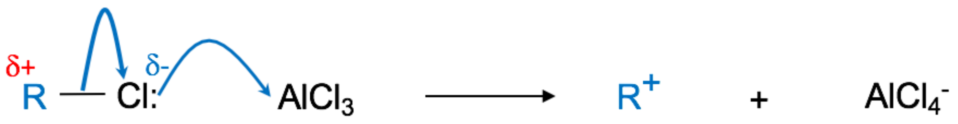
Reaction Type:

Electrophilic substitution

Reaction:

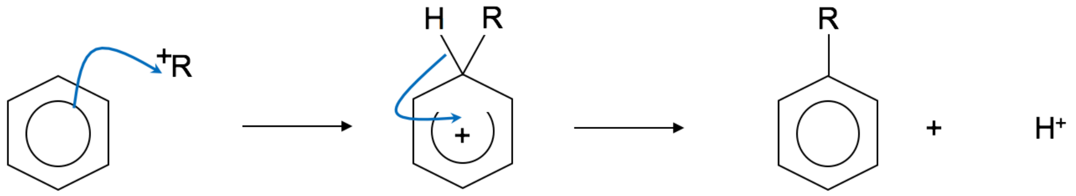
a) Generation of the electrophile:

Halogenoalkanes are not polar enough to react with benzene, a (+) charge is required:



Carbocation is the electrophile

b) Electrophilic Substitution Steps



c) Regeneration of the catalyst

$$H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$$

- The H^+ generated will react with $AlCl_4^-$ forming $AlCl_3$. This means $AlCl_3$ is a catalyst.
- $AlCl_3$ is often referred to as a halogen carrier

4) Halogenation:

Reagents and conditions:

Halogen, Cl_2 and $AlCl_3$ (**Halogen carrier** / catalyst) / Heat under reflux

Overall Equation:

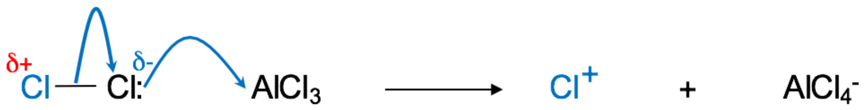
Reaction Type:

Electrophilic substitution

Reaction:

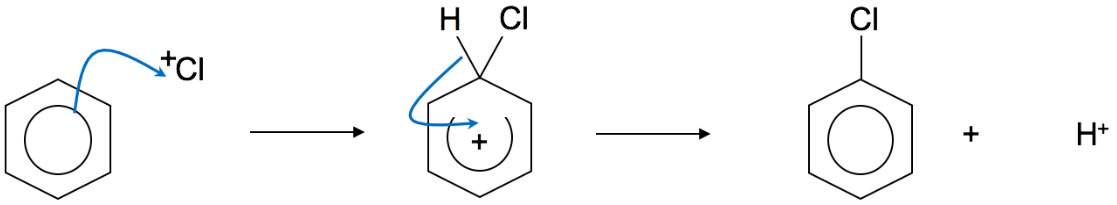
a) Generation of the electrophile:

Halogens are non polar so do not react with benzene, a (+) charge is required:



Chloronium is the electrophile

b) Electrophilic Substitution Steps



c) Regeneration of the catalyst

$$H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$$

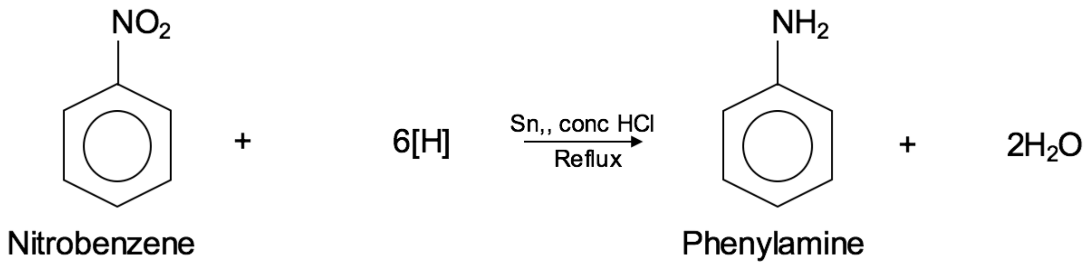
- The H^+ generated will react with $AlCl_4^-$ forming $AlCl_3$. This means $AlCl_3$ is a catalyst.
- $AlCl_3$ is often referred to as a halogen carrier

5) Reduction of nitrobenzene → Phenylamine: *In the specification*

Reagents and conditions:

i) Sn and concentrated HCl / Heat under reflux: Gives the salt of the amine
ii) Add NaOH: Gives the amine

Overall Equation:

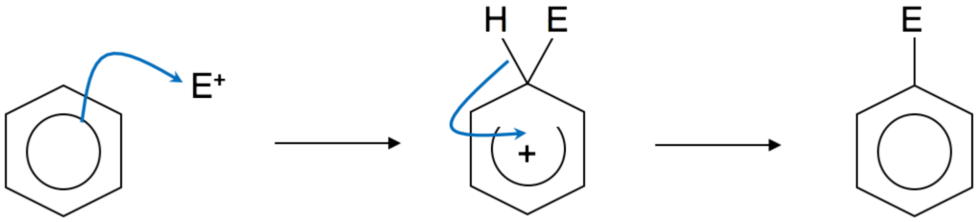


Reaction Type:

Reduction

Summary:

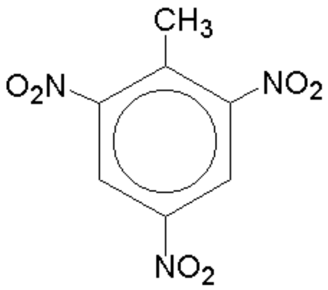
- They all undergo the following mechanism:



- They all require a catalyst to generate a (+) charge:
- They only ever mono substitute (unless extremely harsh conditions)

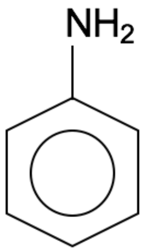
Uses:

Nitration of methylbenzene



- Methyl benzene used to be called toluene. Toluene is slightly more reactive than benzene.
- The nitration of toluene forms nitro toluene.
- This is multiply nitrated in the 2,4,6 position because toluene is more reactive:

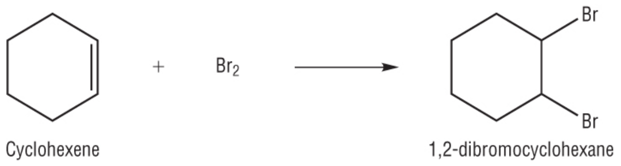
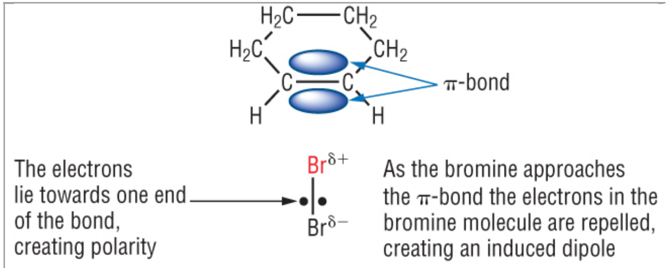
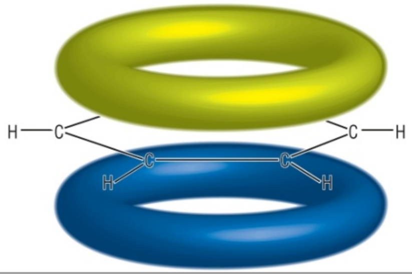
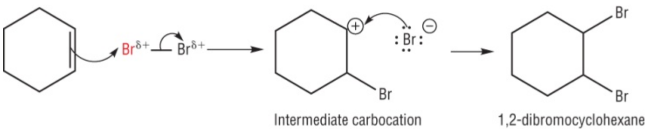
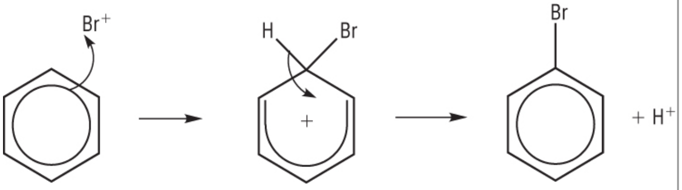
Phenylamine



- Used in the manufacture of dyes

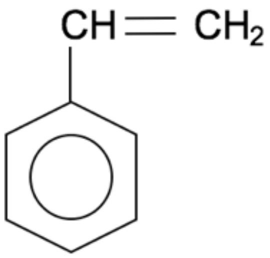
Comparing the reactivity of alkenes and benzene

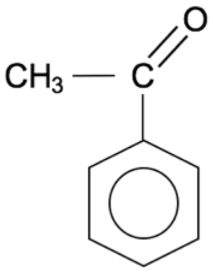
Cyclohexene vs Benzene

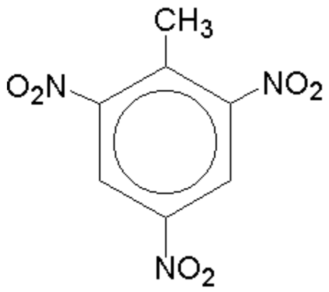
Cyclohexene	Benzene
• Will decolourise bromine water:	• Only reacts with bromine with a halogen carrier:
 **Addition reaction**	 **Substitution reaction**
	
High electron density: localised electrons	**Low electron density:** delocalised electrons
• **Reacts readily** as it can attract electrophiles more readily	• **Requires a catalyst** to produce a (+) ion in order to react with benzene
The mechanism: 	**The mechanism:** $AlBr_3 + Br_2 \rightarrow AlBr_4^- + Br^+$  $AlBr_4^- + H^+ \rightarrow AlBr_3 + HBr$
Electrophilic addition	**Electrophilic substitution**

Questions:

1) Name the following molecules:







2) Draw the following molecules:

Phenol

1,3 dimethyl benzene

2,4,6 trinitro phenylamine

3) Write balanced chemical reactions for the following:
   a. Benzene and nitric acid

   b. Benzene and propanoyl chloride

   c. Benzene and bromoethane

   d. Benzene and iodine

   e. The reduction of nitro benzene

f. For each of the following write down the reactants and conditions
    a) Benzene to nitrobenzene

    b) Benzene to ethyl benzene

    c) Benzene to chlorobenzene

    d) Benzene to phenyl ethanone

    e) Reduction of nitrobenzene

4) Draw the mechanism for (a) and (b) in question 3. For each include the following:
    - A reaction for the generation of the electrophile
    - A reaction for the regeneration of the catalyst