RAFFLES INSTITUTION
YEAR 5 H2 CHEMISTRY 2017
Lecture Notes 12 – Arenes

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Ms Lee Mei Yin

A Content

Arenes (exemplified by benzene and methylbenzene)

1. Introduction
2. Nomenclature of Benzene Derivatives
3. Benzene – Physical Properties
4. Structure of Benzene
5. Electrophilic Substitution Reactions of Benzene
6. Reaction with Concentrated Nitric Acid
7. Reaction with Halogens
8. Friedel-Crafts Alkylation & Acylation
9. Other Reactions of Benzene
10. Methylbenzene
11. Reactions of the Side Chain in Alkylbenzenes
12. Electrophilic Substitution of the Benzene Ring in Methylbenzenes
13. Effect of Substituent Groups
14. Summary

B Learning outcomes

Candidates should be able to:

- (a) understand mechanisms in terms of organic structure and bonding
- (b) recognise that the mechanisms of polar reactions involve the flow of electrons from electron-rich to electron-poor sites
- (c) explain, in terms of delocalisation of π electrons, the difference between benzene and alkene:
  - (i) reactivity towards electrophiles
  - (ii) preference of benzene to undergo substitution rather than addition reaction
- (d) describe the chemistry of the benzene ring as exemplified by the following reactions of benzene and methylbenzene:
  - (i) electrophilic substitution reactions with chlorine and with bromine (recognise the use of Lewis acid as catalysts)
  - (ii) nitration with concentrated nitric acid (recognise concentrated sulfuric acid as a Brønsted-Lowry acid catalyst)
  - (iii) Friedel-Crafts alkylation with halogenoalkanes (recognise the use of Lewis acid as catalysts)
- (e)
  - (i) describe the mechanism of electrophilic substitution in arenes, using the mono-bromination of benzene as an example
  - (ii) describe the effect of the delocalisation of electrons in arenes in such reactions
- (f) describe the chemistry of the alkyl side-chain of benzene ring as exemplified by the following reactions of methylbenzene:
  - (i) free-radical substitution by chlorine and by bromine
  - (ii) complete oxidation to give benzoic acid
- (g) predict whether halogenation will occur in the side-chain or aromatic nucleus in arenes depending on reaction conditions
- (h) apply the knowledge of positions of substitution in the electrophilic substitution reactions of monosubstituted arenes

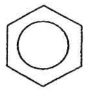
C References

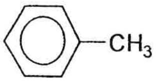
- A-Level Chemistry (by Ramsden)
- Chemistry in Context (by Hill and Holman)
- Organic Chemistry (by David Klein)
- Organic Chemistry (by L.G.Wade)
- Website: www.chemguide.co.uk

1 INTRODUCTION

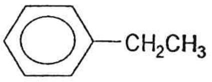
Arenes (also referred to as **aromatic hydrocarbons**) are hydrocarbons based on the **benzene ring as a structural unit**.

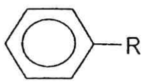
Examples of arenes (or aromatic hydrocarbons):

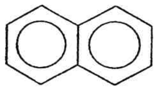

benzene


methylbenzene

toluene


ethylbenzene


alkylbenzene
–R = alkyl group


naphthalene

The term **'aromatic'** (fragrant) was originally used because the first benzene-like compounds isolated have pleasant smells. However since the vapours are toxic, it is unwise to smell them.

The term '**aromatic**' has been retained to indicate certain chemical characteristics rather than odorous properties. An aromatic compound has **special stability**. For example, benzene is more stable than if it were to be formulated as a triene (*refer to Section 4.2*).

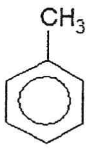
Aromatic compounds are benzene and those compounds possessing the ring structure of benzene or other molecular structures that resemble benzene in structure and chemical behaviour.

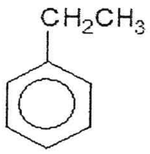
The chemistry of arenes will be exemplified by the reactions of **benzene** and **methylbenzene**.

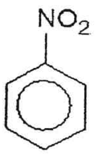
2 NOMENCLATURE OF BENZENE DERIVATIVES

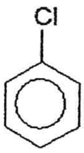
2.1 Monosubstituted benzene derivatives

- For many of these derivatives, the name of the substituent group is added as a prefix to the word *–benzene*. Below are several examples.

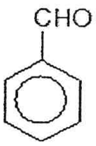

methylbenzene
(or toluene)

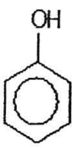

ethylbenzene

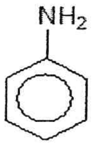

nitrobenzene

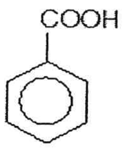

chlorobenzene

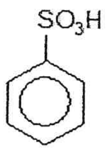
- Other derivatives have special names which may show no resemblance to the name of the attached substituent group. Some examples are given below.


benzaldehyde


phenol

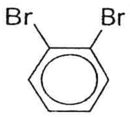

phenylamine
(aniline)

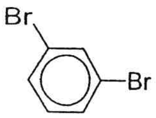

benzoic acid
(benzenecarboxylic acid)

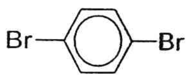

benzenesulfonic
acid

2.2 Disubstituted benzene derivatives

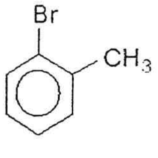
- For disubstituted benzene derivatives, numbers can be used to indicate the relative positions of the two substituents.

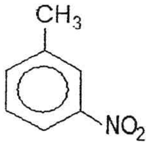

1,2-dibromobenzene
ortho

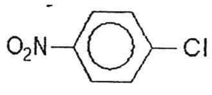

1,3-dibromobenzene
meta


1,4-dibromobenzene
para

- If the two substituent groups are different, the names of the groups prefix benzene in alphabetical order.

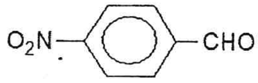

2-bromomethylbenzene
1-bromo-2-methylbenzene

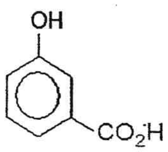

3-nitromethylbenzene
1-methyl-3-nitrobenzene


4-chloronitrobenzene
1-chloro-4-nitrobenzene

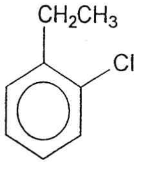
- If one of the two substituents is the kind that gives a special name to the molecule, then the compound is named as a derivative of that special compound. If both substituents give derivatives with special names, then preference is given to the substituent of highest nomenclature priority.

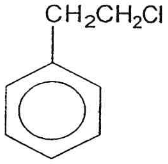

2-bromophenol

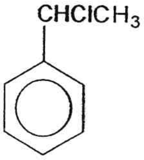

4-nitrobenzaldehyde


3-hydroxy benzoic acid

- Examples of substituents on a side chain:

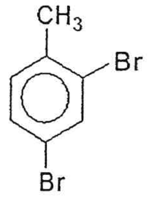

2-chloroethylbenzene
1-chloro-2-ethyl benzene

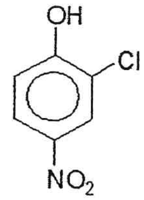

(2-chloroethyl)benzene

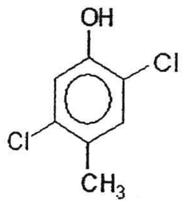

(1-chloroethyl)benzene

2.3 Polysubstituted benzene derivatives

- If three or more groups are attached to the benzene ring, the numbering is in such a way as to keep the prefix numbers as low as possible and with preference given to the group of highest nomenclature priority.
- If one of the groups present gives rise to a compound with a special name, then only two positions of substitution are mentioned.

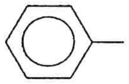
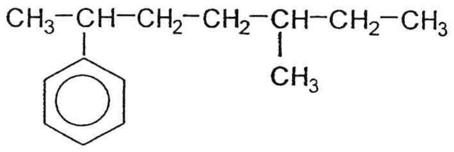
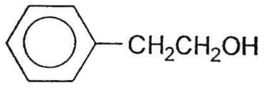
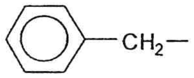
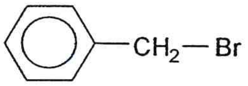

2,4-dibromomethylbenzene
2,4-dibromo-1-methylbenzene


2-chloro-4-nitrophenol


2,5-dichloro-4-methylphenol

2.4 The phenyl and aryl groups

- Benzene ring is treated as a substituent and is called a **phenyl group** when
  - the substituent on the benzene ring has more than six carbon atoms
  - the highest priority functional group is not a substituent on the benzene ring
- Phenyl and substituted phenyl groups are called **aryl groups**.

phenyl group  or C_6H_5-	 5-methyl-2-phenylheptane  2-phenylethanol
benzyl group  or $C_6H_5CH_2-$	 benzyl bromide or (bromomethyl)benzene

3 BENZENE – PHYSICAL PROPERTIES

- Benzene is a colourless liquid with a characteristic odour.
- It is non-polar, insoluble in water and less dense than water. predominant IMF : id-id interactions .
- It is soluble in all organic solvents, and is itself a good solvent for organic compounds.
- It freezes at 5.5 °C and boils at 80 °C.
- Like all aromatic compounds, it burns with a smoky and luminous flame, owing to its relatively high carbon content.

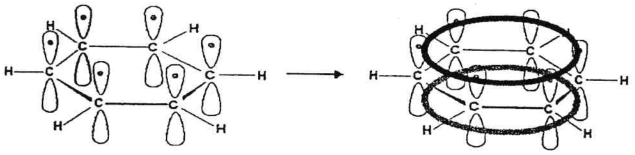
Benzene is a useful chemical!	**Benzene is a TOXIC chemical!**
Benzene is widely used in the United States; it ranks in the top 20 chemicals for production volume. Some industries use benzene to make other chemicals which are used to make plastics, resins, and nylon and synthetic fibers. Benzene is also used to make come types of rubbers, lubricants, dyes, detergents, drugs, and pesticides. Natural sources of benzene include volcanoes and forest fires. Benzene is also natural part of crude oil, gasoline, and cigarette smoke.	Both the liquid and the vapour are highly poisonous, so that benzene must be used with care. It is somewhat **carcinogenic** (cancer-causing) and can induce anaemia and even leukaemia. 

4 STRUCTURE OF BENZENE

Candidates should be able to explain, in terms of delocalisation of π electrons, the difference between benzene and alkene:
- reactivity towards electrophiles
- preference of benzene to undergo substitution rather than addition reaction

4.1 Resonance Structure of Benzene

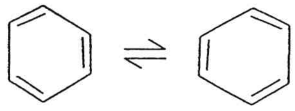
Each of the six carbon atoms in benzene is **sp^2 hybridised**. There are **three sp^2 hybrid orbitals** and **one unhybridised p orbital** for each carbon atom.

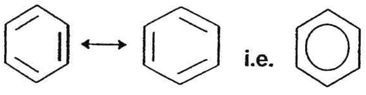
Three sp^2 hybrid orbitals	One unhybridised p orbital
• Each C atom has **three sp^2 hybrid orbitals** that are arranged in a **trigonal planar** manner. ➲ Two sp^2 hybrid orbitals are used to overlap head-on with the sp^2 hybrid orbitals of two adjacent C atoms to form **two C–C σ bonds.** ➲ One sp^2 hybrid orbital is used to overlap head-on with the 1s orbital of the H atom to form the **C–H σ bond**. ➲ The benzene molecule is entirely planar ➲ All bond angles in the molecule are **120°**. trigonal planar	• Each carbon atom also has an **unhybridised p orbital** occupied by a single electron. • Each singly-filled p orbital **overlaps sideways** (π bonding) with the adjacent p orbital on either side.  • This **continuous overlap of the p-orbitals** results in **a cloud of cyclic delocalised π electrons** above and below the plane of the ring, i.e. resonance is present in benzene. The unique properties of benzene are a result of the resonance it possesses.

4.2 Experimental Evidence of Resonance in Benzene

(a) Carbon-carbon bond lengths

If benzene were to have a Kekulé structure (i.e. the cyclohexa-1,3,5-triene structure), there should be two kinds of carbon-carbon bonds in benzene: C–C bonds and C=C bonds. This is **not** the case.

 Kekulé benzene	2 types of carbon-carbon bonds

 i.e. modern benzene (resonance hybrid)	All the carbon-carbon bonds are identical

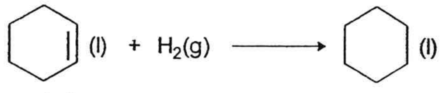
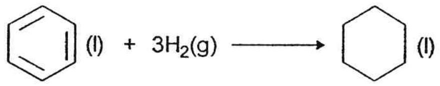
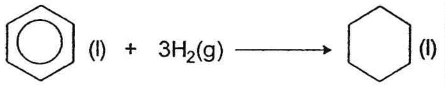
X-ray diffraction studies actually show that **all the carbon-carbon bonds in benzene are identical and equal in length**. This agrees with the description of benzene as a resonance hybrid of two Kekulé structures.

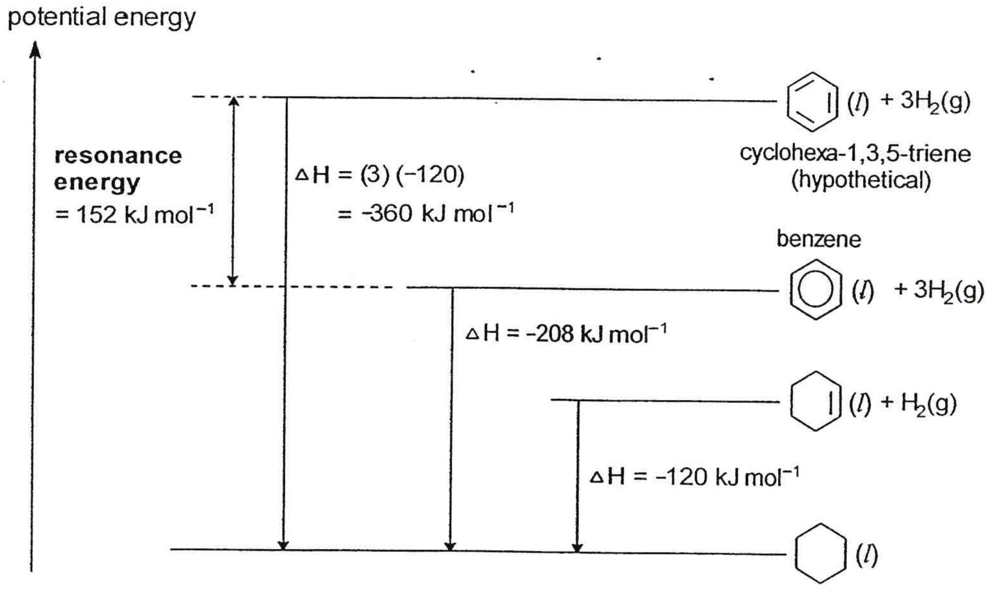
Compound	Bond	Bond length/nm
cyclohexane	carbon-carbon single bond C–C	0.154
cyclohexene	carbon-carbon double bond C=C	0.133
benzene	carbon-carbon bond C$\overset{\cdots}{-}$C	0.139

The measured carbon-carbon bond length (0.139 nm) in benzene is intermediate between the length of a C–C bond (0.154 nm) and that of a C=C bond (0.133 nm).

⇒ This indicates that the bonds have partial double bond character.

(b) Enthalpy change of hydrogenation of benzene

 cyclohexene	• **Experimentally**, enthalpy change of hydrogenation of cyclohexene = –120 kJ mol^{-1}.
 cyclohexa-1,3,5-triene	• If benzene were to have the cyclohexa-1,3,5-triene structure, then its **expected** enthalpy change of hydrogenation = (3) (enthalpy change of hydrogenation of cyclohexene) = (3) (–120) = –360 kJ mol^{-1}
 benzene	• **Experimentally**, enthalpy change of hydrogenation of benzene = –208 kJ mol^{-1} • That is less exothermic than the expected value of –360 kJ mol^{-1}.



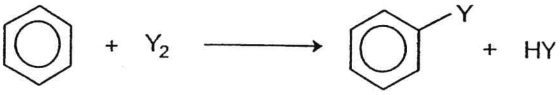
- The Kekulé structures, which contain localized π bonds, are not accurate representations of benzene.
- Instead, benzene has a structure in which the **six π electrons are delocalized**. It is the **delocalisation of the six π electrons** that confers **extra stability** on benzene and gives benzene its **aromatic character**.
- The extra stability of benzene is reflected by its **resonance energy** (or **delocalisation energy** or **stabilisation energy**), as shown in the diagram above.

(c) Benzene undergoes substitution rather than addition reactions

If benzene were cycohexa-1,3,5-triene, it is expected to undergo addition reactions which are characteristic of the alkenes. However, under conditions that cause an alkene to undergo rapid addition, benzene either reacts not at all or very slowly.

If benzene undergoes addition reactions, its overall aromatic character (i.e. delocalisation of six π electrons) is destroyed, removing the extra stability associated with the delocalisation of the six π electrons.

Hence, the majority of reactions that benzene undergoes involve **substitution in the ring**, which takes place with **overall retention of aromatic character**, i.e. retaining the delocalization of the six π electrons in the continuously overlapping p-orbitals.



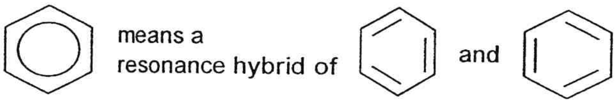
SUMMARY

The following properties are a result of the aromatic character of benzene:

- All carbon-carbon bonds in benzene are equal and are intermediate in length between single and double bonds.
- The enthalpy change of hydrogenation of benzene is less exothermic than expected.
- Benzene undergoes substitution reactions rather than addition reactions.

Representation of the Benzene ring

The benzene is represented by a regular hexagon containing a circle. This representation is useful since it emphasizes the equivalence of the various carbon-carbon bonds.



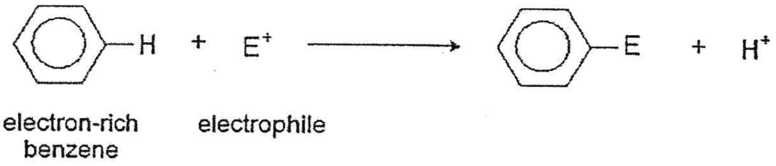
- It is understood that a hydrogen atom is attached to each angle of the hexagon, i.e. each carbon atom, unless another atom or group is indicated.
- The straight lines represent the σ bonds joining the carbon atoms.
- The circle represents the cloud of six delocalised π electrons.

5 ELECTROPHILIC SUBSTITUTION REACTIONS OF BENZENE

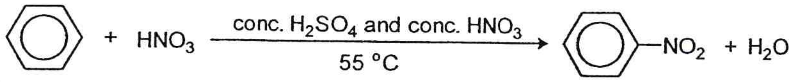
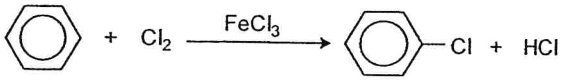
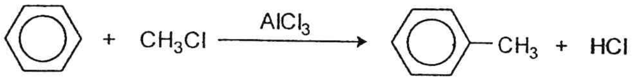
Candidates should be able to
- understand mechanisms in terms of organic structure and bonding
- recognise that the mechanisms of polar reactions involve the flow of electrons from electron-rich to electron-poor sites
- describe the chemistry of the benzene ring (as exemplified by the following reactions of benzene and methylbenzene) as involving electrophilic substitution reactions
- describe the effect of the delocalisation of electrons in arenes in such reactions

- The availability of six π electrons in benzene makes the benzene ring electron rich. The benzene ring thus serves as a source of electrons for electrophilic reagents.

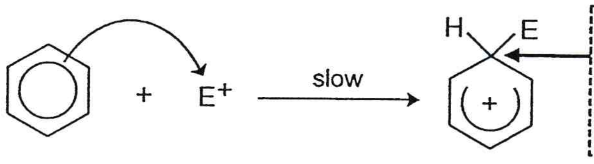
- The main reactions of benzene are characterised by **electrophilic substitution** in the benzene ring in which benzene reacts with an electrophile (E^+) which replaces one or more hydrogen atoms in the ring.

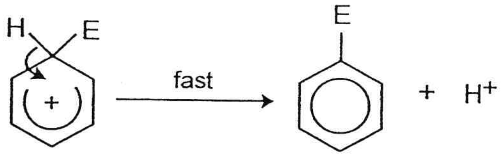


- Examples of electrophilic substitution reactions of benzene (and related aromatic compounds) are:

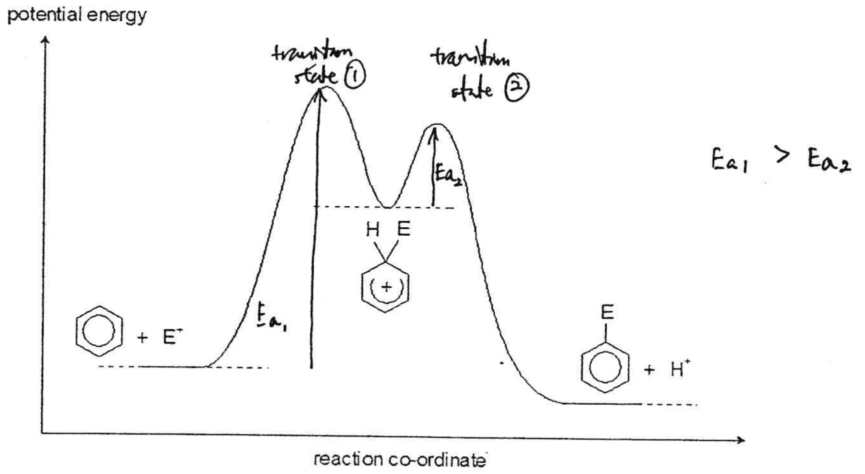
1	nitration	
2	halogenation (e.g. chlorination)	
3	Friedel-Crafts alkylation	

- Each electrophilic substitution reaction of benzene involves essentially the following steps:

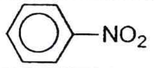
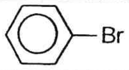
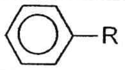
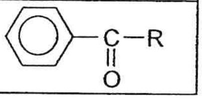
Generation of the electrophile E^+	• The electrophile, E^+, is first generated in the reaction mixture. • This is followed by a **two-step** electrophilic substitution reaction mechanism.
Electrophilic attack by E^+ on the benzene ring to form a carbocation	**Step 1**  a carbocation ➲ This carbon atom is sp^3 **hybridised.** (tetrahedral) ➲ The other 5 carbon atoms remain **sp^2 hybridised.** (trigonal planar) • This step is the **slow step i.e. the rate-determining step** because it involves the destruction of the aromaticity of the benzene ring (i.e. it destroys the extra stability associated with the delocalisation of the six π electrons in the benzene ring). • In this step, the electrophile attacks the electron-rich benzene ring and takes two electrons of the six-electron π system to form a σ bond to one carbon atom of the benzene ring. • The aromatic character of the benzene ring is destroyed and a **carbocation** is formed. This carbocation is resonance-stabilised but **not aromatic.**

Loss of proton from the carbocation to form the product	**Step 2**  • This step is a **fast step**. • In this step, the carbocation intermediate loses a proton from the carbon atom that bears the electrophile. • The two electrons that bonded this proton to carbon become a part of the delocalised π-electron system. • The **aromatic character of the benzene ring is restored** and the substituted product is formed.

Energy Profile



Summary of electrophilic substitution reactions of benzene

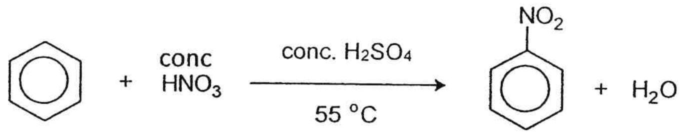
Reaction	**Reagent**	**Catalyst**	**Condition**	**Electrophile**	**Organic product**
Nitration	conc. HNO_3	conc. H_2SO_4	55 °C	NO_2^+	
Halogenation (e.g. bromination)	Br_2	$FeBr_3$	–	Br^+ (for simplicity)	
Friedel-Crafts alkylation	$R–Cl$	$AlCl_3$		R^+	
Friedel-Crafts acylation	$R-\underset{\underset{O}{\|}}{C}-Cl$	$AlCl_3$		$R-\overset{+}{\underset{\underset{O}{\|}}{C}}$	

6 REACTION WITH CONCENTRATED NITRIC ACID

Candidates should be able to describe the chemistry of the benzene ring as exemplified by the following reactions of benzene and methylbenzene:

- nitration with concentrated nitric acid (recognise concentrated sulfuric acid as a Brønsted-Lowry acid catalyst)

6.1 The overall equation



nitrobenzene
(a yellow oil)

A nitrating mixture, containing **concentrated nitric(V) acid** and **concentrated sulfuric(VI) acid** carefully mixed together, is added to the benzene.

The mixture is then refluxed in a water bath maintained at **55–60 °C**. Keeping the temperature below 60 °C minimises the formation of a dinitrated product.

6.2 The reaction mechanism: Electrophilic Substitution

6.2.1 Bronsted-Lowry acid and base

In the nitration of benzene, the electrophile is generated from the reaction between a *Bronsted-Lowry acid* and a *Bronsted-Lowry base*.

A Bronsted-Lowry acid is a proton (H^+) donor.

A Bronsted-Lowry base is a proton (H^+) acceptor.

6.2.2 Reaction mechanism

The nitration of benzene involves the following stages:

1) Generation of the electrophile, NO_2^+

$$2H_2SO_4 + HNO_3 \rightleftharpoons \overset{(E^+)}{NO_2^+} + 2HSO_4^- + H_3O^+$$

Steps involved in generation of the electrophile NO_2^+:

In the nitrating mixture, the HNO_3 acid acts as a Bronsted-Lowry base and accepts a proton from the Bronsted-Lowry acid H_2SO_4.

$$H_2SO_4 + HNO_3 \rightleftharpoons H_2NO_3^+ + HSO_4^- \qquad (1)$$

The reaction leads eventually to the formation of the **nitronium ion** (or nitryl ion).

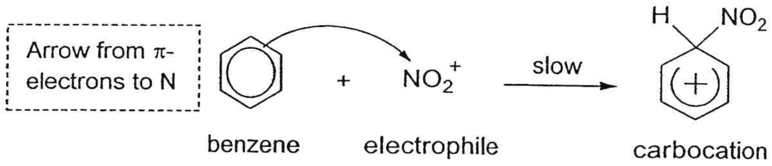
$$H_2NO_3^+ \rightleftharpoons \mathbf{NO_2^+} + H_2O \qquad (2)$$
$$H_2SO_4 + H_2O \rightarrow HSO_4^- + H_3O^+ \qquad (3)$$

Adding up (1) to (3) gives the overall equation for generation of electrophile

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

2) A two-step electrophilic substitution reaction mechanism then follows:

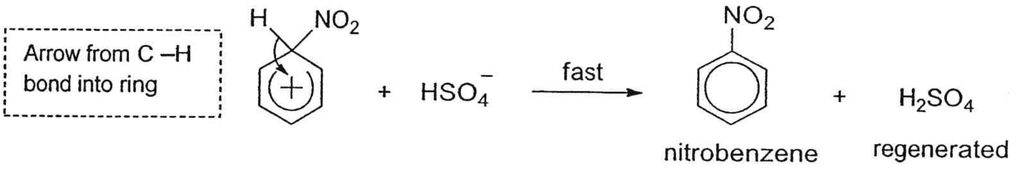
Step 1: Electrophilic attack by NO_2^+

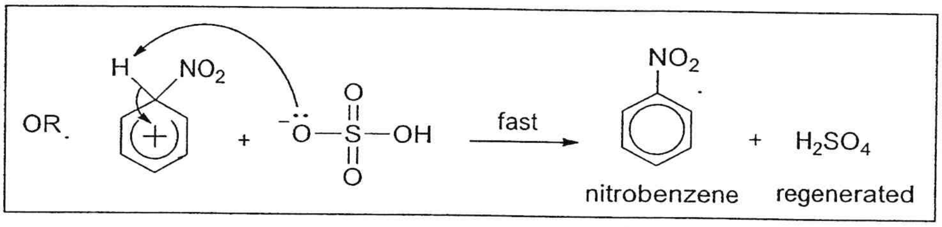


- In this slow step, the NO_2^+ ion acts as an electrophile and attacks the electron-rich benzene ring.
- 2 of the 6 π electrons in the benzene ring are used to form the C–N bond. Hence the aromatic character of the ring is destroyed.

  ⇒ this is the slow step of the reaction mechanism
- A carbocation is formed. Note that the carbon atom bearing the $-NO_2$ group in the carbocation is sp^3 hybridised. The shape with respect to this carbon atom is tetrahedral. The rest of the carbon atoms on the benzene ring remain as sp^2 hybridised.

Step 2: Loss of a proton from carbocation

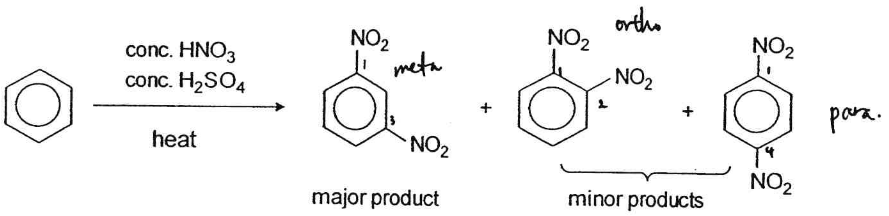




- In this fast step, the unstable carbocation loses a proton to the HSO_4^- ion to form nitrobenzene, thus regaining the aromatic character.
- H_2SO_4 (catalyst) is regenerated.

6.3 Electrophilic Substitution of more than one nitro group

- During the nitration of benzene using the nitrating mixture, small quantities of white crystals of 1,3-dinitrobenzene (m.p. 90 °C) are almost invariably formed.
- 1,3-dinitrobenzene can also be prepared as shown below:



- Formation of 1,3,5-trinitrobenzene requires reacting benzene with fuming HNO_3 and conc. H_2SO_4 for five days at 110 °C. Even under these conditions, the yield is only about 40 percent.

7 REACTION WITH HALOGENS

Candidates should be able to
- describe the chemistry of the benzene ring as exemplified by the following reactions of benzene and methylbenzene: electrophilic substitution reactions with chlorine and with bromine (recognise the use of Lewis acid as catalysts)
- describe the mechanism of electrophilic substitution in arenes, using the mono-bromination of benzene as an example

7.1 Lewis acid and base

$F_3B \leftarrow :NH_3$ (form adduct)
lewis acid lewis base

$H^+ \leftarrow :OH^-$ (from H_2O)
lewis acid. lewis base

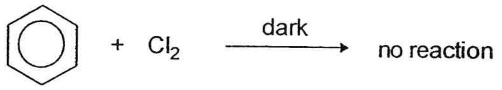
The halogenation of benzene requires the use of a *Lewis acid* as a catalyst.

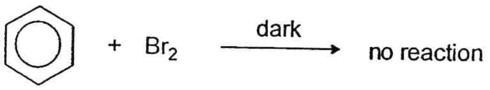
A Lewis acid is an electron - pair acceptor.

A Lewis base is an electron - pair donor.

7.2 Halogenation: Generation of Electrophile

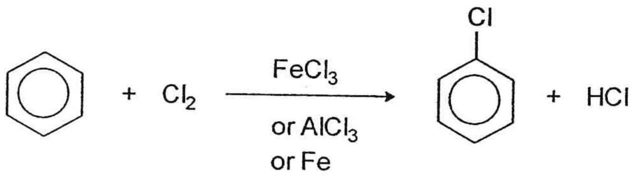
Benzene does not react with chlorine or bromine in the dark.



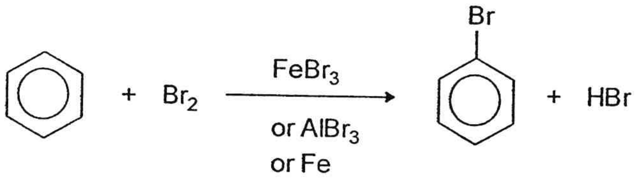


Note:
- The π-electron cloud in an alkene is easily broken when reacting with halogens. However, the same cannot be said for arenes.
- The extra stability associated with the delocalization of the 6 π-electrons in benzene requires the use of a **stronger electrophile** in order to disrupt the π-electron cloud.

In the presence of a suitable **Lewis acid catalyst** such as $AlCl_3$ or $FeCl_3$, benzene undergoes **electrophilic substitution** reaction with chlorine at room temperature.

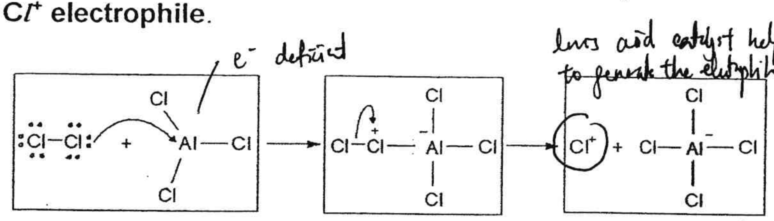


In a similar way, benzene reacts with bromine to form bromobenzene and hydrogen bromide in the presence of $AlBr_3$ or $FeBr_3$.



Note:
- Analogous reactions with I_2 and F_2 are not synthetically useful because I_2 is too unreactive and F_2 reacts too violently.

The **catalyst** is thought to work by inducing polarisation in the halogen molecule by accepting a lone pair of electrons from it. Hence the catalyst functions as a **Lewis acid**, generating the **Cl^+ electrophile**.



$Cl_2 + AlCl_3 \rightleftharpoons Cl^+ + [AlCl_4]^-$ $\underbrace{\qquad}_{[AlCl_4]^-}$

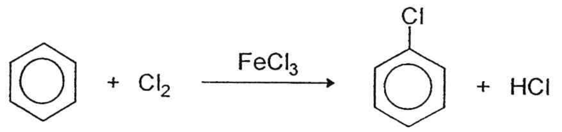
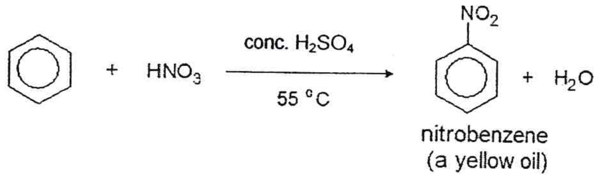
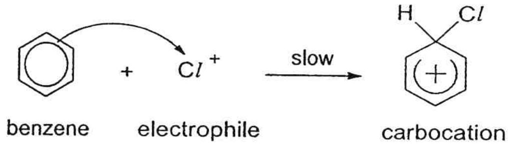
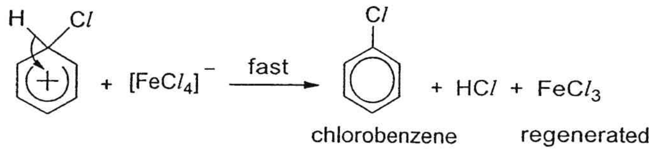
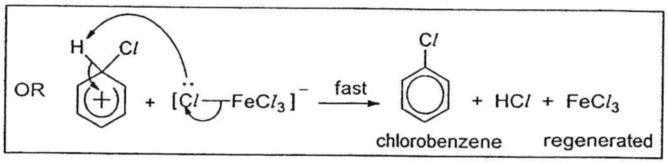
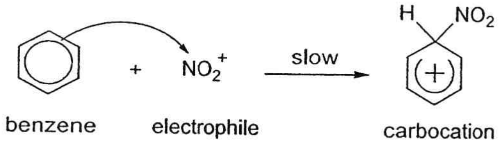
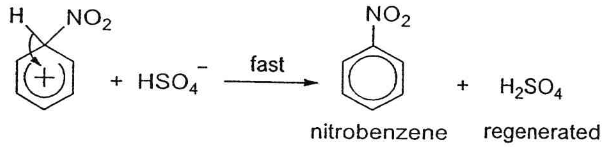
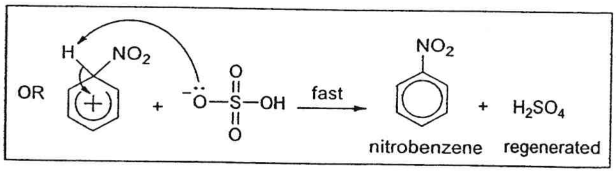
Note:

- $AlCl_3$ catalyst reacts readily with water.
  $AlCl_3(s) + 6H_2O(l) \longrightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$
  $[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(aq)$
- Hence the reaction can only proceed under **anhydrous** condition.

Iron filings can be used for the reaction since it is converted into $FeCl_3$ or $FeBr_3$ in the reaction mixture (i.e. $FeCl_3$ is often generated *in situ* from Fe and Cl_2 while $FeBr_3$ from Fe and Br_2).

$$2Fe + 3Br_2 \longrightarrow 2FeBr_3$$
$$2Fe + 3Cl_2 \longrightarrow 2FeCl_3$$

7.3 The reaction mechanism: Electrophilic Substitution

Halogenation of benzene	**Nitration of benzene (for comparison)**
Overall reaction:  	**Overall reaction:** 
Reaction Mechanism: **Generation of the electrophile, Cl^+** $Cl_2 + FeCl_3 \rightleftharpoons Cl^+ + [FeCl_4]^-$ **Step 1:**  **Step 2:**  	**Reaction Mechanism:** **Generation of the electrophile, NO_2^+** $2H_2SO_4 + HNO_3 \rightleftharpoons NO_2^+ + 2HSO_4^- + H_3O^+$ **Step 1:**  **Step 2:**  

Marking points for mechanism drawing:

✓ Name of mechanism
✓ Equation for generation of electrophile
✓ Correct curly arrows
✓ Correct intermediate
✓ Label slow/fast steps

8 ELECTROPHILIC SUBSTITUTION: FRIEDEL-CRAFTS ALKYLATION & ACYLATION

Candidates should be able to describe the chemistry of the benzene ring as exemplified by the following reactions of benzene and methylbenzene:

- Friedel-Crafts alkylation with halogenoalkanes (recognise the use of Lewis acid as catalysts)

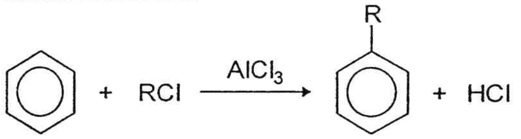
Friedel–Crafts Alkylation

Alkylation with a <u>halogenoalkane</u> and a trace amount of **anhydrous *AlCl₃*** as catalyst is often referred to as a **Friedel-Crafts alkylation**, after Charles Friedel, a French chemist, and James Crafts, an American chemist, who developed this reaction in 1877.

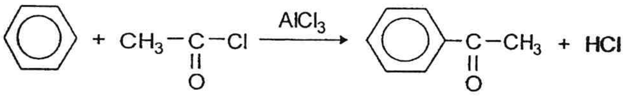
Friedel–Crafts Acylation

Acylation is similar to that of alkylation except that an **<u>acid halide</u>** (RCOX or ArCOX) instead of a halogenoalkane (RX) is used. The acid halide provides the acyl group needed for the reaction.

<u>The overall reaction</u>



<u>The overall reaction</u>



Note: $AlCl_3$ catalyst <u>reacts readily with water</u>.
Hence the reaction can only proceed under **anhydrous** condition.

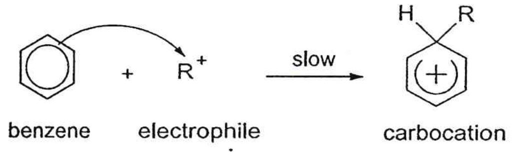
<u>Reaction mechanism:</u>

Electrophilic Substitution

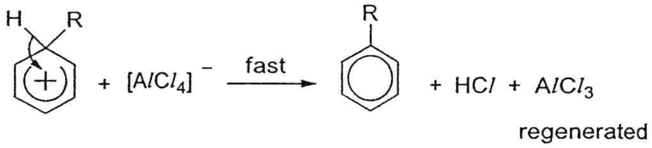
Generation of the electrophile R^+

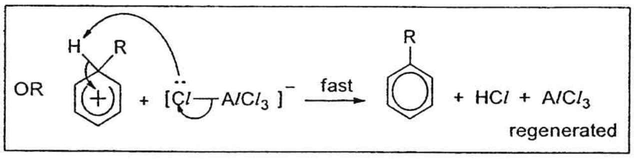
$$R–Cl + AlCl_3 \rightleftharpoons R^+ + [AlCl_4]^-$$

Step 1:



Step 2:

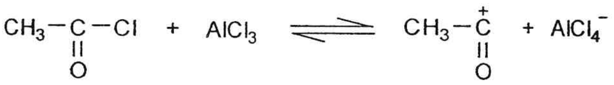




<u>Reaction mechanism:</u>

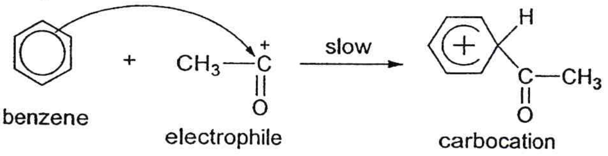
Electrophilic Substitution

Generation of the electrophilic acylium ion

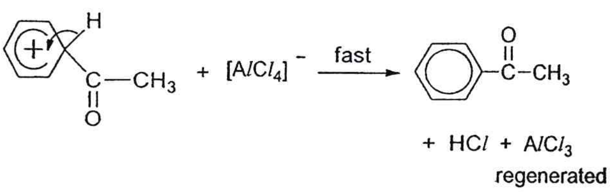


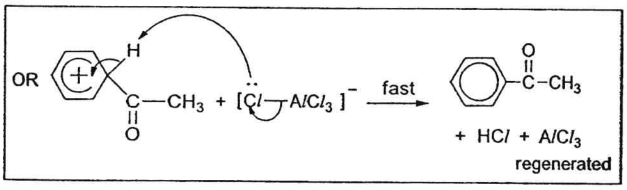
$$CH_3–\underset{\underset{O}{||}}{C}–Cl + AlCl_3 \rightleftharpoons CH_3–\underset{\underset{O}{||}}{\overset{+}{C}} + AlCl_4^-$$

Step 1:



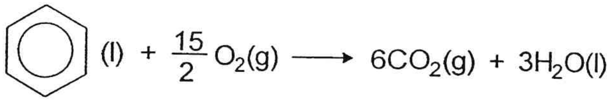
Step 2:





9 OTHER REACTIONS OF BENZENE

9.1 Combustion

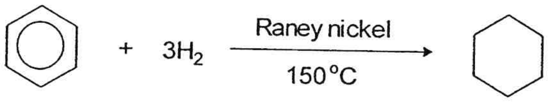


Benzene burns in air with a sooty, smoky flame. This sort of flame is characteristic of all hydrocarbons containing a high percentage of carbon.

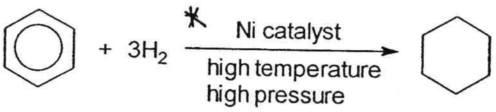
9.2 Reduction (catalytic hydrogenation)

Benzene undergoes **addition reaction** with **hydrogen** in the **presence of nickel catalyst** at considerably **higher temperature and pressure** than for alkenes.

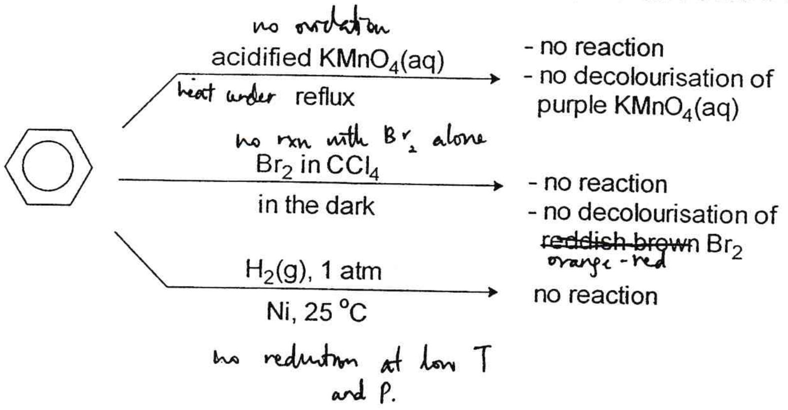
⇒ The higher temperature is needed because extra energy must be supplied to break up the delocalised π-electron system.

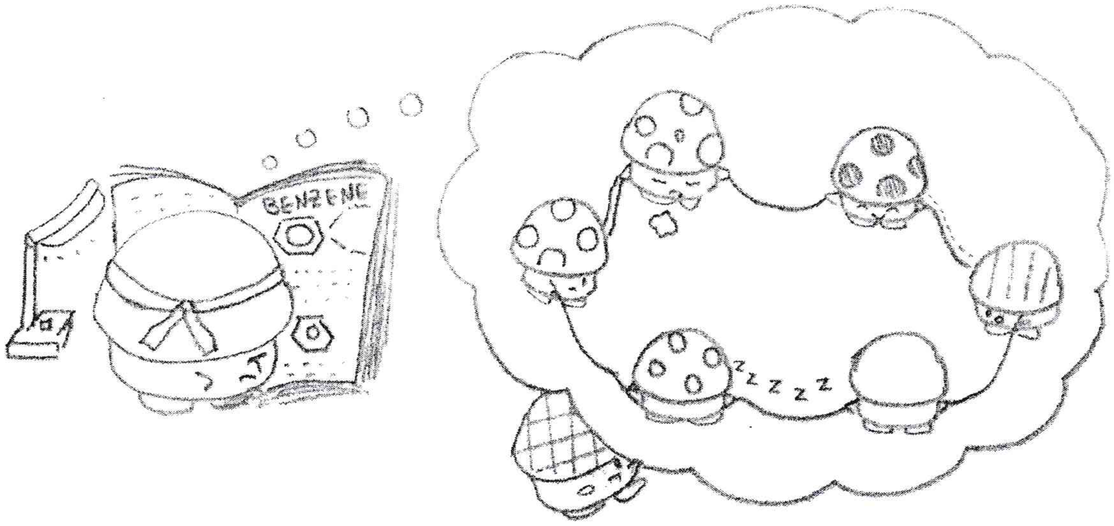


Or simply



9.3 Reactions that benzene DOES NOT undergo



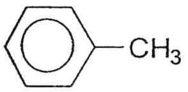


10 METHYLBENZENE

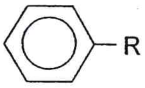
Candidates should be able to
- describe the chemistry of the alkyl side-chain of benzene ring as exemplified by the following reactions of methylbenzene:
  (i) free-radical substitution by chlorine and by bromine
  (ii) complete oxidation to give benzoic acid
- predict whether halogenation will occur in the side-chain or aromatic nucleus in arenes depending on reaction conditions

10.1 Introduction

Methylbenzene (C_7H_8) is the simplest alkylbenzene. Its structural formula is shown below.



methylbenzene



where
—R is an alkyl group

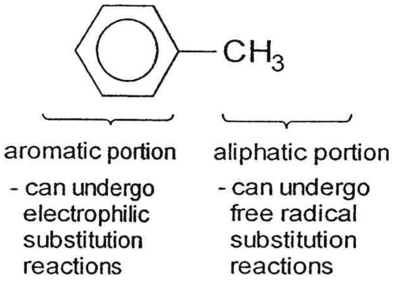
alkylbenzene

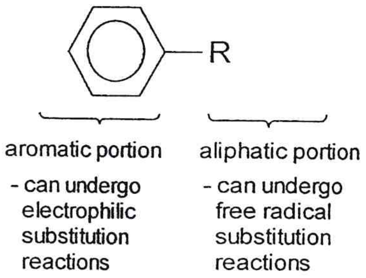
- Like benzene, methylbenzene is a colourless liquid which is insoluble in water but soluble in organic solvents. It is itself a useful solvent.
- It melts at –95 °C and boils at 111 °C.
- When combusted, it burns with a sooty flame indicating that it has a relatively high C:H ratio.
- Industrially, methylbenzene is obtained both from coal and from petroleum in the same way as benzene.

10.2 Reactions of methylbenzene and other alkylbenzenes

Methylbenzene has an **aromatic** portion (the benzene ring) and an **aliphatic** portion (the methyl group).

⇒ These two portions make different contributions to the chemical properties of methylbenzene and have a modifying effect on one another.





Methylbenzene undergoes two main types of reactions:

❶ reactions of the alkyl side chain ➲ free radical substitution
➲ oxidation

❷ reactions of the benzene ring ➲ electrophilic substitution
(*similar to benzene but at* ***milder*** *conditions*)

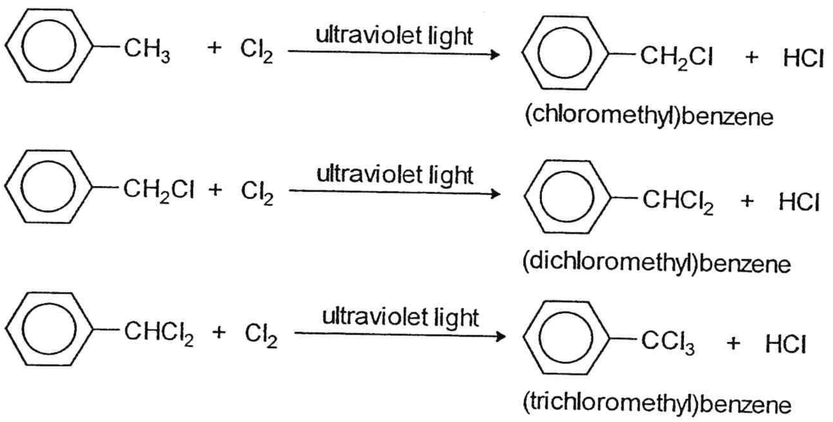
11 REACTIONS OF THE SIDE CHAIN IN ALKYLBENZENES

Candidates should be able to
- describe the chemistry of the alkyl side-chain of benzene ring as exemplified by the following reactions of methylbenzene:
  (i) free-radical substitution by chlorine and by bromine
  (ii) complete oxidation to give benzoic acid
- predict whether halogenation will occur in the side-chain or aromatic nucleus in arenes depending on reaction conditions

11.1 Free radical substitution of the alkyl side chain

- The $-CH_3$ group in methylbenzene shows reactions expected of an alkyl group, for example, it can undergo **free radical substitution reaction** with chlorine.

- The reaction occurs when chlorine is bubbled into boiling methylbenzene which is exposed to sunlight or ultraviolet light.



- Bromination of methylbenzene takes place under similar conditions, forming the corresponding bromine derivatives.

- The conditions employed here favour the formation of free radicals, and the reaction proceeds in a similar way to the halogenation of alkanes (i.e. via **free radical substitution mechanism**).

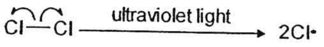
■ Worked Example 1 ■

Describe the mechanism for the reaction between methylbenzene and chlorine in the presence of ultraviolet light to produce (chloromethyl)benzene.

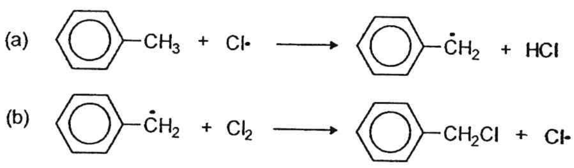
Solution:

Mechanism: Free radical substitution

Step 1: Initiation

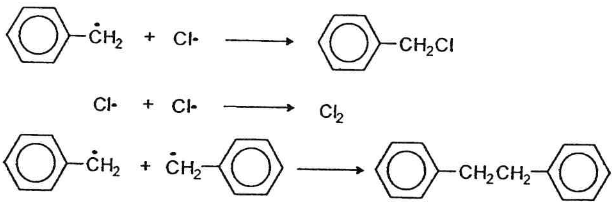


Step 2: Propagation



Then (a), (b), (a), (b), ...

Step 3: Termination

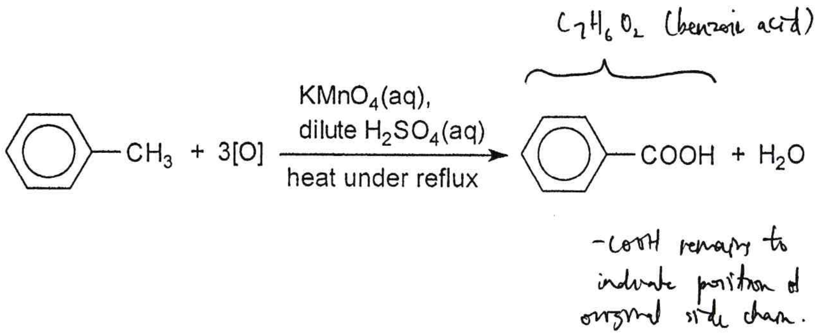
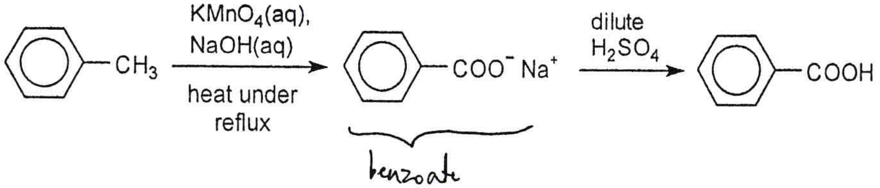
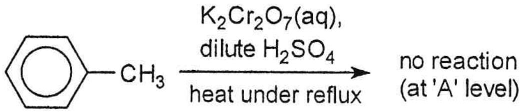


11.2 Oxidation of the alkyl side chain

- Although alkanes and benzene are quite unreactive toward the usual oxidising agents (e.g. acidified $KMnO_4$), the benzene ring renders an aliphatic side chain quite susceptible to oxidation.

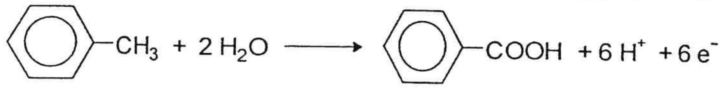
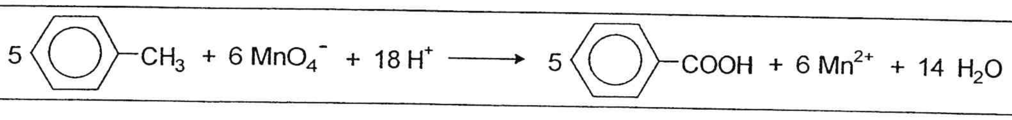
> **Note:** The side chain is oxidised, with **only a carboxylic acid group (–COOH) remaining** to indicate the position of the original side chain.

- This oxidation reaction is useful for the synthesis of carboxylic acids and the identification of alkylbenzenes.

Reagents and Conditions	Reaction (if any)	Observations
$KMnO_4(aq)$, $H_2SO_4(aq)$, heat	 $C_7H_6O_2$ (benzoic acid) -COOH remains to indicate position of original side chain.	• **Decolourisation** of purple $KMnO_4$ (if it is the limiting reagent). • Formation of a white precipitate of benzoic acid. upon cooling. **Note**: Benzoic acid has limited solubility in water as its large non-polar benzene ring interferes with the formation of hydrogen bonding between the $-CO_2H$ group and water. Hence, benzene is soluble in hot water but has poor solubility in cold water. It appears as a **white precipitate** when the reaction mixture is cooled.
$KMnO_4(aq)$, $NaOH(aq)$, heat	 benzoate	• **Decolourisation** of purple $KMnO_4$ (if it is the limiting reagent). • Formation of a brown-black ppt **of MnO_2.** • Formation of a white precipitate of benzoic acid **upon cooling and acidification.**
$K_2Cr_2O_7(aq)$, $H_2SO_4(aq)$, heat	 	Cr^{3+} • Orange $K_2Cr_2O_7(aq)$ **does not turn green.**

11.2.1 Balancing equations using half equation method

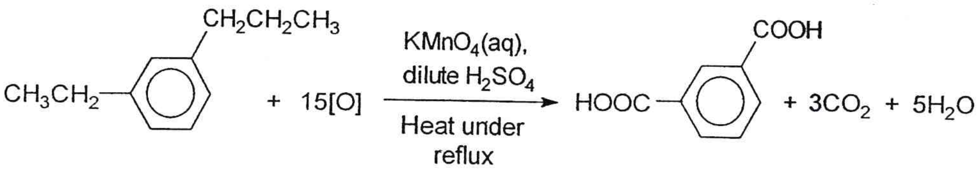
For *stoichiometric calculations*, the following equations are required to derive the stoichiometric ratios of the oxidising agent and reducing agent.

Oxidation half-equation:	
Reduction half-equation:	$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$
Overall equation:	

11.2.2 Oxidation of longer alkyl chains

- Ethylbenzene or any other benzene derivative with an alkyl side chain (however long) will produce the same product, **benzoic acid**.
- The **rest of the alkyl side chain** is destroyed, usually forming **carbon dioxide and water**.

Example:

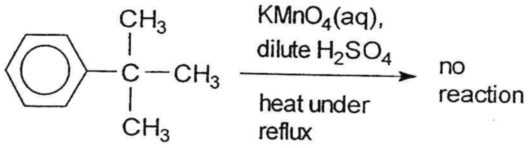


Note: Only a carboxylic acid group (i.e. –COOH) remains to indicate the position of the original side chain.

11.2.3 Criteria for oxidation of side chains on benzene

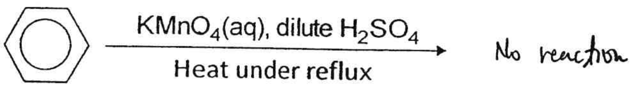
/ must have at least 1 H atom bonded to it.

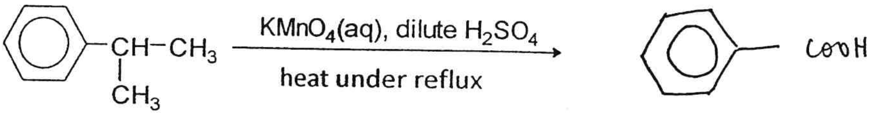
- Alkylbenzenes **without a H atom bonded to the benzylic carbon atom** (i.e. the carbon atom that is bonded to the benzene ring) **do not undergo oxidation** when heated with acidified $KMnO_4$.

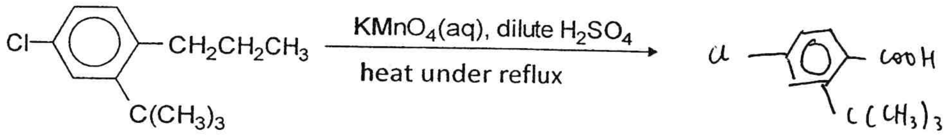


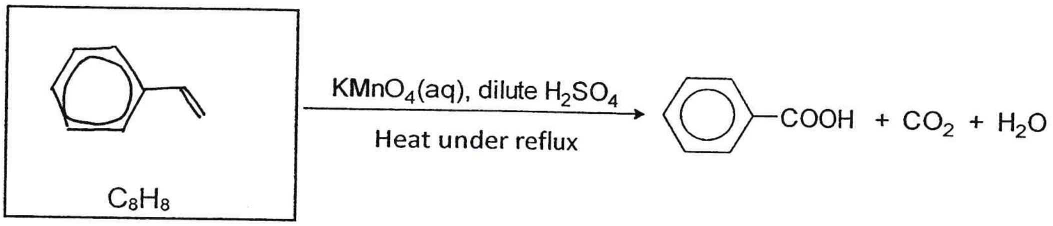
- The other criteria will be discussed in the later topics of Organic Chemistry.

Exercise 1: Identify the organic reactants or products for the following reactions.
(Note: Equations are not balanced)

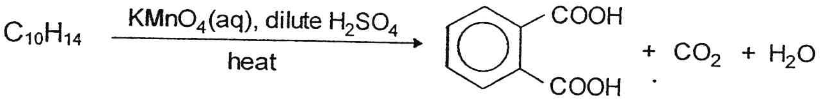
1


2


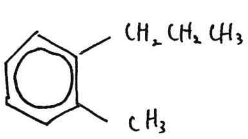
3


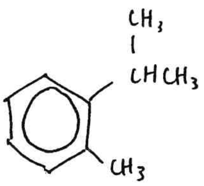
4


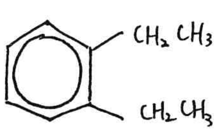
Exercise 2: Identify the reactant of the following reaction
(Note: Equations are not balanced)

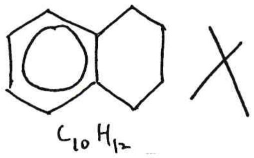


Possible structures of the reactant, C$_{10}$H$_{14}$:
(Hint: There are 3 possible structures)

①


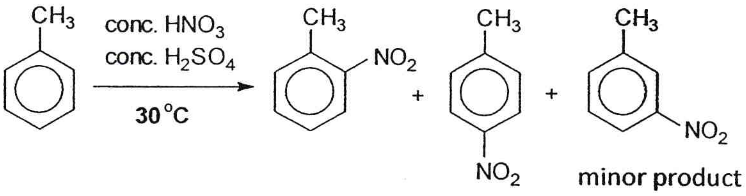
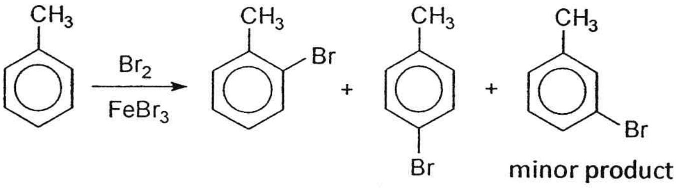
②


③




12 ELECTROPHILIC SUBSTITUTION OF THE BENZENE RING IN METHYLBENZENES

- Consider the following electrophilic substitution reactions of methylbenzene:

nitration		**Note:** • Reaction takes place at **30 °C**. • A mixture of products is obtained
halogenation		**Note:** • **Faster** rate of reaction relative to benzene. • A mixture of products is obtained.

- The presence of the $-CH_3$ group in methylbenzene affects both the **reactivity** and **orientation** of the electrophilic substitution reaction.

  Using the nitration of methylbenzene as an example:

Effect on Reactivity (i.e. the rate of the nitration reaction)	**Effect on Orientation** (i.e. the site of electrophilic attack)
• A **lower temperature (30 °C)** is used for the nitration of methylbenzene (whereas nitration of benzene requires 55 – 60 °C). • This shows that methylbenzene is **more reactive** than benzene towards nitration. • In this case, the $-CH_3$ group is said to be an **activating group**.	• The major products of mono-nitration of methylbenzene are 2-nitromethylbenzene and 4-nitromethylbenzene. • This shows that substitution by the $-NO_2$ group occurs **chiefly at 2- and 4- positions** relative to the $-CH_3$ group. • As such the $-CH_3$ group is described as **2,4-directing** (or ortho, para-directing).

substituents affect orientation (site of electrophilic attack).

13 EFFECTS OF SUBSTITUENT GROUPS

Candidates should be able to apply the knowledge of positions of substitution in the electrophilic substitution reactions of monosubstituted arenes.

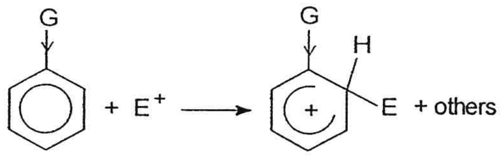
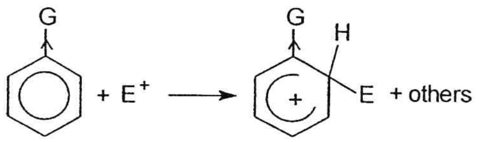
When an electrophilic reagent attacks an aromatic ring, it is the group already attached to the ring that determines

➲ **how readily** the attack occurs (i.e. the **reactivity** of the ring), and

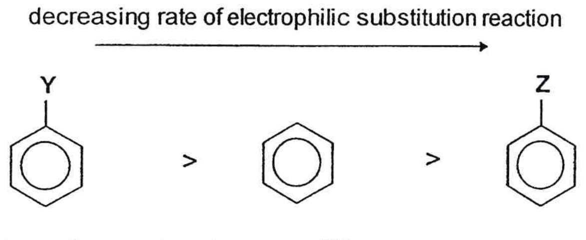
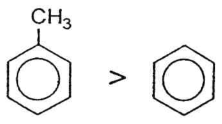
➲ the **position** of substitution.

13.1 Relative reactivity

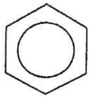
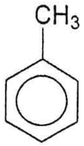
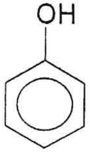
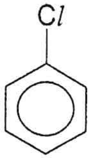
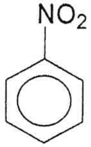
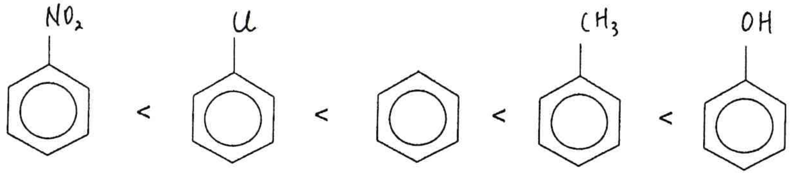
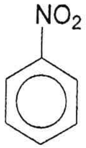
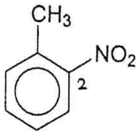
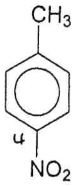
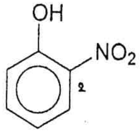
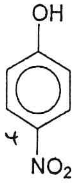
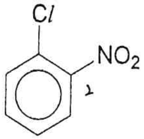
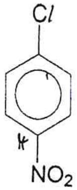
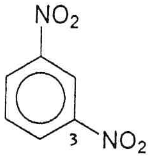
- Reactivity in electrophilic substitution depends on the tendency of a substituent group to release or withdraw electrons.
  - A group that donates electrons or delocalize electrons into the ring **activates** the benzene ring towards electrophilic substitution reaction.
  - A group that withdraws electrons **deactivates** the benzene ring towards electrophilic substitution reaction.

Activating groups	**Deactivating groups**
• An **activating group** is **electron-donating**. It - **increases the electron density** in the benzene ring and makes the ring more susceptible to electrophilic attack. - helps to **disperse the positive charge** in the intermediate **carbocation** and leads to the stabilisation of the carbocation	• A **deactivating group** is **electron-withdrawing**. It - **decreases the electron density** in the benzene ring and makes the ring less susceptible to electrophilic attack. - tends to **intensify the positive charge** in the intermediate **carbocation** and leads to the destabilisation of the carbocation
A group attached to a benzene ring is classified as **activating** if it activates the benzene ring towards electrophilic attack, i.e. the ring is more reactive than benzene towards electrophilic substitution reactions.	A group attached to a benzene ring is classified as **deactivating** if it deactivates the benzene ring towards electrophilic attack, i.e. the ring is less reactive than benzene towards electrophilic substitution reactions.
• Examples of activating group: $-NH_2$, $-OH$, $-CH_3$	• Examples of deactivating group: $-NO_2$, $-COOH$, $-Cl$
	 where G is C*l*, in this example.

- Relative rates of electrophilic substitution

 **Y** is an electron-donating group and hence is an activating group. **Z** is an electron-withdrawing group and hence is a deactivating group.	**Note:**  Methylbenzene is more reactive than benzene towards electrophilic substitution reactions because the $-CH_3$ group is an electron-donating group and hence an activating group. It increases the electron density in the benzene ring and makes it more susceptible to electrophilic attack.

- Example: Nitration of benzene ring

Compound					
Nature of substituent	—	Activating	Strongly activating	Deactivating	Strongly deactivating
Reagents	Concentrated nitric acid	Concentrated nitric acid	Dilute nitric acid	Concentrated nitric acid	Concentrated nitric acid
Conditions	Concentrated sulfuric acid catalyst, 55 – 60 °C	Concentrated sulfuric acid catalyst, 30 °C	Room temperature	Concentrated sulfuric acid catalyst, > 55°C	Concentrated sulfuric acid catalyst, high temperature (95 °C)
Reactivity					
Major product(s)		 	 	 	

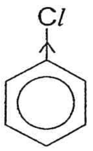
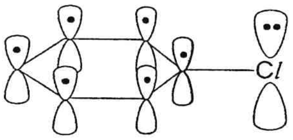
Note: The $-CH_3$, $-OH$, $-Cl$ groups are 2,4-directing while the $-NO_2$ group is 3-directing (*refer to Section 13.2*)

Question: What makes a substituent on a benzene ring electron-donating or electron-withdrawing?

Substituents on a benzene ring donate or withdraw electrons through **inductive** and **resonance** effects.

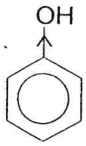
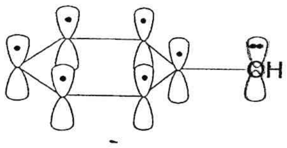
	Inductive Effect	**Resonance effect**
	• An **inductive effect** is the donation or withdrawal of electrons **through σ bonds** due to the electronegativity difference between atoms.	• A **resonance effect** is the donation or withdrawal of electrons **through π bonds** due to the <u>continuous p-orbital overlap</u> of the substituent and the benzene ring. This results in delocalisation of electrons, either towards or away from the benzene ring.
Electron-donating	Example: $-CH_3$ • Alkyl groups have a sp^3 carbon. Since sp^3 orbitals have less s-character, its electrons are less tightly held and more easily donated to the benzene ring. • The substituent is said to be electron-donating **by inductive effect.**	Example: –OH (*refer to pg 25*) • If a substituent has a lone pair of electrons on the atom that is directly attached to the benzene ring, - the lone pair is usually in a p-orbital, and - can be delocalised into the ring. • The substituent is said to be electron-donating by **resonance effect.**
Electron-withdrawing	Example: –C*l* (*see below*) • Atoms such as O, N and C*l* are more electronegative than C atom (on benzene ring). They pull electron density away from C through the **σ bond.** • The substituent is said to be electron-withdrawing by **inductive effect.**	Examples: –C=O, $-NO_2$ • If a substituent is directly attached to the benzene ring by an atom that is doubly or triply bonded to a more electronegative atom, the π electrons of the ring can be delocalised onto the substituent. • The substituent is said to be electron-withdrawing by **resonance effect.**

- Consider chlorobenzene and phenol where there is competition between electron-withdrawing inductive effect and the electron-donating resonance effect.

Inductive effect	**Resonance effect**
	
• The C*l* atom is more electronegative than C. • Hence the –C*l* group is **electron-withdrawing by inductive effect.**	• A lone pair of electrons on the C*l* atom can interact with the delocalised π-electron cloud of the benzene ring and delocalises into the ring. ⇒ This increases the electron density in the benzene ring. • Hence the –C*l* group is **electron-donating by resonance effect.**

Note:

- In this case, the inductive effect is <u>stronger</u> than the resonance effect.
- This is because C*l* is in Period 3 ⇒ its p-orbitals are more diffuse leading to a less effective side-on overlap with the p-orbitals of the benzene ring.
- Hence the **overall effect of the –C*l* group in chlorobenzene is <u>electron-withdrawing</u>.**
- The **–C*l* group decreases the electron density** in the benzene ring and makes the ring less susceptible to electrophilic attack. It is said to be a **<u>deactivating group</u>**.

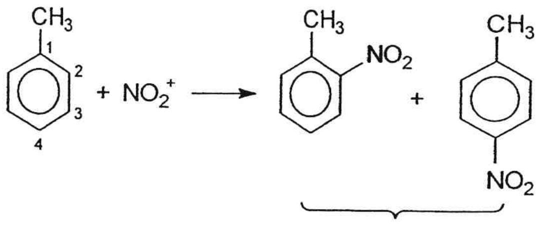
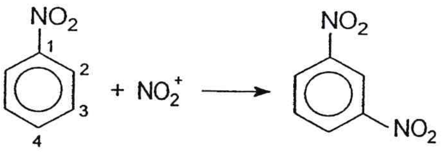
Inductive effect	Resonance effect
	
• The O atom is more electronegative than C. • Hence the –OH group is **electron-withdrawing by inductive effect.**	• A lone pair of electrons on the O atom can interact with the delocalised π-electron cloud of the benzene ring and delocalises into the ring. ⇒ This increases the electron density in the benzene ring. • Hence the –OH group is **electron-donating by resonance effect.**

Note:

- In this case, the resonance effect is stronger than the inductive effect.
- Hence the **overall effect of the –OH group in phenol is electron-donating.**
- The **–OH group increases the electron density** in the benzene ring and makes the ring more susceptible to electrophilic attack. It is said to be a **strongly activating group**.

13.2 Orientation

- A substituent group in the benzene ring not only activates or deactivates the ring, it also controls the position of entry of an incoming group.
- Depending on the position it directs an incoming group to, a substituent group may be classified as
  - a **2,4-directing group** (or ortho, para-directing group) or
  - a **3-directing group** (or meta-directing group).

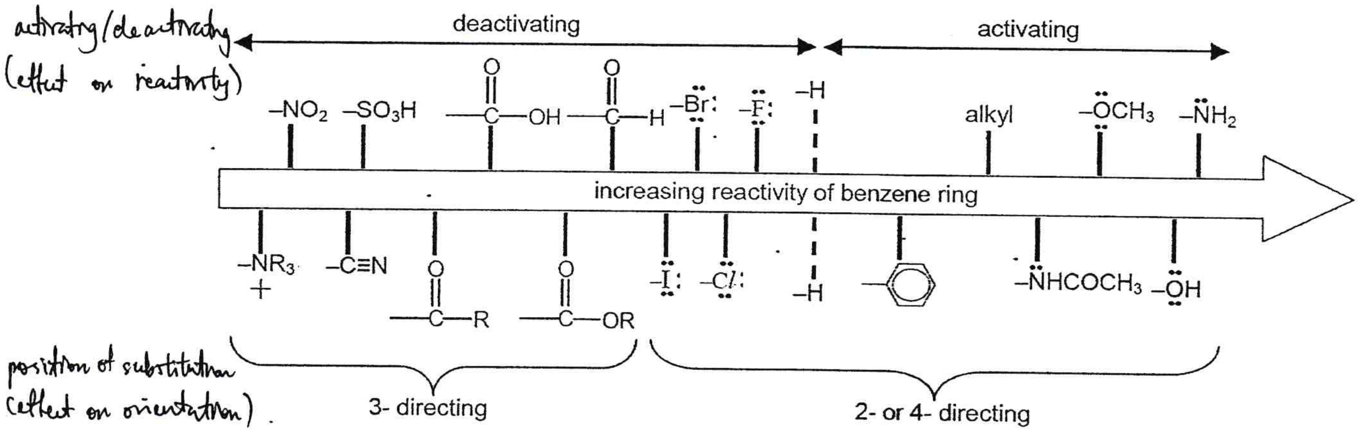
2,4-directing group	3-directing group
• A **2,4-directing group** (e.g. $-CH_3$) causes an electrophile to attack chiefly at 2-position and 4-position relative to it. ⇒ It directs the incoming group mainly to the 2- and 4- positions relative to it.	• A **3-directing group** (e.g. $-NO_2$) causes an electrophile to attack **chiefly** at 3-position relative to it. ⇒ It directs the incoming group mainly to the 3-position relative to it.
• Examples of 2,4-directing group: $-NH_2$, $-OH$, $-CH_3$, $-Cl$	• Examples of 3-directing group: $-COOH$, $-NO_2$, $-CHO$
 major products	 major product

13.3 Classification of substituent groups

Refer to the *Data Booklet* section 8 on **'The orientating effect of groups in aromatic substitution reactions'**

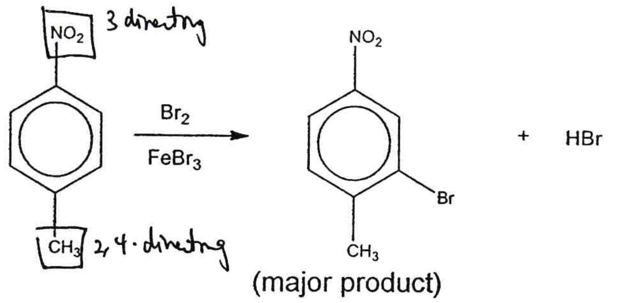
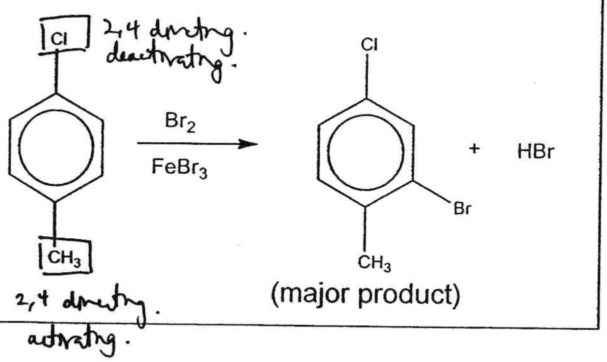
Effect of groups on electrophilic aromatic substitution:

Substituent group	Effect on reactivity	Effect on orientation	Remarks
$-NH_2$ $-NHR$ $-NR_2$ $-OH$	strongly activating	2,4-directing	• Each substituent has a lone pair on an atom that is bonded to the carbon atom of the aromatic ring. • Each substituent can donate electrons by resonance effect (delocalize electrons into the ring).
$-OCH_3$ ($-OCH_2CH_3$, etc.) $-NHCOCH_3$	moderately activating	2,4-directing	
$-C_6H_5$ $-CH_3$ ($-CH_2CH_3$, etc.)	weakly activating	2,4-directing	
$-H$	Standard for comparison		
$-F$, $-Cl$, $-Br$, $-I$	weakly deactivating	2,4-directing	• The halogen atoms are different from the other substituents.
$-COOH$ ($-COOR$) $-SO_3H$ $-CHO$, $-COR$	deactivating	3-directing	• Each substituent is unsaturated and does not have an atom with a lone pair bonded directly to the benzene ring.
$-NO_2$ $-NR_3^+$ $-CF_3$, $-CCl_3$	strongly deactivating	3-directing	



A classification of substituents based on how each group affects the reactivity of the benzene ring towards electrophilic substitution

If there are two substituent groups in the benzene ring and their <u>directing effects oppose each other</u>, the **directing effect of the more powerful activating group wins**.

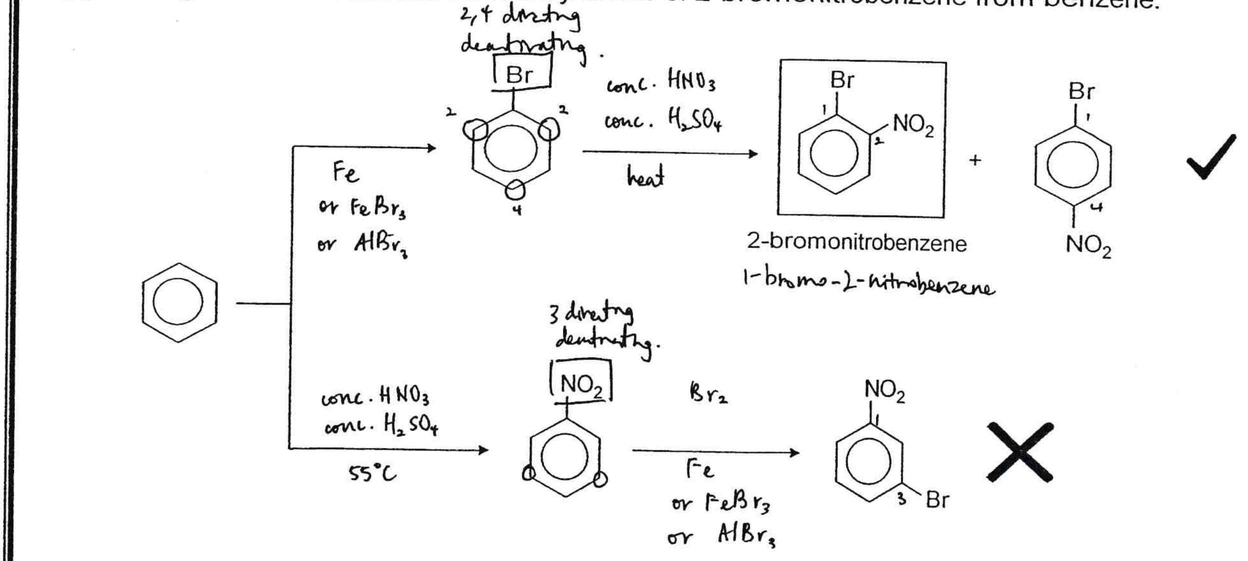
Both groups direct to same position	Opposing effects:
 (major product)	 (major product)

13.4 Orientation and Synthesis

The order in which the various substituents are introduced into the benzene ring is important.

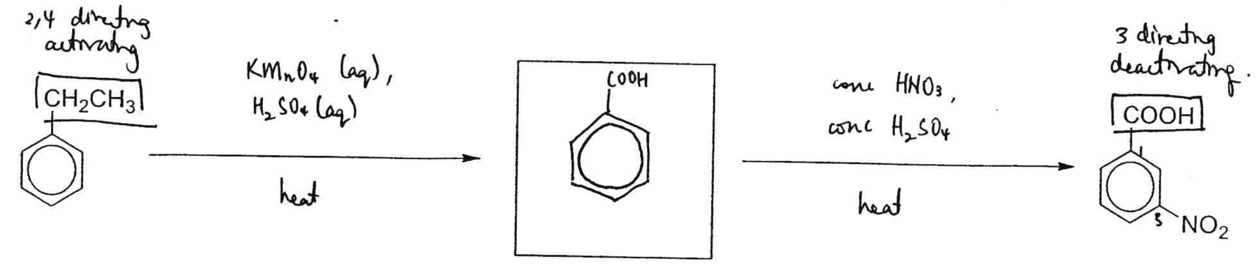
■ Worked Example 2 ■

Suggest reagents and conditions for the synthesis of 2-bromonitrobenzene from benzene.

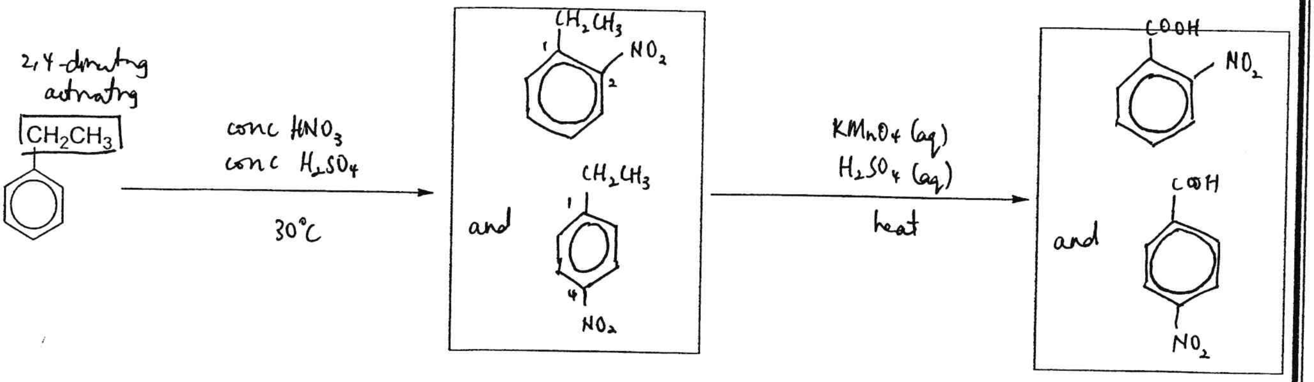


Exercise 3:

Suggest reagents and conditions for the synthesis of 3-nitrobenzoic acid from ethylbenzene.

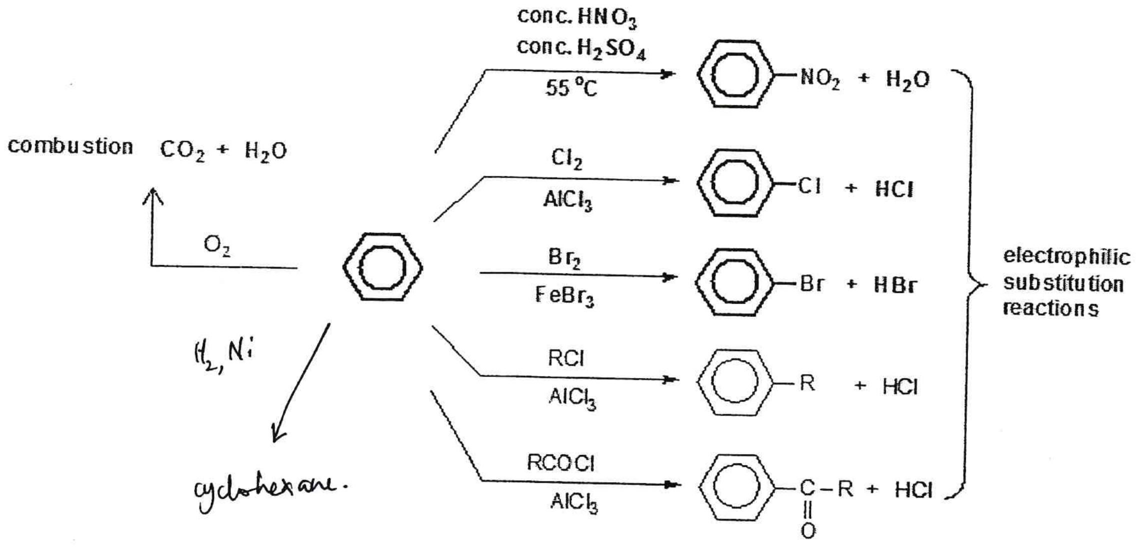


What would happen when the two synthesis steps are swapped?

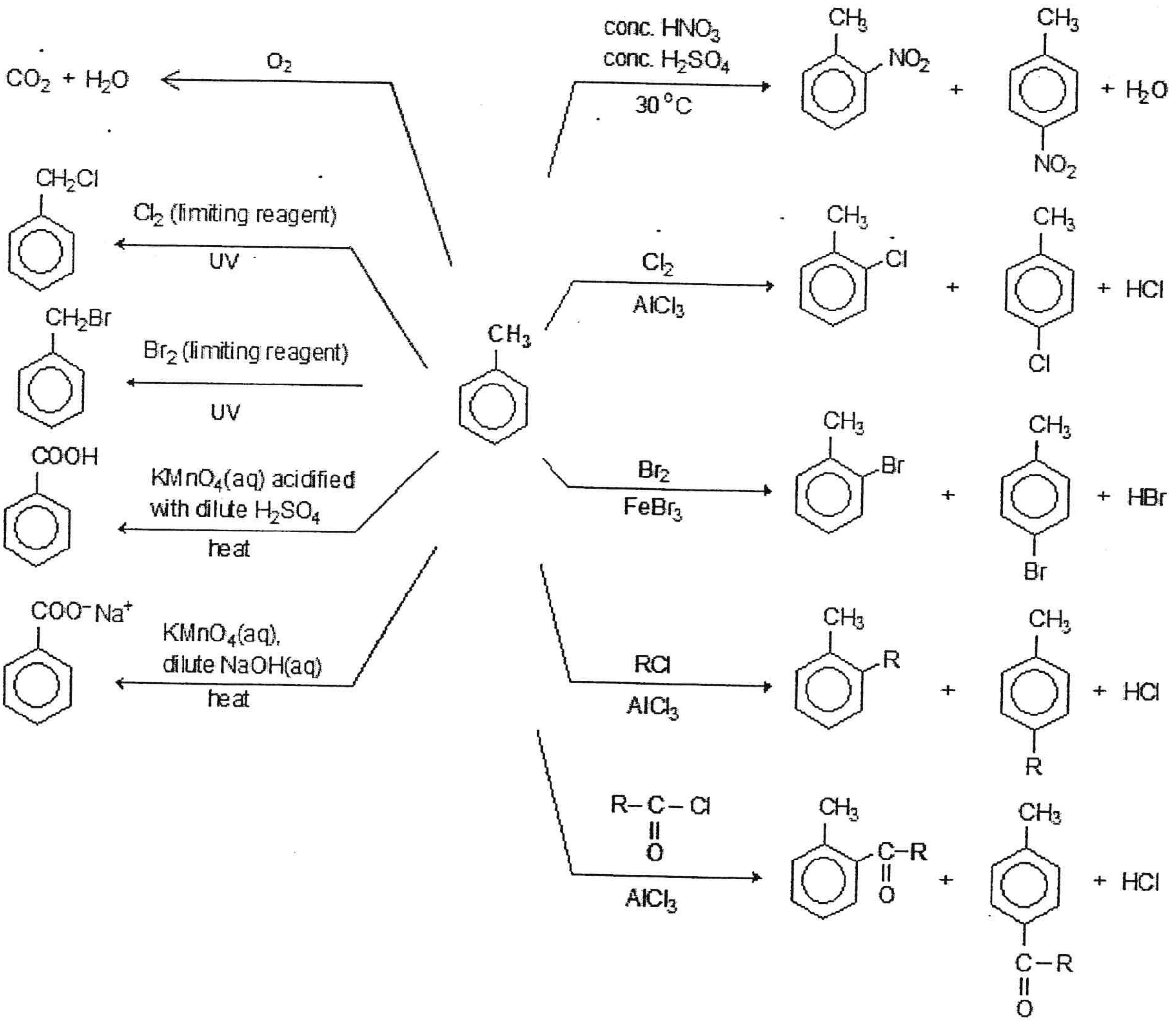


14 SUMMARY

14.1 Some reactions of benzene

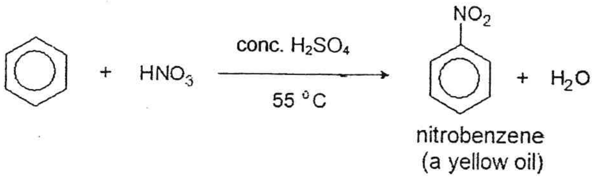


14.2 Some reactions of methylbenzene



14.3 Electrophilic Substitution Reactions

Nitration of benzene:

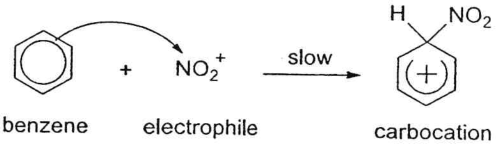


Reagents and conditions:
conc HNO_3, conc H_2SO_4, 55 – 60 °C

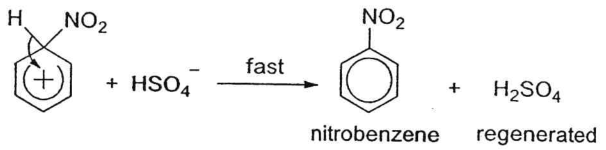
Electrophilic Substitution

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

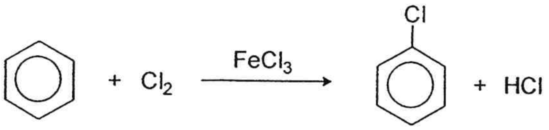
Step 1:



Step 2:



Chlorination of benzene:

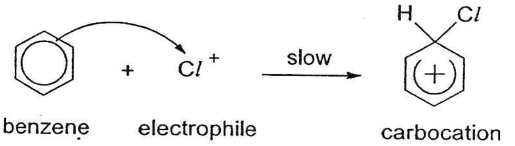


Reagents and conditions: Cl_2, $FeCl_3$

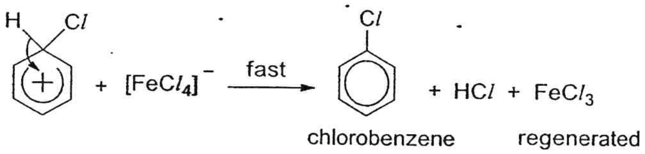
Electrophilic Substitution

$$Cl_2 + FeCl_3 \rightleftharpoons Cl^+ + [FeCl_4]^-$$

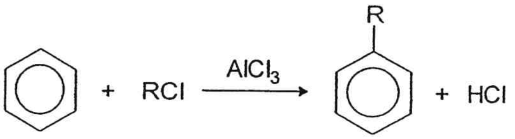
Step 1:



Step 2:



Friedel–Crafts Alkylation

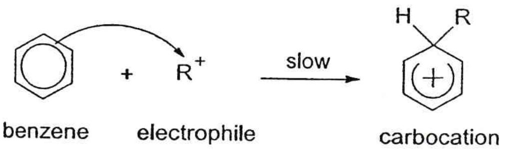


Reagents and conditions: RCl, $AlCl_3$

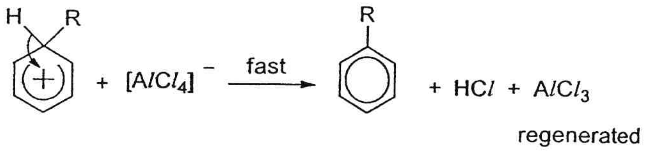
Electrophilic Substitution

$$R\text{–}Cl + AlCl_3 \rightleftharpoons R^+ + [AlCl_4]^-$$

Step 1:



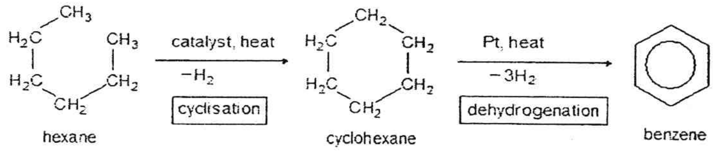
Step 2:



OPTIONAL READING

- **Industrial sources of Benzene**

(a) From petroleum by catalytic reforming of hexane

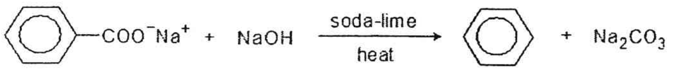


(b) From coal tar by fractional distillation of coal tar

- **Laboratory preparation of Benzene** *(not in the syllabus but can be tested)*

Owing to the abundance of benzene from industrial sources, it is rarely prepared in the laboratory, and the following reactions tend to be of academic interest only.

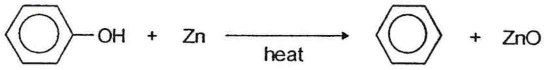
(a) Decarboxylation of a sodium benzoate



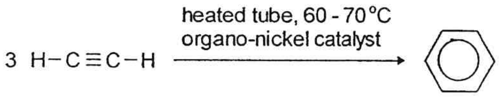
Note: Soda-lime is a mixture of sodium and calcium hydroxides made by adding concentrated sodium hydroxide solution to quicklime. It functions as sodium hydroxide. It may be preferable to sodium hydroxide as a reagent because it is not deliquescent, it attacks glass less readily and it has a higher melting point.

- **Decarboxylation** is a reaction in which the elements of carbon dioxide are removed from a compound.

(b) Reduction of phenol

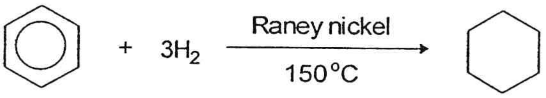


(c) Polymerisation of ethyne



- **Reduction of benzene**

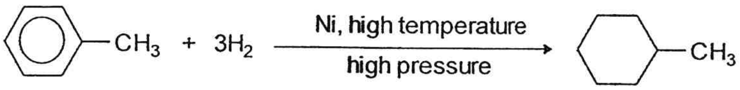
Benzene undergoes addition reaction with hydrogen in the presence of nickel catalyst at considerably higher temperatures than for alkenes. The higher temperature is needed because extra energy must be supplied to break up the delocalised π-electron system.



The catalyst, Raney nickel, is a form of nickel with an extremely high surface area for catalytic activity. The catalytic hydrogenation of benzene is important industrially in the manufacture of cyclohexane, from which nylon is made. Other catalyst that can be used: Pt or Pd

- **Reduction of methylbenzene**

Methylbenzene reacts with hydrogen under the same conditions (i.e. catalyst + high temperature + high pressure) as benzene. Thus if a mixture of methylbenzene vapour and hydrogen is passed over finely divided nickel at 180 °C, methylcyclohexane is produced.



Other catalysts: Pt or Pd

- **Free radical addition of benzene**