RAFFLES INSTITUTION
YEAR 5 H2 CHEMISTRY 2022
Lecture Notes 13 – Arenes

A Content

Arenes (exemplified by benzene and methylbenzene)

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

B Learning outcomes

Candidates should be able to:

(a) 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

(b) 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)

(c) (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

(d) 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

(e) predict whether halogenation will occur in the side-chain or aromatic nucleus in arenes depending on reaction conditions

(f) apply the knowledge of positions of substitution in the electrophilic substitution reactions of monosubstituted arenes

C References

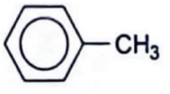
- A-Level Chemistry (by Ramsden)
- Chemistry in Context (by Hill and Holman)
- Organic Chemistry (by David Klein)
- Organic Chemistry (by L.G.Wade)
- Website: www.chemguide.co.uk

1 INTRODUCTION

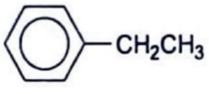
Arenes (also referred to as aromatic hydrocarbons) are hydrocarbons based on the **benzene ring** as a structural unit.

Examples of arenes (or aromatic hydrocarbons):

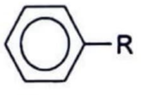

benzene



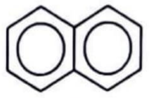
methylbenzene



ethylbenzene



alkylbenzene
–R = alkyl group


naphthalene

The term 'aromatic' indicates 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 cyclotriene (*refer to Section 4.2*).

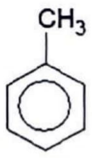
Aromatic compounds are compounds possessing the ring structure of benzene or other molecular structures that resemble benzene in structure and chemical behaviour.

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

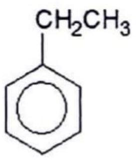
2 NOMENCLATURE OF BENZENE DERIVATIVES

2.1 Monosubstituted benzene derivatives

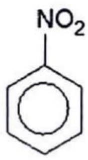
- For many of these derivatives, the name of the substituent group is added as a prefix to the word *–benzene*. Below are several examples.



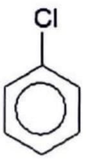
methylbenzene
(or toluene)



ethylbenzene

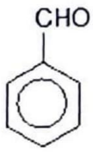


nitrobenzene

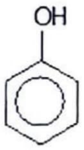


chlorobenzene

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

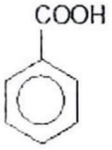


benzaldehyde

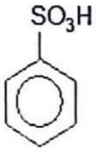


phenol

phenylamine
(aniline)



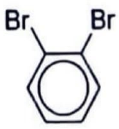
benzoic acid
(benzenecarboxylic acid)

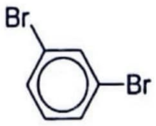


benzenesulfonic
acid

2.2 Disubstituted benzene derivatives

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

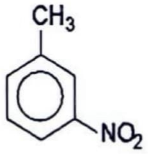

1,2-dibromobenzene

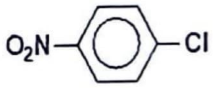

1,3-dibromobenzene


1,4-dibromobenzene

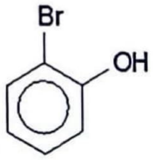
- If the two substituent groups are different, the names of the groups prefix benzene in alphabetical order.


1-bromo-2-methylbenzene
(2-bromomethylbenzene)

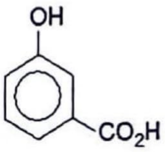

1-methyl-3-nitrobenzene
(3-nitromethylbenzene)


1-chloro-4-nitrobenzene
(4-chloronitrobenzene)

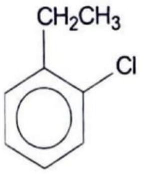
- If one of the two substituents is the kind that gives a special name to the molecule, then the compound is named as a derivative of that special compound. If both substituents give derivatives with special names, then preference is given to the substituent of highest nomenclature priority.

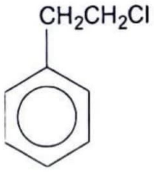

2-bromophenol

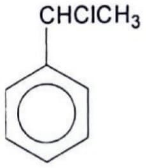

4-nitrobenzaldehyde


3-hydroxybenzoic acid

- Examples of substituents on a side chain:

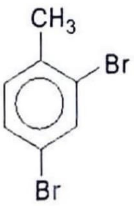

1-chloro-2-ethylbenzene
(2-chloroethylbenzene)

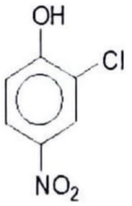

(2-chloroethyl)benzene

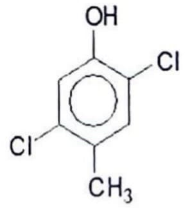

(1-chloroethyl)benzene

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.

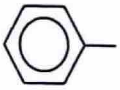
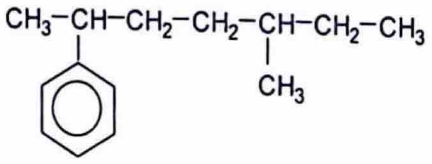
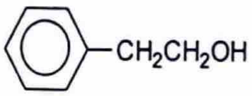
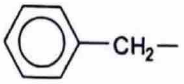
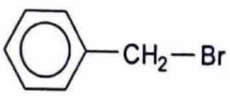

2,4-dibromo-1-methylbenzene
(2,4-dibromomethylbenzene)


2-chloro-4-nitrophenol


2,5-dichloro-4-methylphenol

2.4 The phenyl and aryl groups

- Benzene ring is treated as a substituent and 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.
- It is soluble in all organic solvents and is 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. 

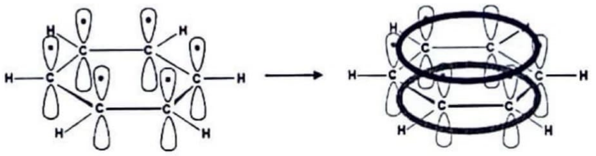
4 STRUCTURE OF BENZENE

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

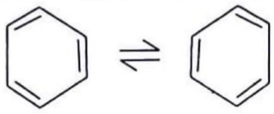
To minimise electronic repulsion, the three region of electron density about each carbon atom in a benzene (C_6H_6) molecule adopt a trigonal planar geometry. Hence, all bond angles in the benzene are 120° and it a planar molecule. Each of the six carbon atoms in benzene is sp^2 hybridised, comprising three sp^2 hybrid orbitals and one unhybridised p orbital.

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.	• Each carbon atom also has an unhybridised p orbital occupied by a single electron. • Each singly-filled p-orbital overlaps side-on with the adjacent p orbital on either side. • This continuous side-on overlap of the p-orbitals results in a cloud of delocalised π electrons above and below the plane of the ring, i.e. resonance is present. (Refer to diagram below)
 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 and energies

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.

 Kekulé benzene	2 types of carbon-carbon bonds

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

However, X-ray diffraction studies 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.

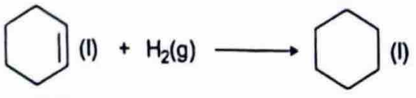
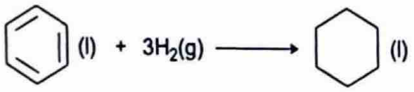
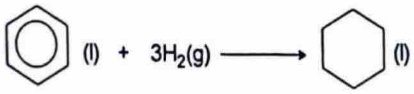
Compound	Bond	Bond length/nm
cyclohexane	carbon-carbon single bond C–C	0.154
cyclohexene	carbon-carbon double bond C=C	0.133
benzene	carbon-carbon bond $C\overset{\cdots}{-}C$	0.139

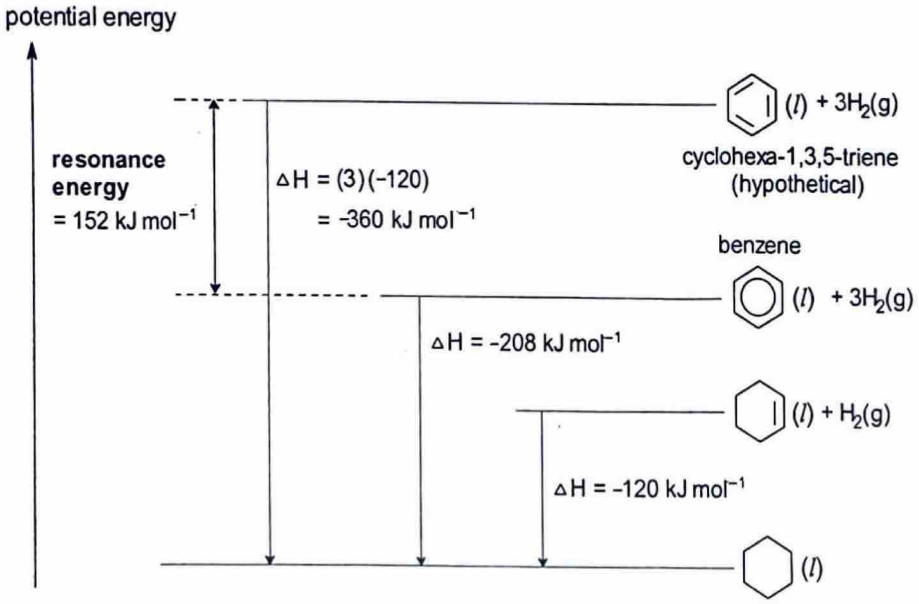
Bond	Bond energy/kJ mol^{-1} (values taken from Data Booklet)
C–C	350
C=C	610
$C\overset{\cdots}{-}C$ in benzene	520

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 carbon-carbon 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} • This is less exothermic than the expected value of –360 kJ mol^{-1}.

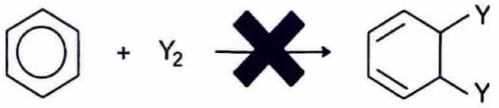


- This shows that the Kekulé structures, which contain localised π bonds, are not accurate representations of benzene.
- Instead, benzene has a structure in which the six π electrons are delocalised. It is the delocalisation of the six π electrons that confers extra stability on benzene and gives benzene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

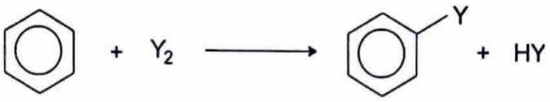
(c) Benzene undergoes substitution rather than addition reactions

If benzene were to have the cyclohexa-1,3,5-triene structure, 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 does not react or reacts very slowly.

If benzene undergoes addition reactions, its overall aromatic character is destroyed. The extra stability associated with the delocalisation of the six π electrons is lost.



Hence, the majority of reactions that benzene undergoes involve substitution in the ring. The delocalisation of the six π electrons in the continuously overlapping p-orbitals, hence its aromatic character, is retained.



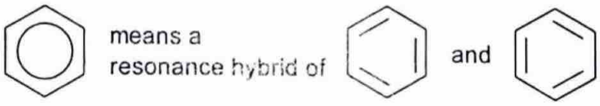
SUMMARY

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

- All carbon-carbon bonds in benzene are equal and intermediate in length between C–C and C=C bonds.
- The enthalpy change of hydrogenation of benzene is less exothermic than expected.
- Benzene undergoes substitution reactions rather than addition reactions to retain its aromaticity.

Representation of the benzene ring (C_6H_6)

Benzene is represented by a regular hexagon containing a circle. This representation is useful since it emphasises the equivalence of all the carbon-carbon bonds.

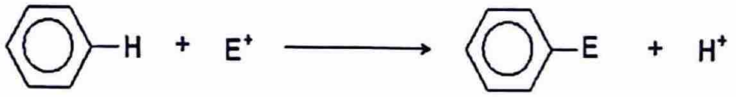


- A hydrogen atom is attached to each vertex of the hexagon, i.e. each carbon atom, unless another atom or group is indicated.
- The straight lines represent the σ bonds joining the carbon atoms.
- The circle represents the cloud of six delocalised π electrons.

5 ELECTROPHILIC SUBSTITUTION REACTIONS OF BENZENE

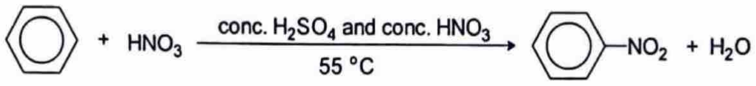
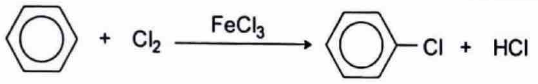
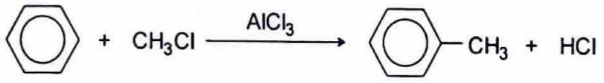
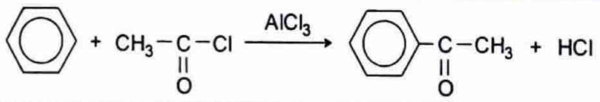
Candidates should be able to
- describe the chemistry of the benzene ring (as exemplified by the following reactions of benzene and methylbenzene) as involving electrophilic substitution reactions
- describe the effect of the delocalisation of electrons in arenes in such reactions

- The availability of six π electrons in benzene makes it electron rich. Hence, benzene attracts electrophiles.
- The main reactions of benzene are characterised by electrophilic substitution in the benzene ring. Benzene reacts with an electrophile (E^+) which replaces one or more hydrogen atoms in the ring.

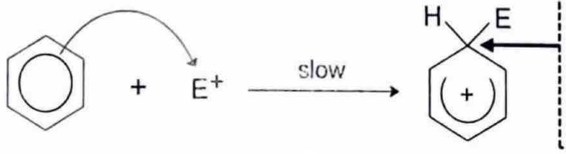


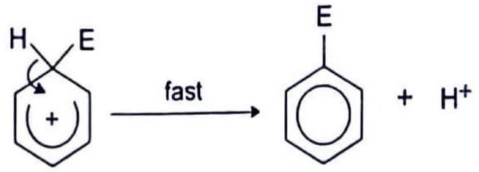
electron-rich benzene **electrophile**

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

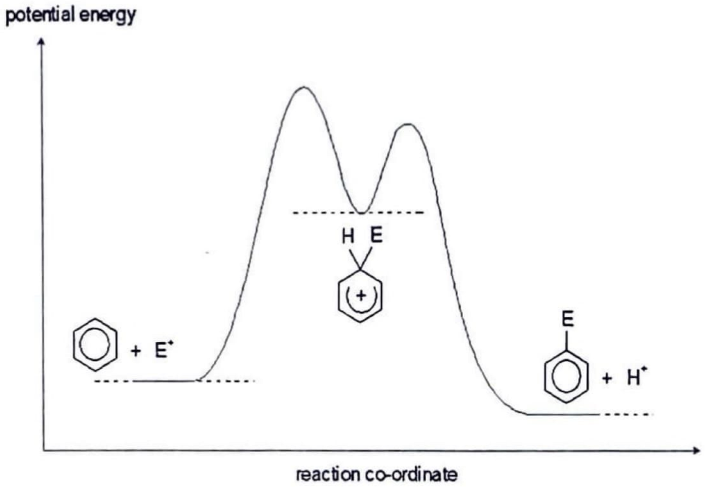
Type of reaction: Electrophilic Substitution		
1	nitration	
2	halogenation (e.g. chlorination)	
3	Friedel-Crafts alkylation	
4	Friedel-Crafts acylation	

- 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**  ➲ This carbon atom is sp^3 hybridised. ➲ The other 5 carbon atoms remain sp^2 hybridised. a carbocation • This step is the slow step i.e. the rate-determining step, because it involves the destruction of the aromaticity of benzene. The extra stability associated with the delocalisation of the six π electrons is lost. • The electrophile attacks the electron-rich benzene ring. This involves the movement of 2 π electrons from the benzene ring to the electrophile, forming a σ bond to one carbon atom of the benzene ring. • A carbocation is formed. This carbocation is resonance-stabilised but not aromatic.

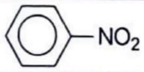
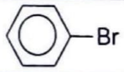
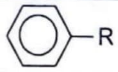
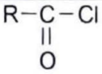
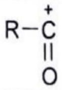
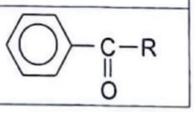
Loss of proton from the carbocation to form the product	**Step 2**  • This step is a fast step. • The carbocation intermediate loses a proton from the carbon atom that bears the electrophile. • The two electrons that bonded this proton to carbon become a part of the delocalised π-electron system. • The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

Energy Profile



Summary of electrophilic substitution reactions of benzene

Type of reaction: Electrophilic Substitution

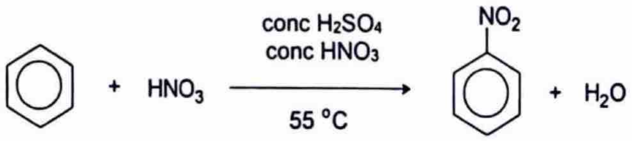
Reaction	Reagent	Catalyst	Condition	Electrophile	Organic product
Nitration	conc. HNO_3	conc. H_2SO_4	55 °C	NO_2^+	
Halogenation (e.g. bromination)	Br_2	$FeBr_3$	--	Br^+ (for simplicity)	
Friedel-Crafts alkylation	R–C*l*	$AlCl_3$		R^+	
Friedel-Crafts acylation	 $R{-}\underset{\overset{\|}{O}}{C}{-}Cl$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

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)

Note: Keeping the temperature below 60 °C minimises the formation of a dinitrated product.

Reagent:	concentrated HNO_3 and concentrated H_2SO_4 (Note: conc H_2SO_4 (aq) or conc HNO_3 (aq) is not accepted)
Condition:	55–60 °C (or heat) - Refer to Section 9.1

6.2 The reaction mechanism: Electrophilic Substitution

6.2.1 Bronsted-Lowry acid and base

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

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

6.2.2 Reaction mechanism

The nitration of benzene involves the following stages:

1) Generation of the electrophile, NO_2^+

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

Steps involved in the generation of the electrophile NO_2^+:

In the nitrating mixture, HNO_3 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), NO_2^+.

$$H_2NO_3^+ \rightleftharpoons \mathbf{NO_2^+} + H_2O \qquad (2)$$

$$H_2SO_4 + H_2O \rightarrow HSO_4^- + H_3O^+ \qquad (3)$$

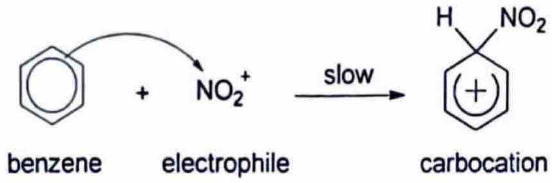
Adding up (1) to (3) gives the overall equation for generation of electrophile.

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

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

Step 1: Electrophilic attack by NO_2^+ (rate-determining / slow step)

Curly arrow from π- electrons to N



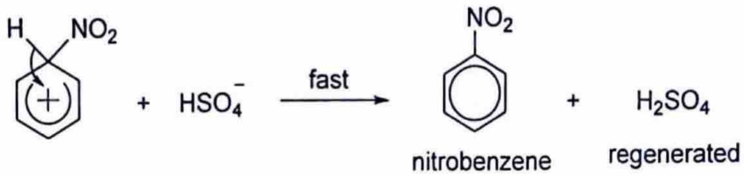
- The NO_2^+ ion acts as an electrophile and attacks the electron-rich benzene ring. 2 of the 6 π electrons in the benzene ring are used to form the C–N bond. Hence, the aromatic character of the ring is destroyed.

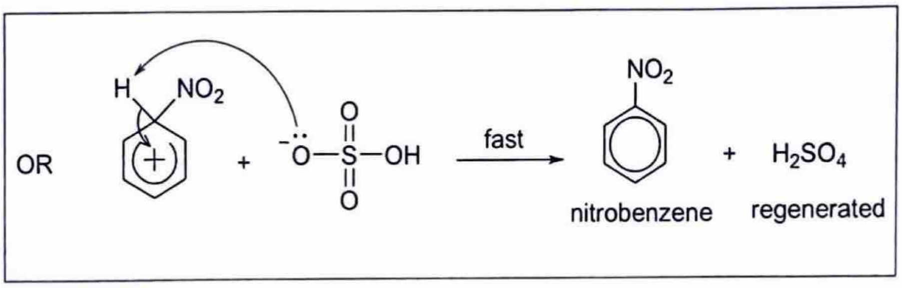
  ⇒ This is the rate-determining / slow step of the reaction mechanism.

- 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 (fast step)

Curly arrow from C–H bond into ring





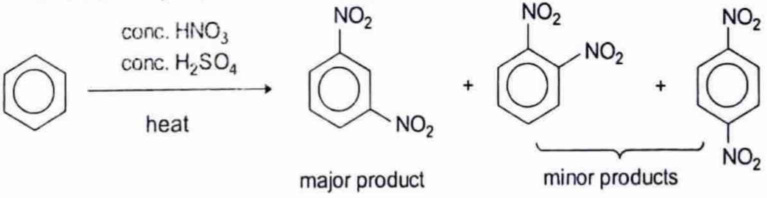
- The unstable carbocation loses a proton to the HSO_4^- ion to form nitrobenzene, thus regaining the aromatic character.

- H_2SO_4 is regenerated. (Note: H_2SO_4 acts as a Bronsted-Lowry acid catalyst.)

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:



(refer to section 9.3 on why 1,3-dinitrobenzene is the major product)

- Formation of 1,3,5-trinitrobenzene requires reacting benzene with fuming HNO_3 and conc. H_2SO_4 at very high temperatures for several days. However, the yield of the reaction is only about 40%.

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

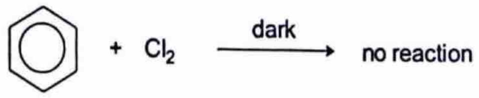
7.1 Lewis acid and base

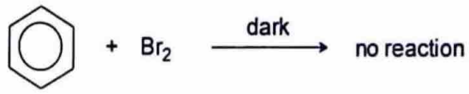
A Lewis acid is an electron pair acceptor. A Lewis base is an electron pair donor.

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

7.2 Halogenation: Generation of Electrophile

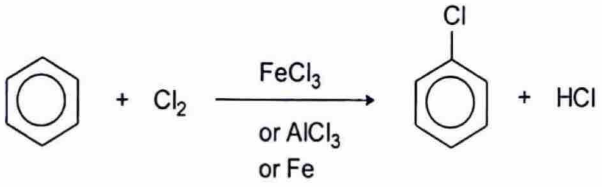
Benzene does not react with chlorine or bromine in the dark.



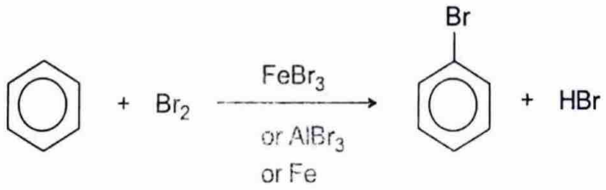


Alkenes react with Cl_2 or Br_2 readily in the dark. However, the extra stability associated with the aromaticity in benzene requires the use of a stronger electrophile in order to disrupt the π-electron cloud.

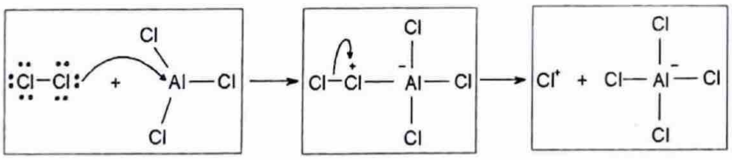
In the presence of a suitable Lewis acid catalyst such as $AlCl_3$ or $FeCl_3$, benzene undergoes electrophilic substitution reaction with chlorine at room temperature.



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



$AlCl_3$ accepts a lone pair of electrons from the halogen molecule, generating the Cl^+ electrophile. Hence, $AlCl_3$ functions as a Lewis acid.



Note:
- $AlCl_3$ catalyst reacts readily with water.

$AlCl_3(s) + 6H_2O(l) \longrightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$

$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(aq)$

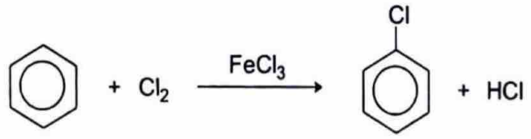
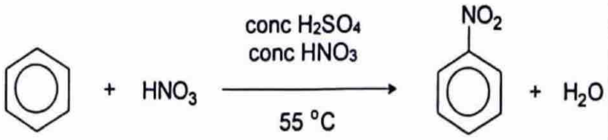
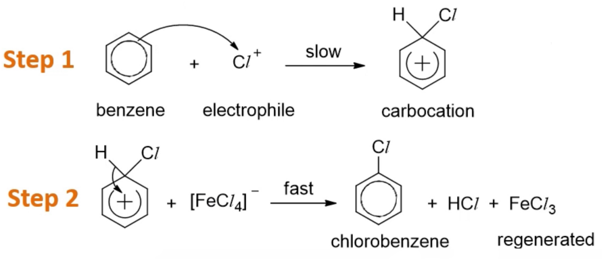
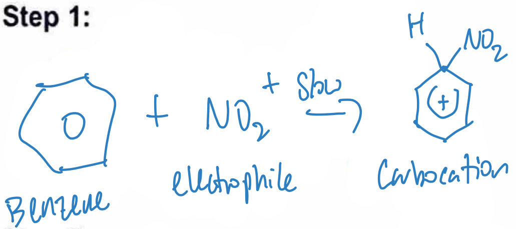
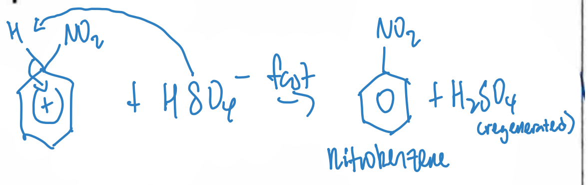
- Hence the reaction can only proceed under anhydrous condition.

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).

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

> **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.

7.3 The reaction mechanism: Electrophilic Substitution

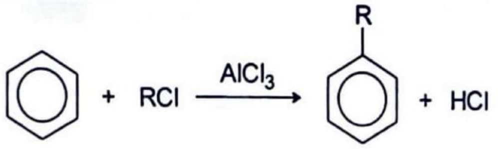
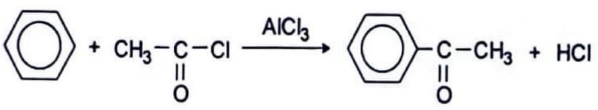
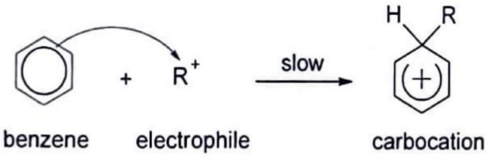
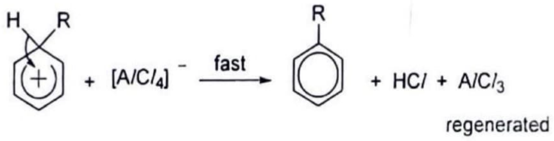
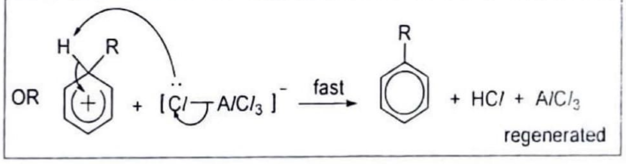
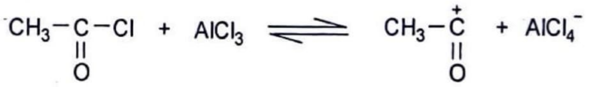
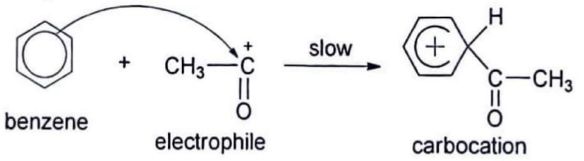
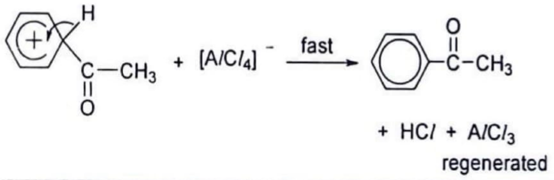
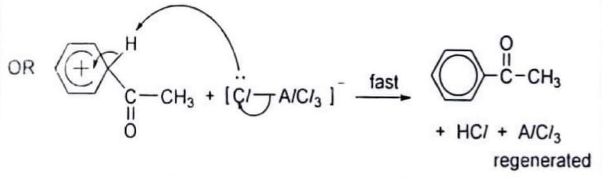
Halogenation of benzene	Nitration of benzene (for comparison)
Overall reaction:  	**Overall reaction:** 
Reaction Mechanism: **Generation of the electrophile, Cl^+** $Cl_2 + FeCl_3 \rightleftharpoons Cl^+ + [FeCl_4]^-$  	**Reaction Mechanism:** **Generation of the electrophile, NO_2^+** $2H_2SO_4 + HNO_3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

> **Show the following 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)

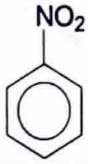
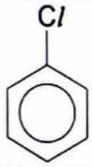
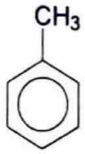
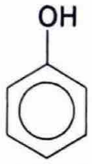
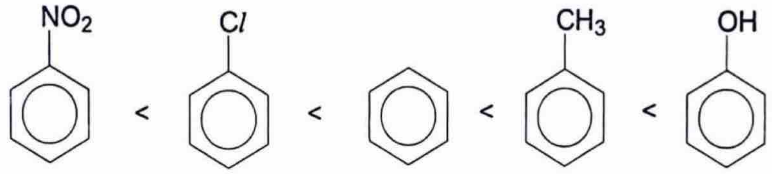
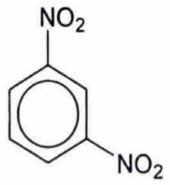
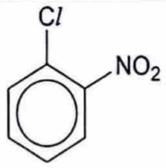
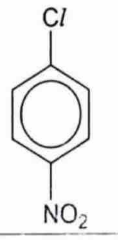
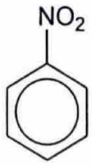
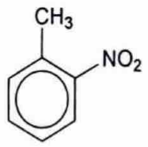
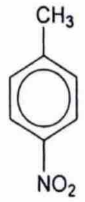
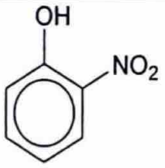
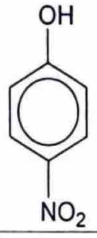
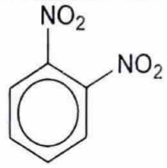
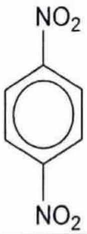
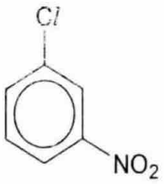
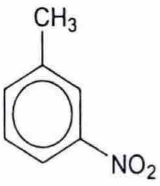
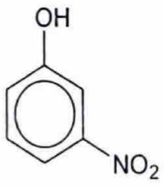
Friedel–Crafts Alkylation	Friedel–Crafts Acylation
Alkylation with a halogenoalkane (RX) and a trace amount of anhydrous $AlCl_3$ as catalyst is often referred to as a Friedel-Crafts alkylation.	Acylation is similar to that of alkylation except that an acid halide (RCOX or ArCOX) instead of a halogenoalkane (RX) is used. The acid halide provides the acyl group needed for the reaction.
The overall reaction:  	**The overall reaction:** 
Reaction mechanism: Electrophilic Substitution **Generation of the electrophile R^+** $R{-}Cl + AlCl_3 \rightleftharpoons R^+ + [AlCl_4]^-$ **Step 1:**  **Step 2:**   	**Reaction mechanism:** Electrophilic Substitution **Generation of the electrophilic acylium ion**  $CH_3COCl + AlCl_3 \rightleftharpoons CH_3C^+O + AlCl_4^-$ **Step 1:**  **Step 2:**  
Role of $AlCl_3$: Lewis acid catalyst	**Role of $AlCl_3$:** Lewis acid catalyst

9 EFFECTS OF SUBSTITUTENT GROUPS

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

9.1 Interpreting Experimental Data

The following table shows the reagents and conditions required for the nitration of various substituted benzenes and the different products obtained.

Compound					
Reagents	Concentrated nitric acid	Concentrated nitric acid	Concentrated nitric acid	Concentrated nitric acid	Dilute nitric acid
Conditions	Concentrated sulfuric acid catalyst, heat (>> 55 °C)	Concentrated sulfuric acid catalyst, heat (> 55°C)	Concentrated sulfuric acid catalyst, 55 – 60 °C	Concentrated sulfuric acid catalyst, 30 °C	Room temperature
Rank the compounds in increasing order of reactivity					
Nature of substituent	Deactivating	Deactivating	—	Activating	Activating
Major product(s)		 		 	 
Minor product(s)	 		---		
Nature of substituent	3-directing	2,4-directing	—	2,4-directing	2,4-directing

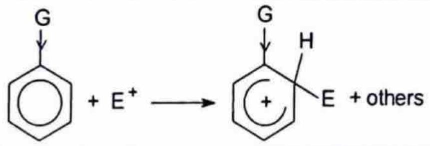
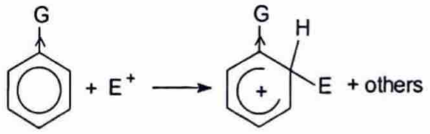
SUMMARY

When an electrophile attacks an aromatic ring, the group already attached to the ring determines

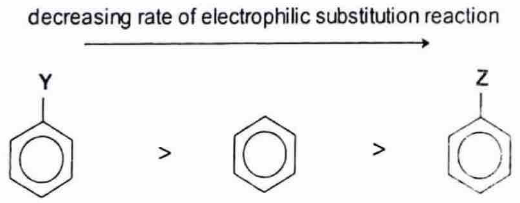
- ➲ how readily the attack occurs (i.e. the reactivity of the ring), and
- ➲ the position of substitution.

9.2 Relative reactivity (i.e. the rate of electrophilic substitution reaction)

- Reactivity in electrophilic substitution depends on the tendency of an existing substituent group to release or withdraw electrons.
  - A group that donates electrons or delocalise electrons into the ring activates the benzene ring towards electrophilic substitution reaction.
  - A group that withdraws electrons deactivates benzene 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. - It helps to disperse the positive charge in the intermediate carbocation and stabilise 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. - It tends to intensify the positive charge in the intermediate carbocation and destabilise the carbocation.
A group attached to a benzene ring is classified as activating if it makes the benzene ring more reactive than benzene towards electrophilic substitution reactions.	A group attached to a benzene ring is classified as deactivating if it makes the ring less reactive than benzene towards electrophilic substitution reactions.
	

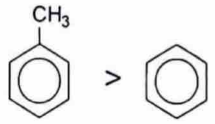
- Relative rates of electrophilic substitution



Y is an electron-donating group and hence it is an activating group.

Z is an electron-withdrawing group and hence is a deactivating group.

Note: Rate of electrophilic substitution



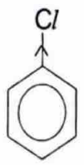
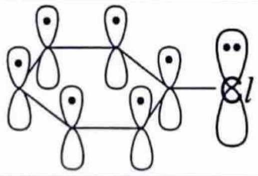
- Recall from section 9.1: Lower temperature (30 °C) is used for the nitration of methylbenzene. Nitration of benzene requires 55 – 60 °C.
- Methylbenzene is more reactive than benzene towards electrophilic substitution reactions because the $-CH_3$ group is an electron-donating group and hence an activating group. It increases the electron density in the benzene ring and makes it more susceptible to electrophilic attack.

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.

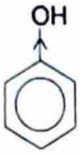
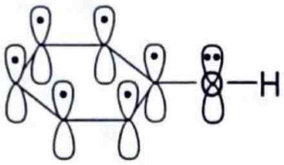
	Inductive Effect	**Resonance effect**
	• An inductive effect is the donation or withdrawal of electrons through σ bonds due to the electronegativity difference between atoms.	• A resonance effect is the donation or withdrawal of electrons through π bonds due to the continuous side-on p-orbital overlap 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. Compared to sp^2 carbon in benzene ring, sp^3 orbitals have less s-character and 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 (*see pg 18*) • 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 benzene 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 stronger than the resonance effect.
- This is because C*l* is in Period 3 and 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 electron-withdrawing.
- 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 **deactivating group**.

<table>
<tr><th>Inductive effect</th><th>Resonance effect</th></tr>
<tr><td></td><td>
</td></tr>
<tr><td>

- The O atom is more electronegative than C.
- Hence, the –OH group is electron-withdrawing by inductive effect.

</td><td>

- 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.

</td></tr>
<tr><td colspan="2">

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**.

</td></tr>
</table>

9.3 Orientation (i.e. the site of electrophilic attack)

- A substituent group in the benzene ring not only activates or deactivates the ring, it also controls the position of of electrophilic attack on the ring.

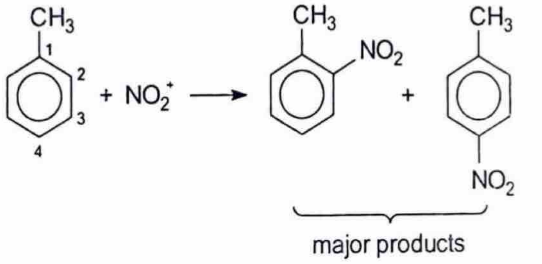
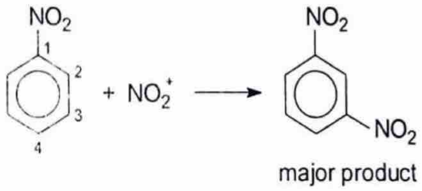
- Depending on the position it directs the electrophilic attack, a substituent group may be classified as
  - a 2,4-directing group (or ortho, para-directing group) or
  - a 3-directing group (or meta-directing group).

<table>
<tr><th>2,4-directing group</th><th>3-directing group</th></tr>
<tr><td>

- A 2,4-directing group (e.g. $-CH_3$) causes an electrophile to attack chiefly at 2-position and 4-position relative to it.

</td><td>

- A 3-directing group (e.g. $-NO_2$) causes an electrophile to attack chiefly at 3-position relative to it.

</td></tr>
<tr><td>
</td><td>
</td></tr>
</table>

9.4 Classification of substituent groups

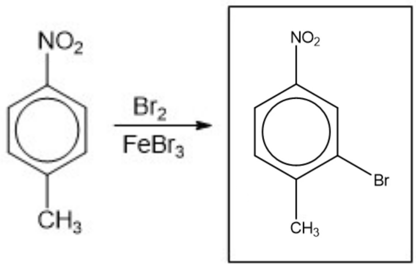
Refer to the *Data Booklet* section 8 on 'The orientating effect of groups in aromatic substitution reactions'

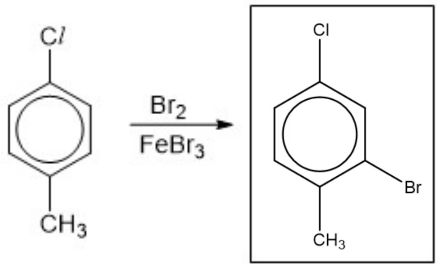
Effect of groups on electrophilic substitution:

Substituent group	Effect on reactivity	Effect on orientation	Remarks
$-NH_2$ $-NHR$ $-NR_2$ $-OH$ $-OCH_3$ ($-OCH_2CH_3$, etc.) $-NHCOCH_3$	activating	2,4-directing	• Each substituent has a lone pair of electrons on an atom that is bonded to the carbon atom of the aromatic ring. • Each substituent donates electrons by resonance effect.
$-C_6H_5$ $-CH_3$ ($-CH_2CH_3$, etc.)	weakly activating	2,4-directing	• Each substituent donates electrons by inductive effect.
$-H$	Standard for comparison		
$-F$, $-Cl$, $-Br$, $-I$	weakly deactivating	2,4-directing	• The halogen atoms are different from the other substituents. (Refer to pg 17)
$-COOH$ ($-COOR$) $-SO_3H$ $-CHO$, $-COR$	deactivating	3-directing	• Each substituent is unsaturated and does not have an atom with a lone pair bonded directly to the benzene ring. • Each substitutent withdraws electrons by resonance effect.
$-NO_2$ $-NR_3^+$ $-CF_3$, $-CCl_3$			

■ **Exercise 1** ■

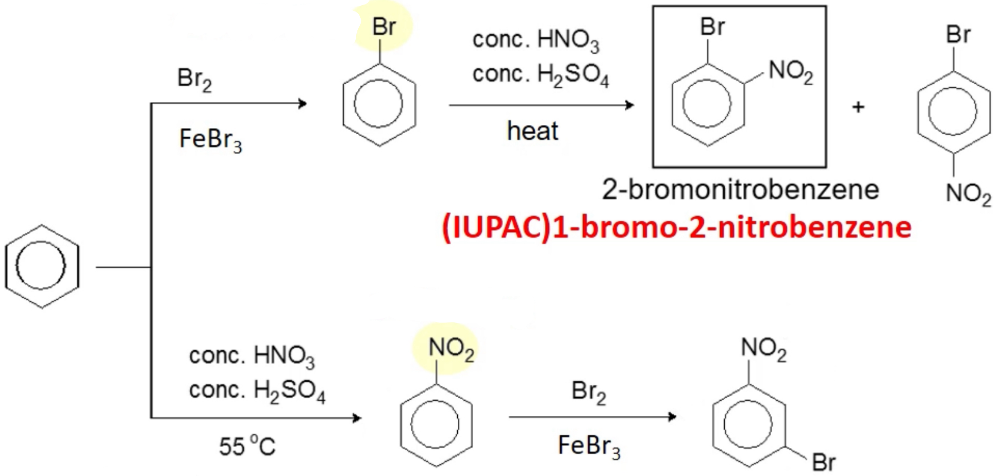
(a) Draw the structure of the **major product** in each of the following reaction.





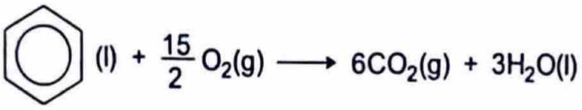
Note: If there are two substituent groups in the benzene ring and their directing effects oppose each other, the directing effect of the more powerful activating group dominates.

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



10 OTHER REACTIONS OF BENZENE

10.1 Combustion

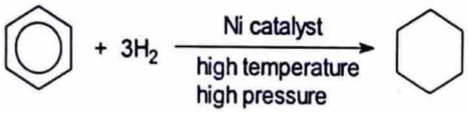


Benzene burns in air with a sooty, smoky flame. This sort of flame is characteristic of all hydrocarbons containing a high percentage of carbon.

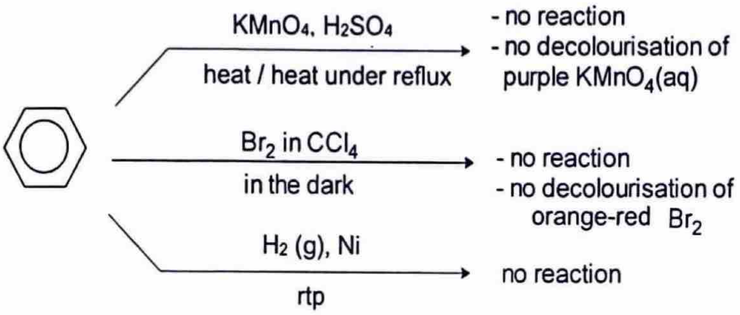
10.2 Reduction (catalytic hydrogenation)

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

⇒ Extra energy must be supplied to break up the delocalised π-electron system.



10.3 Reactions that benzene DOES NOT undergo

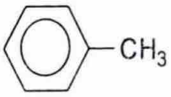


11 METHYLBENZENE

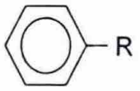
Candidates should be able to
- describe the chemistry of the alkyl side-chain of benzene ring as exemplified by the following reactions of methylbenzene:
  - (i) free-radical substitution by chlorine and by bromine
  - (ii) complete oxidation to give benzoic acid
- predict whether halogenation will occur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

11.1 Introduction

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



methylbenzene



where
—R is an alkyl group

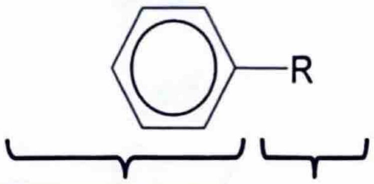
alkylbenzene

- 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.

11.2 Reactions of methylbenzene and other alkylbenzenes

Alkylbenzenes, such as methylbenzene, has an aromatic portion (the benzene ring) and an aliphatic portion (the alkyl group).

⇒ These two portions contribute to the chemical properties of alkylbenzenes.



Aromatic portion
- Contains benzene ring
- Undergoes electrophilic substitution reactions (refer to sections 5 and 9)

Aliphatic portion
- Alkyl side chain
- Undergoes
  - Free radical substitution reaction
  - Oxidation

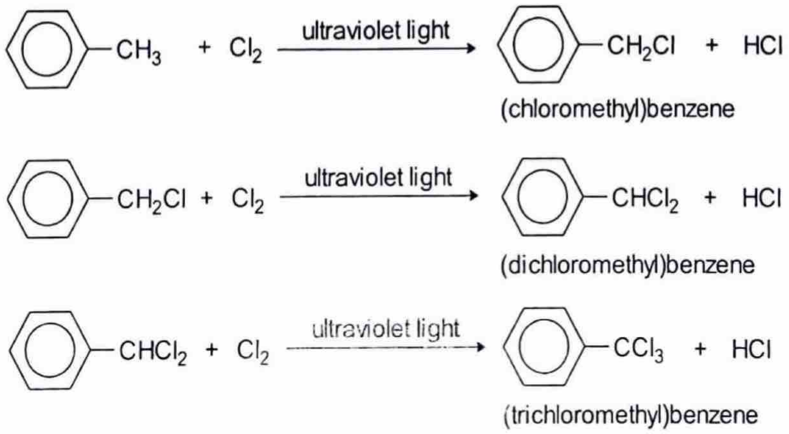
12 REACTIONS OF THE SIDE CHAIN IN ALKYLBENZENES

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

12.1 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 methylbenzene under heat or ultraviolet light.



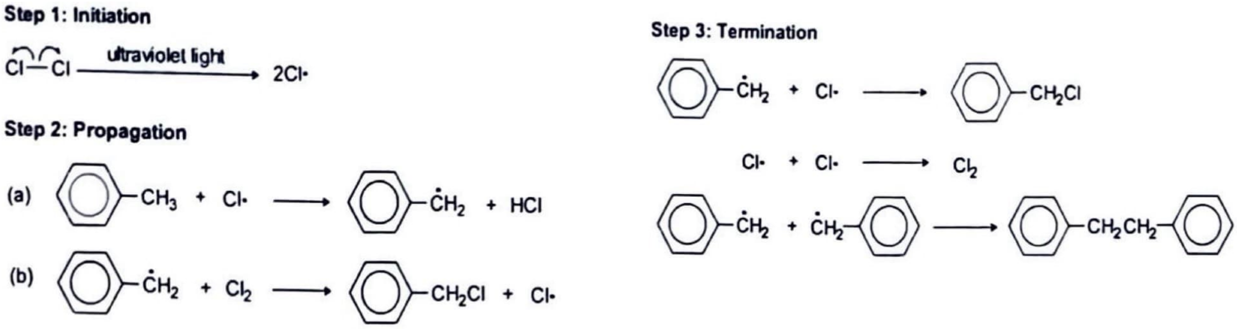
Note:
Bromination of methylbenzene takes place under similar conditions, forming the corresponding bromine derivatives.

■ Exercise 2 ■

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



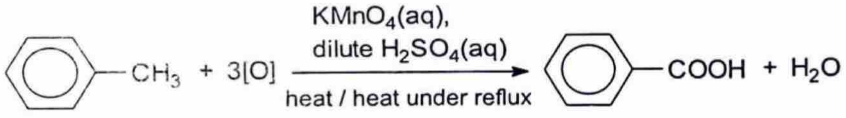
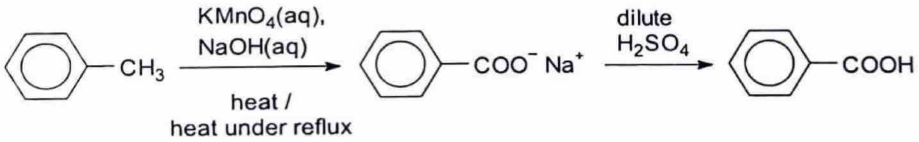
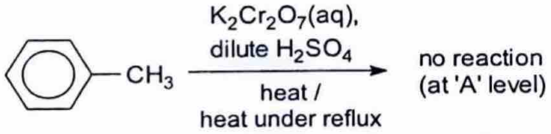
Then (a), (b), (a), (b), ...

12.2 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.

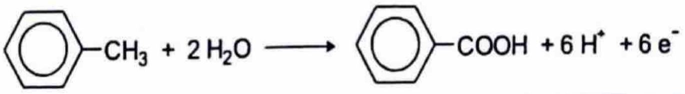
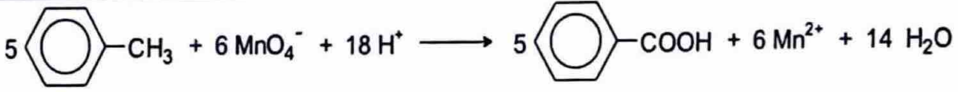
> **Note:** The side chain is oxidised, with only a carboxylic acid group (–COOH) remaining to indicate the position of the original side chain.

- 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		• decolourisation of purple KMnO4 (if it is the limiting reagent). • Formation of a white ppt 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, benzoic acid is soluble in hot water but has poor solubility in cold water. It appears as a white ppt when the reaction mixture is cooled.
$KMnO_4$(aq), NaOH(aq), heat		• Decolourisation of purple $KMnO_4$ (if it is the limiting reagent). • Formation of a black-brown ppt of MnO_2. • Formation of a white ppt of benzoic acid upon cooling and acidification.
$K_2Cr_2O_7$(aq), H_2SO_4(aq), heat		• Orange $K_2Cr_2O_7$(aq) does not turn green.

12.2.1 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.

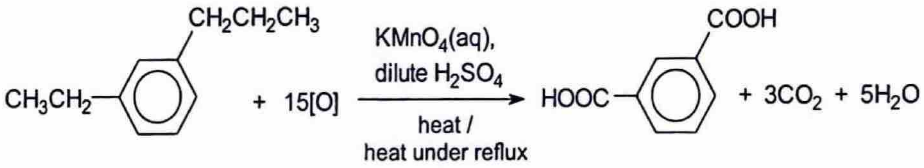
<table>
<tr><td>Oxidation half-equation:</td><td>
</td></tr>
<tr><td>Reduction half-equation:</td><td>$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$</td></tr>
<tr><td>Overall equation:</td><td>

This equation is required only when stoichiometric calculations are assessed. Generally, organic oxidation equations are written in the manner illustrated in 12.2.2.</td></tr>
</table>

12.2.2 Oxidation of longer alkyl chains

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

Example:

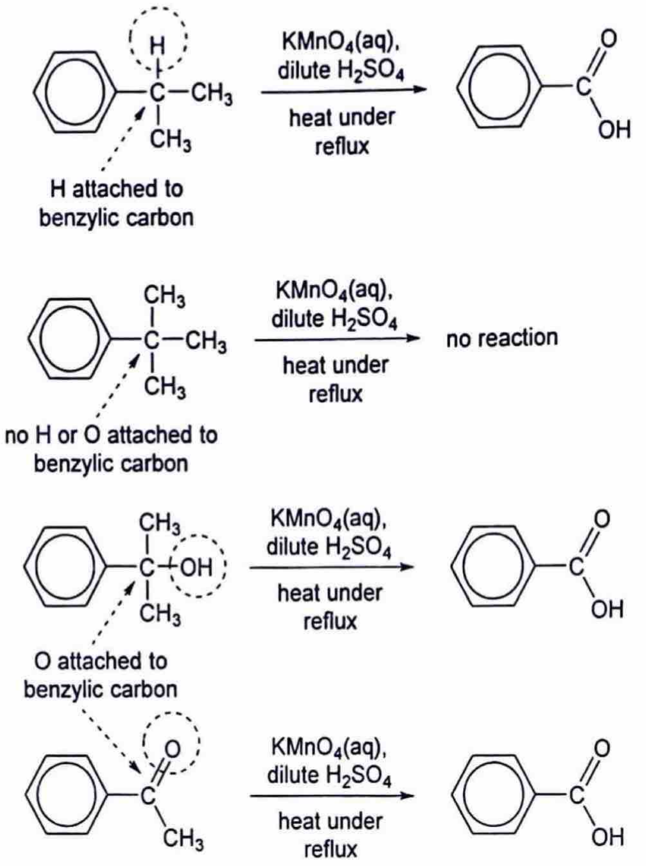


> **Note:** Only the carboxylic acid group (i.e. –COOH) remains to indicate the position of the original side chain.

12.2.3 Criteria for oxidation of side chains on benzene

- Alkylbenzenes with a hydrogen or oxygen atom bonded to the benzylic carbon atom (i.e. the carbon atom that is bonded to the benzene ring) can undergo oxidation when heated with acidified $KMnO_4$.

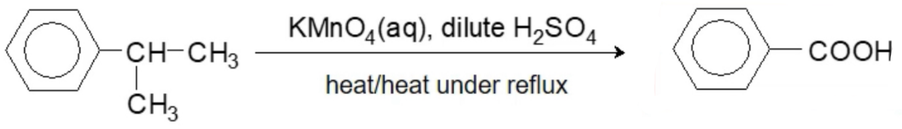
  Examples:



- The oxidation of side chains containing a benzylic oxygen atom will be discussed further in the topic on Carboxylic Acids and Derivatives.

Exercise 3: Identify the organic reactants or products for the following reactions.
(Note: Equations are not balanced)

1



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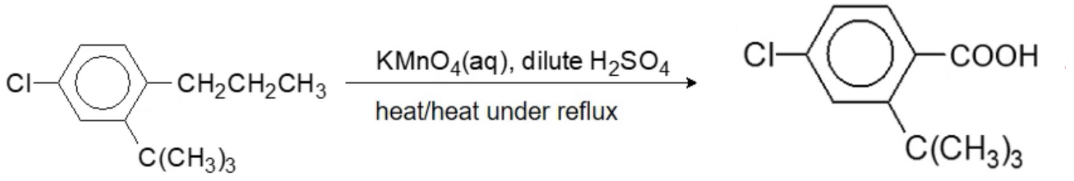

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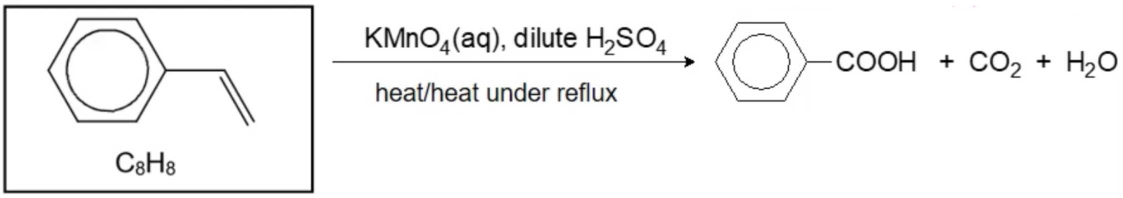
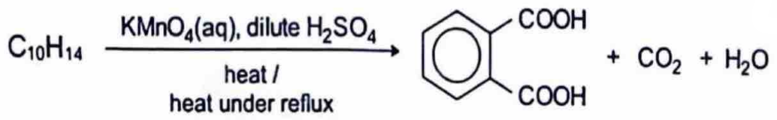


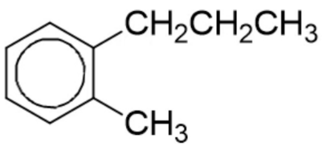
Exercise 4: Identify the reactant of the following reaction.

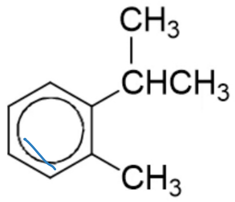
(Note: Equations are not balanced)

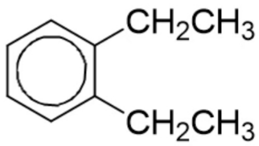


Possible structures of the reactant, $C_{10}H_{14}$:

(Hint: There are 3 possible structures)

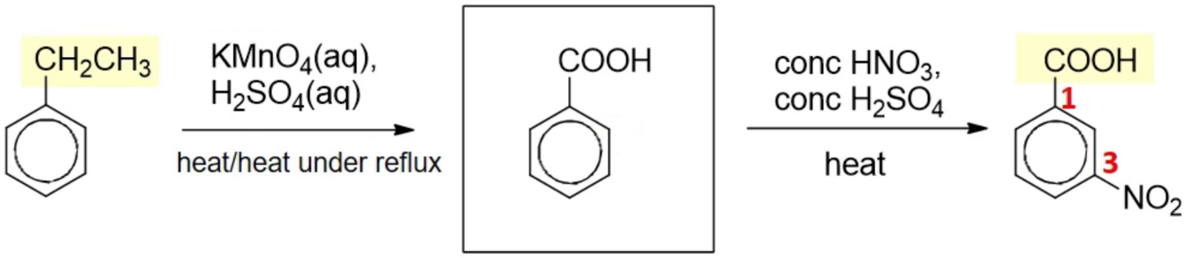






Exercise 5:

3-nitrobenzoic acid can be prepared from ethylbenzene in a two-step synthesis. Suggest reagents and conditions for the synthesis.

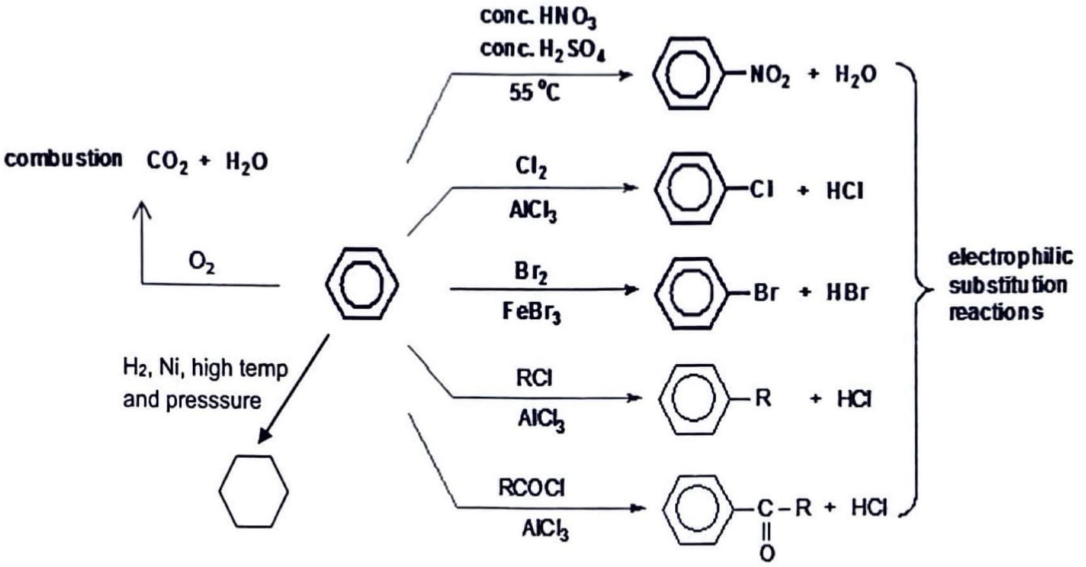


Is there any difference if the two steps were swapped?

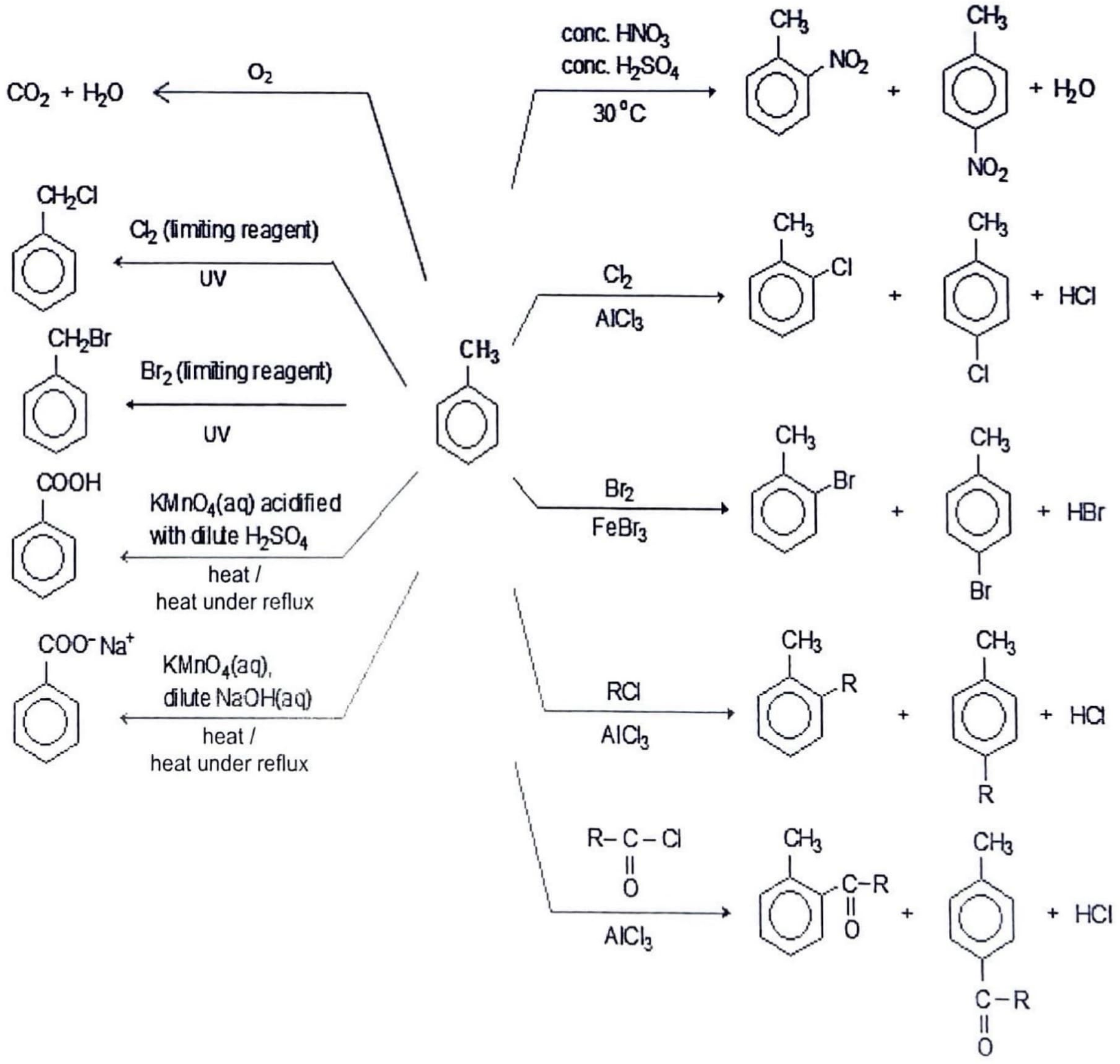
Yes. 2-nitro benzoic acid or 4-nitro benzoic acid would be formed instead of 3-nitro benzoic acid

13 SUMMARY

13.1 Some reactions of benzene



13.2 Some reactions of methylbenzene



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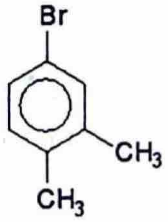
Tutorial 13 – Arenes

Self-Check Questions

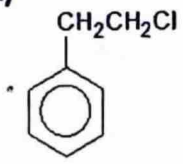
1 **(a)** Draw all the eight benzene ring-containing isomers with molecular formula C_9H_{12} and name them by the IUPAC system.

(b) Name each of the following compounds:

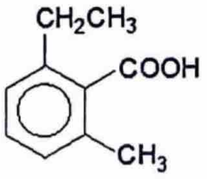
(i)



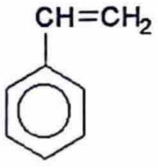
(ii)



(iii)



(iv)



(c) Write the structural formula for each of the following compounds:

(i) (dichloromethyl)benzene

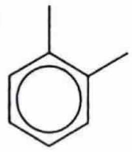
(ii) 1-bromo-2-cyclohexylbenzene

(iii) 2,4,6-tribromophenol

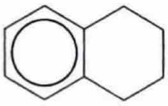
(iv) 2-chloro-4-methylbenzoic acid

2 Draw the structural formulae of the organic products obtained when each of the following arenes are heated under reflux with excess acidified $KMnO_4(aq)$.

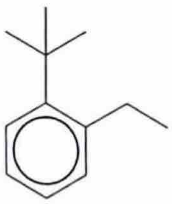
(a)



(b)



(c)



3 Benzene, cyclohexene and cyclohexane react with Cl_2 under different conditions. For each reaction:

(a) State the reaction conditions.
(b) Write down the overall equation.
(c) Identify the type of reaction.
(d) Describe the mechanism.

4 Benzene, ethylbenzene and benzoic acid exhibits different reactivity towards nitration. Arrange these compounds in decreasing order of reactivity and explain your answer.

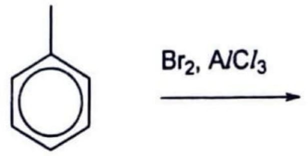
5 Suggest a simple chemical test to distinguish between the following pairs of compounds.

(a) benzene and cyclohexene **(b)** benzene and ethylbenzene

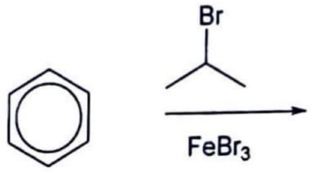
Practice Questions

1 For each of the following electrophilic substitution reactions, identify the electrophile and draw the structure of the major organic product(s) if any.

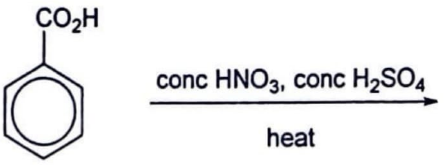
(i)



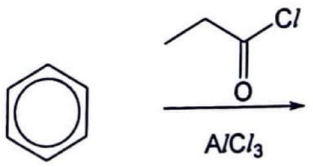
(ii)



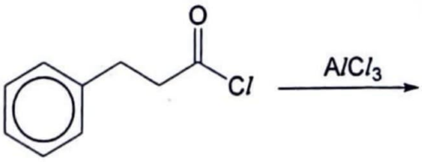
(iii)



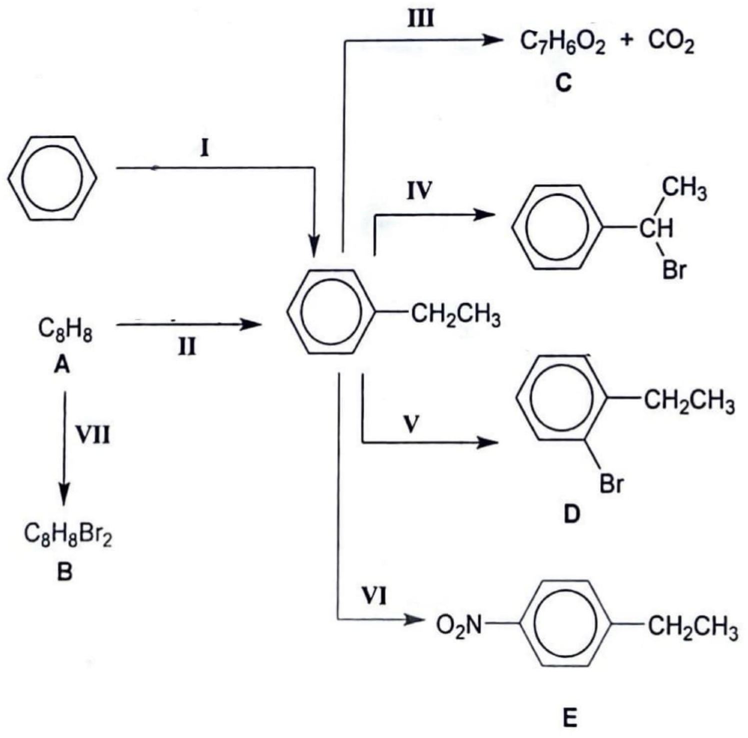
(iv)



(v)



2 Some chemical transformations of ethylbenzene are given below.



(a) For the above reaction scheme,
- suggest the reagents and conditions for reactions **I** to **VII**,
- name the type of reaction in each case, and
- identify compounds **A**, **B** and **C**.

(b) Using the [O] notation, write a balanced equation for reaction **III**.

(c) There are two other positional isomers of **D**. Draw their structural formulae, and suggest which one is more likely to be formed along with **D** in reaction **V**.

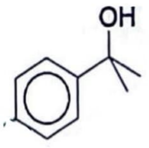
(d) Ethylbenzene and **A** react with bromine under different conditions. Compare and account for the difference in conditions used in
(i) reactions **IV** and **VII**.
(ii) reactions **V** and **VII**.

(e) Describe the mechanism involved in each of the following reactions: **I**, **IV**, **V** and **VI**.

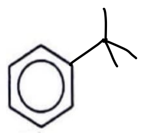
3 Suggest a simple chemical test to distinguish between the following pairs of compounds.

(a) methylbenzene and cyclohexane **(b)** benzene and cyclohexane

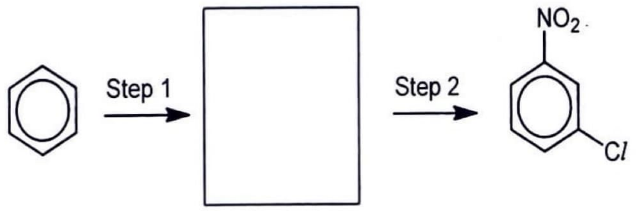
(c)



and



4 State the reagents and conditions needed for the following conversions. Draw the structure of the intermediate in each case.

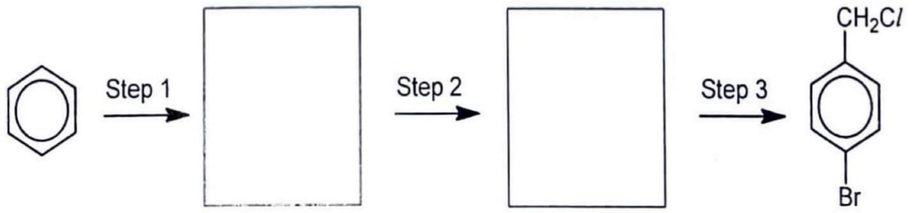


(a)

Reagents and conditions

Step 1: ____________________

Step 2 : ____________________



(b)

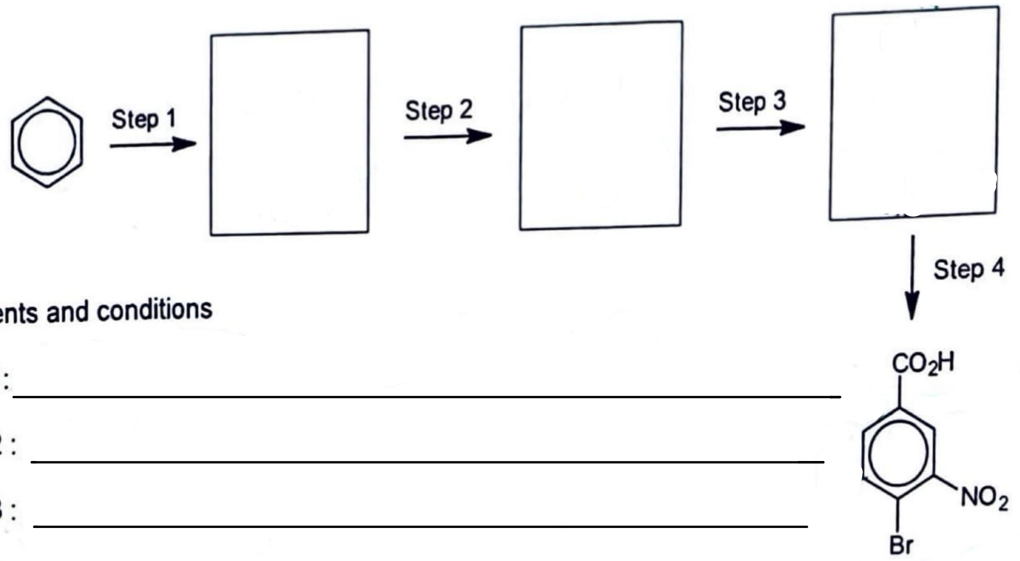
Reagents and conditions

Step 1: ____________________

Step 2 : ____________________

Step 3 : ____________________

(c)



Reagents and conditions

Step 1: ____

Step 2 : ____

Step 3 : ____

Step 4 : ____

Structural Elucidation Questions (Question 5 and 6)

If reasoning or explanation is required for structural elucidation questions, you are encouraged to present your answers with the aid of a table as shown below.

Evidence / Information	Deduction and explanation
A, **B** and **C** are structural isomers of cyclohexene.	**A**, **B** and **C** have the molecular formula, C_6H_{10}.
$C_6H_{10} + 2Br_2 \xrightarrow[\text{dark}]{\text{in } CCl_4}$ product **A**	**Electrophilic addition** occurs.

① Evidence / Information
- Quote / extract information from the question briefly either in words or using equations.

② Deduction and explanation
Include the following here:
- **type of reaction** that occurs
- **no. and type of functional group** that is responsible for the reaction
- any other relevant structural features of the reactant or product molecules based on the stated evidence

③ Draw the structural formulae of the unknown compounds.

④ Write the relevant equations, if required.

5 Compound **P** has molecular formula C_8H_8. **P** instantly decolourises a solution of bromine in tetrachloromethane. When **P** is heated under reflux with alkaline potassium manganate(VII) and the resultant solution acidified, a white crystalline precipitate **Q** with molecular formula $C_7H_6O_2$ is obtained. In the presence of platinum catalyst at 25 °C, **P** reacts with hydrogen in a 1:1 molar ratio to form compound **R**. In the dark, **R** gives no apparent reaction with bromine until a little iron powder is added: dense white fumes, **S**, then appear. Two isomeric compounds, **T** and **U**, are also obtained from the reaction.

(a) With the aid of a suitable diagram, explain the phrase, *heated under reflux*, and state the significance of such a heating process.

(b) Identify the compounds **P**, **Q**, **R**, **S**, **T** and **U**, and explain the reactions described with the aid of relevant equations. *You may make use of the template provided on the next page.*

Evidence	**Deductions**
P has molecular formula of C_8H_8	
P instantly decolourises Br_2 in CCl_4.	
P $\xrightarrow[\text{then } H^+]{\text{alkaline } KMnO_4\text{, heat under reflux}}$ **Q** $C_7H_6O_2$	
P + H_2 $\xrightarrow{Pt,\ 25\ ^\circ C}$ **R** (1:1 ratio)	
R $\xrightarrow{Br_2}$ No reaction $\xrightarrow{Fe}$ **dense white fumes, S** **+ T** and **U**	

Structures:

P	Q	R	S	T	U

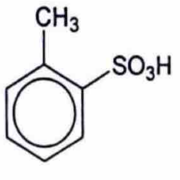
6 Hydrocarbons **A**, **B**, **C** and **D** have the same molecular formula C_9H_{10}. All decolourise Br_2 in CCl_4 rapidly at room temperature. **A** and **B** are cis-trans isomers with **B** having a lower volatility. When heated under reflux separately with acidified $KMnO_4$(aq), **A**, **B** and **C** each gives a compound **W**, $C_7H_6O_2$, while **D** gives a compound **X**, $C_8H_6O_4$. **X** undergoes nitration to yield only one mono-nitrated product, **Y**.

(a) Give the structural formulae of the hydrocarbons **A** to **D** and the compounds **W**, **X** and **Y**.

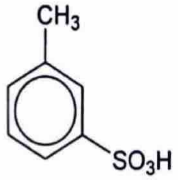
(b) Another structural isomer **E** does not react with bromine in the dark but reacts with hot acidified potassium manganate(VII) to yield a dicarboxylic acid **Z**. Identify **E** and **Z**.

7 **[N2018/II/4(b), (c)]**

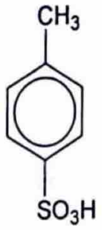
(a) Methylbenzene reacts with fuming sulfuric acid, $H_2S_2O_7$, to form a mixture of three isomers, **G**, **H** and **J**, in equilibrium.



G



H



J

(i) Explain why **H** is the isomer least likely to be formed in this reaction. [1]

(ii) Suggest why there is a lower concentration of **G** than of **J** in the equilibrium mixture. [1]

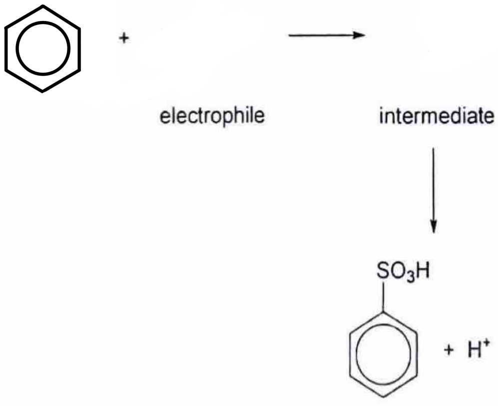
(b) Under different conditions, benzene will also react with fuming sulfuric acid, $H_2S_2O_7$.

$$C_6H_6 + H_2S_2O_7 \longrightarrow C_6H_5SO_3H + H_2SO_4$$

Assuming that fuming sulfuric acid ionises as shown.

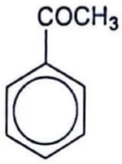
$$H_2S_2O_7 \rightleftharpoons HSO_4^- + SO_3H^+$$

(i) Complete the following diagram to suggest a mechanism for this reaction. Show the displayed structure of the electrophile, the structure of the intermediate and the movement of electron pairs by using curly arrows. [3]



(ii) When fuming sulfuric acid reacts with alkenes, addition reactions occur. Explain why benzene does **not** undergo addition reactions with fuming sulfuric acid. [2]

(iii) **K** also undergoes a reaction with fuming sulfuric acid.



K

Suggest the order of reactivity of benzene, methylbenzene and **K** with fuming sulfuric acid. Explain your answer. [2]