20

AROMATIC HYDROCARBONS

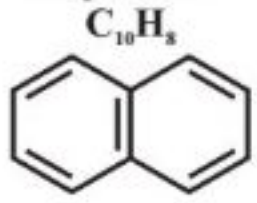
Student Learning Outcomes

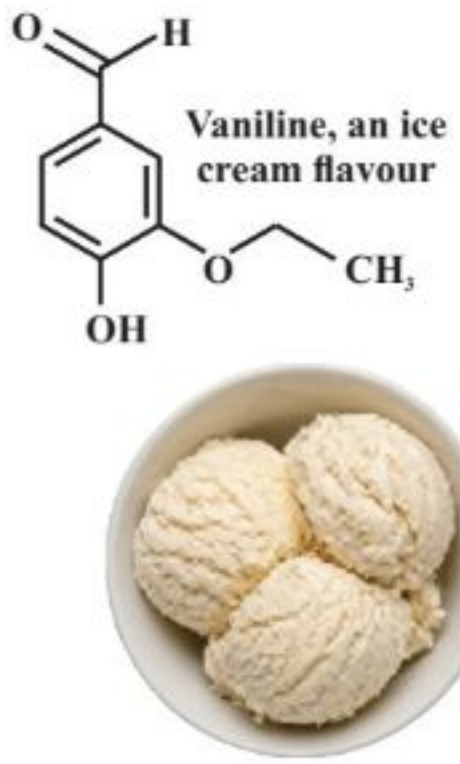
[C-12-D-21 to C-12-D-29]

- Explain the shape of the benzene molecule (molecular orbital aspect).
- Define resonance, resonance energy and relative stability of benzene.
- Compare the reactivity of benzene with alkanes and alkenes.
- Describe the mechanism of substitution reactions with chlorine and bromine, including the formation of ortho, para, and meta isomers, and predict the major product(s) of the reaction.
- Explain the mechanism of nitration, including the formation of a neutronium ion, and predict the major product(s) of the reaction.
- Explain the mechanism of Friedel-Crafts alkylation and acylation, respectively, including the role of the Lewis acid catalyst, and predict the major product(s) of the reaction.
- Explain the mechanism of side chain oxidation, including the formation of benzoic acid, and predict the major product(s) of the reaction.
- Explain the mechanism of hydrogenation, including the role of a metal catalyst, and predict the major product(s) of the reaction, which is cyclohexane.
- Describe the mechanism of electrophilic aromatic substitution, including the role of the electrophile and the formation of a sigma complex, and predict the major product(s) of the reaction based on the directing effects of substituents on the aromatic ring.

Benzene is one of the most important organic compounds with the chemical formula C_6H_6. It is the simplest aromatic hydrocarbon. **Benzene** derived products are well known to be **pleasantly fragrant**. For this reason, organic compounds containing benzene rings were classified as being "**aromatic**" **(sweet smelling)** amongst scientists in the early 19th century. Many **aromatic** compounds are **sweet/pleasant smelling**, such as **vanilla.** Organic hydrocarbons containing one or more benzene rings are known as **arenes**. However, the term **'aromatic'** continues to be used today in order to designate molecules with benzene and benzene-like rings in their structures that are not good-smelling, rather have foul smells.

Napthalene
$C_{10}H_8$





Vaniline, an ice cream flavour

Did You Know?

Saying that only aromatic compounds smelling good and sweet is wrong. Non-aromatic compounds, such as camphor, extracted from the camphor laurel tree, release a strong, minty aroma, yet it lacks the benzene ring in its structure.

20.1 STRUCTURE OF BENZENE

After the discovery of benzene, its molecular formula was found to be C_6H_6. Following this, many scientists attempted to figure out its structure. Some scientists presented linear structures. But, these were soon rejected as they could not explain the properties of benzene.

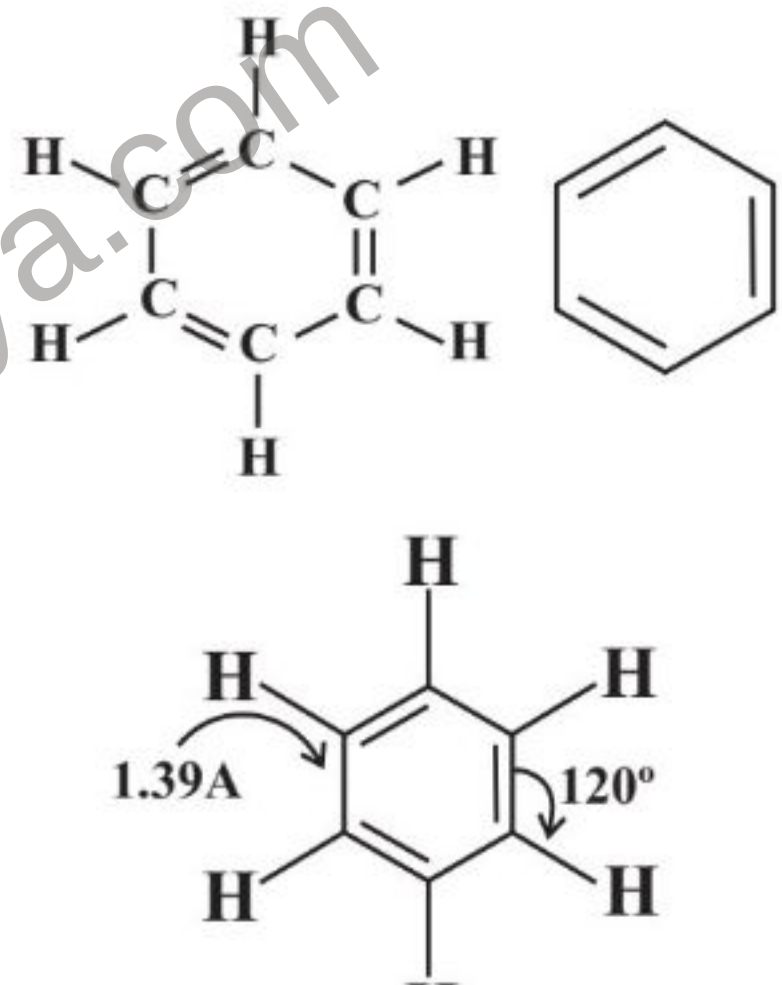
The structure of benzene remained a mystery until 1865 when a German professor August Kekule elucidated it as a six membered cyclic compound having alternate single and double bonds as below.

Kekule structure of benzene

This structure explained many properties of benzene successfully.

There were, however, a number of problems with Kekule's structure in that it didn't fully explain the physical and chemical properties of benzene.

X-ray studies of benzene exhibits a planar configuration characterized by a regular hexagon comprising six sp^2 hybridized carbon atoms. As illustrated, each carbon atom is connected to three additional atoms with bond angles of 120° for C–C–C and H–C–C. The length of the C–H bond is 109 pm, while the length of the C–C bond is 139 pm, falling between the single bond lengths of sp^3 hybridized carbons (154 pm) and sp^2 hybridized carbons (133 pm). All C-C and C-H bond lengths are 1.3970 A and 1.090 A, respectively.



Bond angles and bond lengths in benzene

20.1.1 Thermodynamic Stability of Benzene and Resonance

Benzene like alkenes have double bonds, however it is much more stable than alkenes. Evidence of the increased stability of benzene is obtained by measuring the heat emitted during the hydrogenation of benzene and cyclic alkenes. These heats of hydrogenation can be related to the relative thermodynamic stability of the compounds. This reaction yields cyclohexane as a common product via catalytic addition of hydrogen. In the following diagram, cyclohexane symbolizes a low-energy reference point. Let us analyse the heats of hydrogenation of different cyclohexenes.

The hydrogenation of cyclohexene results in the formation of cyclohexane and releases 120 kJ mol⁻ of energy. From this, we could expect that cyclohexadiene would yield 240 kJ mol⁻ on complete hydrogenation, while the hypothetical 1,3,5-cyclohexatriene would produce 360 kJ mol⁻ as shown in **Figure 20.1**.

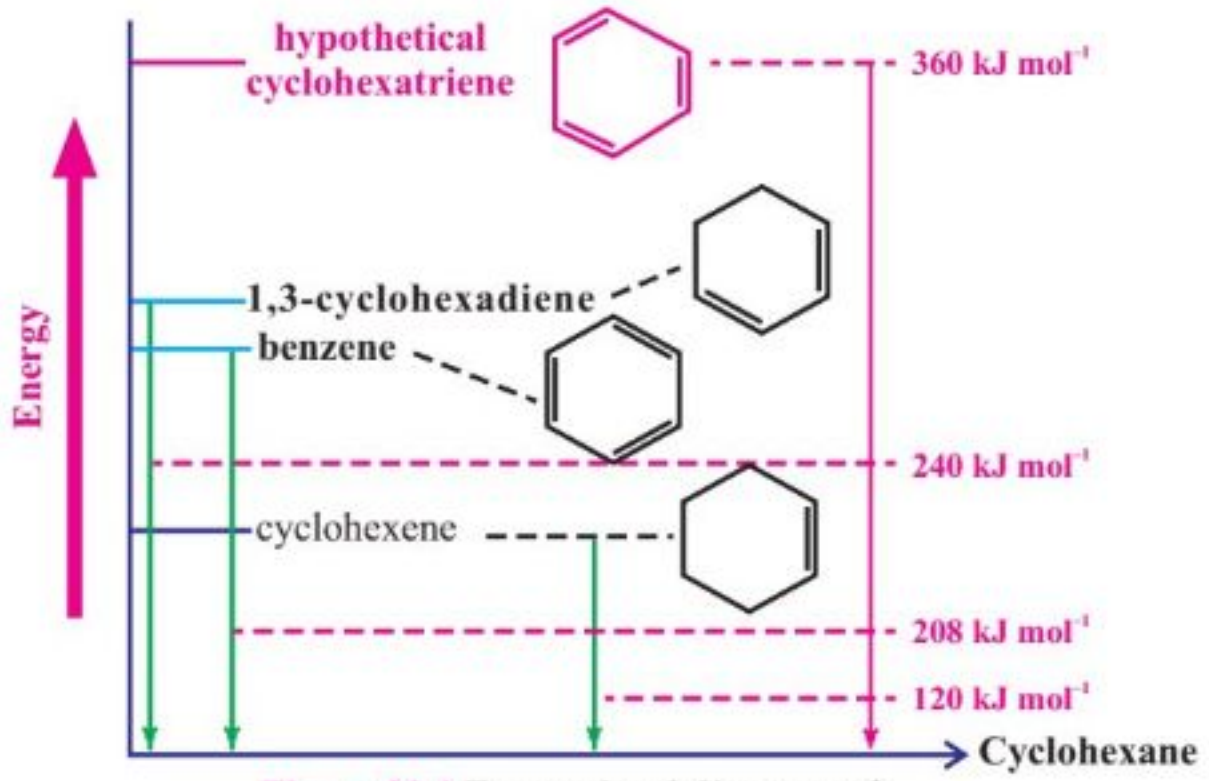


Figure 20.1 Energy level diagram of hydrogenation of cyclohexenes and benzene

Following this, we must expect that heat of hydrogenation of benzene would be much higher if it were a cyclohexene too. Its heat of hydrogenation would be equal to the hypothetical cyclohexatriene as shown in the above diagram. Benzene, however, has much lower heat of hydrogenation (208 kJ mol⁻) exhibiting an exceptional stability. This heat is 158.5 kJ mol⁻ lower than expected. It shows benzene is much more stable than the hypothetical cyclohexatriene.

This stability is explained based on the delocalisation of π electrons. According to the modern concept, all the benezene π electrons are delocalised over the ring through the π orbital overlap on all the six carbon atoms. The actual heat of hydrogenation of benzene is 152 kJ mol⁻ lower than the theoretical value. This energy is called the resonance energy (delocalisation energy) of benzene. This concept of delocalisation is explained in the next topic (20.1.2)

20.1.2 Atomic Orbital Structure of Benzene

The hexagonal frame work of benzene ring can be conveniently explained by using hybridization approach. According to this, each carbon atom in benzene is sp^2 hybridized. The three sp^2 hybrid orbitals on each carbon are utilized to form three σ-bonds, two with adjacent carbon atoms and one with a hydrogen atom. Since all the sp^2 orbitals are in the same plane, therefore, all the carbon and hydrogen atoms of this σ framework are coplanar at 120°.

The six unhybrid '2p' orbitals, one from each carbon, are perpendicular to this sigma framework and parallel to each other overlap sideways to form a π-electron cloud above and below the plane of the benzene ring making it a conjugated molecule. Due to this overlap six electrons are shared equally among all the six carbons and this is known as delocalization of π electron.

Table: 20.1

Bond	Bond Length
C – C	154 pm
C = C	133 pm
C ≡ C	120 pm

This delocalization causes all the six C - C bond lengths to be same (139 pm). Benzene is thus represented as a hexagon with a circle inscribed, where the circle represents delocalized π electrons.

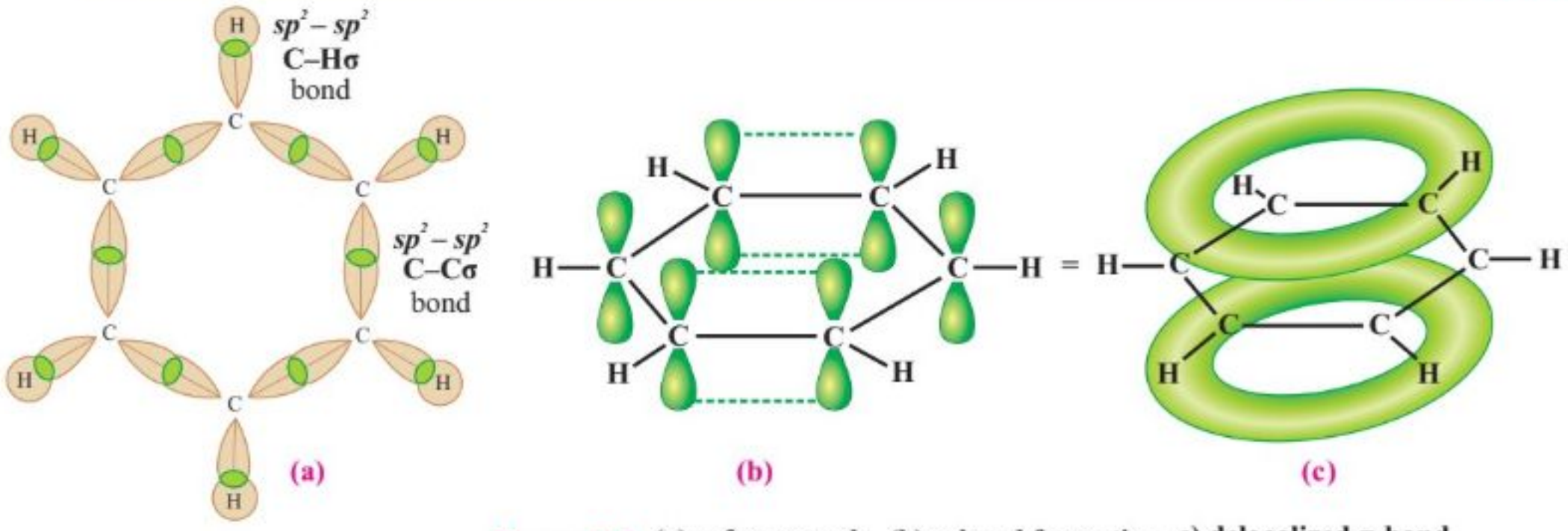


Figure 20.1 (a) σ-framework (b) π-bond formation c) delocalized π-bond

Quick Check 20.1

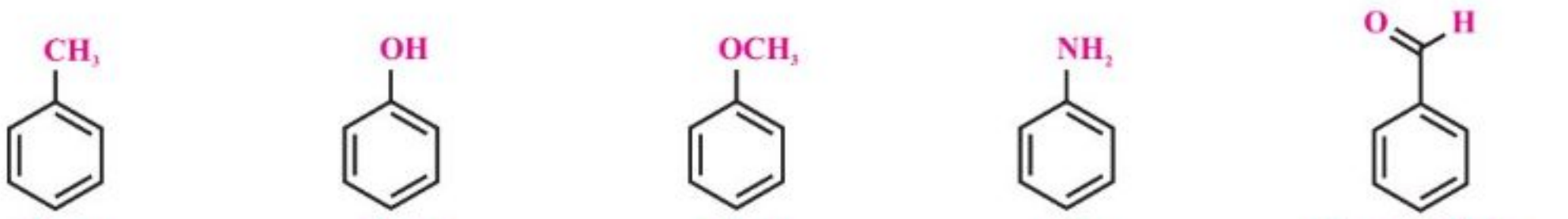
a) The delocalization (resonance) energy of benzene is about 152 kJ mol^{-1}. Explain what that means and how it affects the reactivity of benzene.
b) The X-ray studies show that benzene has a planar structure. If benzene were not planar, what difference in the reactivity of benzene would be seen?
c) Why all the bonds in the benzene ring are of equal bond length?
d) How the atomic orbital concept explains the delocalization of π electrons in benzene?

20.2 NOMENCLATURE OF BENZENE DERIVED COMPOUNDS

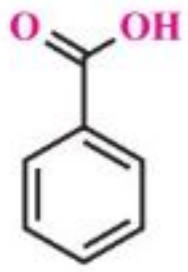
Aromatic hydrocarbons that contain only one benzene ring in this structure are known as **monocyclic aromatic hydrocarbons**. We will look into nomenclature of monocyclic aromatic compounds first. There are two styles of naming benzene derivatives. One in which the compound is named with the suffix 'benzene' and one with no benzene (special name).

When a single substituent is present on a benzene, it is a **monosubstituted benzene.**

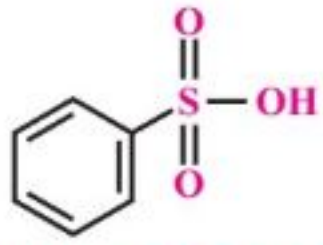
- Most of the monosubstituted benzenes are named with the base name 'benzene' and using the substituent group as a prefix, such as chlorobenzene, nitrobenzene and methyl benzene.
- Many monosubstituted benzenes have common names; some of these names have been included in IUPAC nomenclature as base names for the structure. e.g, phenol, toluene, aniline, etc. Common names in bold face given below are considered to be IUPAC correct base names for structures. The substituent in a monosubstituted benzene is always at C-1, so there is no need to number its location.
- Some benzene derivatives have special names , which are accepted as IUPAC names, e.g., benzene carboxylic acid, benzene sulphonic acid, etc.



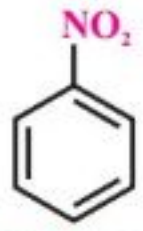
toluene (methylbenzene) | **phenol** (benzenol) | **anisole** (methoxybenzene) | aniline (benzenamine) | **benzaldehyde** (benzenecarbaldehyde)



benzoic acid
(benzenecarboxylic acid)



benzene sulphonic acid



nitrobenzene

chlorobenzene

Common names of monosubstituted benzenes.

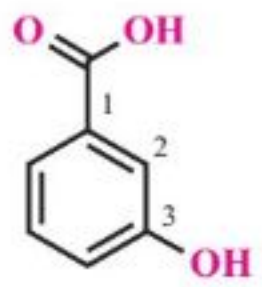
Disubstituted benzenes are compounds when two substituents are present on the benzene ring. They are named according to the following rules.

- The carbon to which a higher priority substituent is attached is C_1. Others are numbered accordingly. The order of priority of substituents (left to right) is:

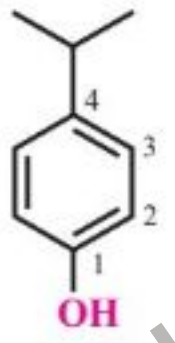
  -COOH, -CN, -CHO, -$COCH_3$, -OH, -NH_2, -OR, -R

- If both substituents are the same priority then the carbon having a substituent lower in alphabets is designated as C_1.

The following examples explain how the disubstituted benzenes are named.



3-hydroxybenzoic acid
acid is higher priority than alcohol.



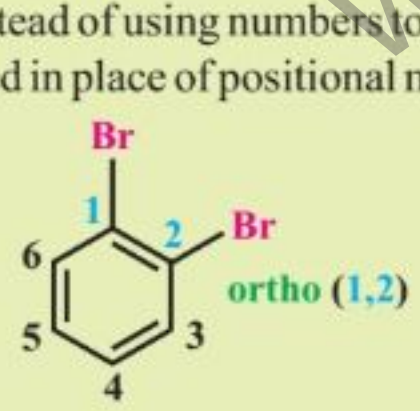
4-isopropylphenol
(4-(1-methylethyl)-phenol)
The phenol alcohol is C-1

1-bromo-2-chlorobenzene
bromo is before chloro in the alphabet

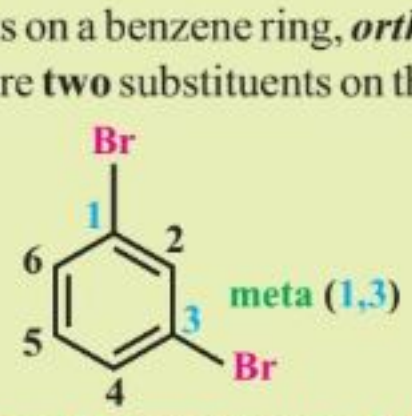
Names of disubstituted benzenes

Did You Know?

Disubstituted benzenes have common names with reference to the relationship between the two substituents. Instead of using numbers to indicate substituents on a benzene ring, ***ortho- (o-), meta- (m-), or para (p-)*** can be used in place of positional markers when there are **two** substituents on the benzene ring.



ortho (1,2)



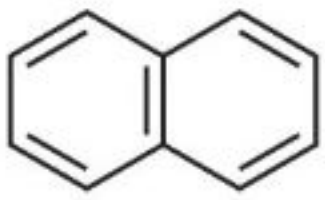
meta (1,3)

ortho (1,3)

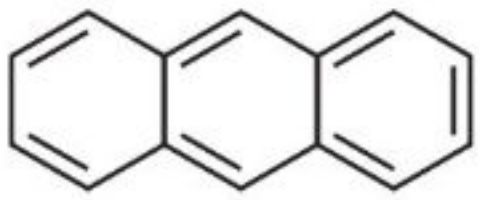
Ortho, meta and para positions of benzene

Aromatic hydrocarbons that contain two or more benzene rings in their molecules are known **as polycyclic aromatic hydrocarbons**.

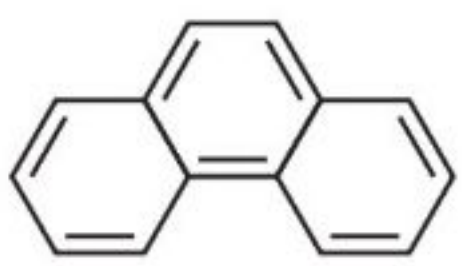
Naphthalene
$C_{10}H_8$



Anthracene
$C_{14}H_{10}$



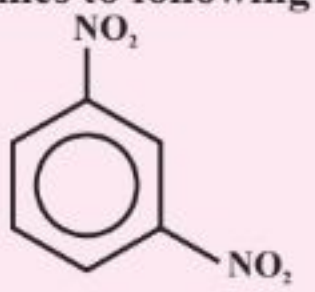
Phenanthrene
$C_{14}H_{10}$

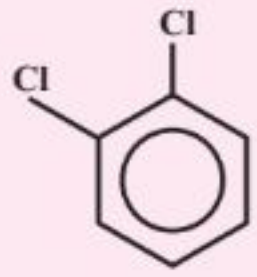


Example of polycyclic benzenes

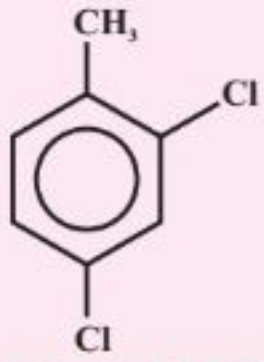
Quick Check 20.2

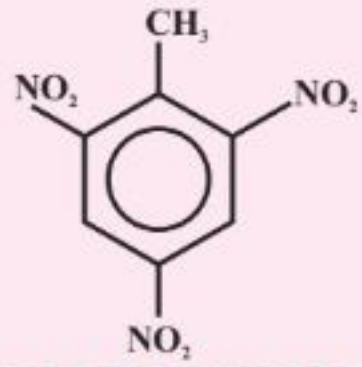
Give names to following arenes:

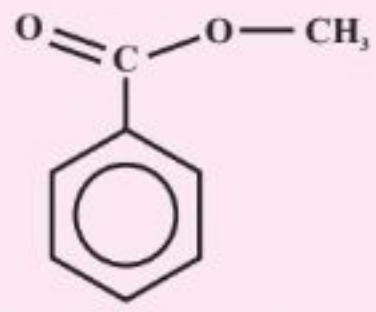
i) 

ii) 

iii) 

iv) 

v) 

vi) 

20.3 COMPARISON OF REACTIVITY OF BENZENE WITH ALKANES AND ALKENES:

Alkanes are generally an unreactive class of organic compounds due to their non-polar nature and the presence of sigma bond only. However, they undergo free radical substitution reactions in the presence of UV light quite easily. Alkenes, on the other hand, are very reactive class of organic compounds due to the presence of π bond and the availability of π electrons for electrophilic reagents. They undergo electrophilic addition reactions easily.

Benzene has three π bonds and, as expected, shows some similarities to alkenes in being reactive towards electrophilic species. However, there are two key differences between their reactions with electrophiles:

- benzene is very stable and thus less reactive.
- Unlike alkenes, it undergoes the electrophilic substitution and not electrophilic addition reactions:

electrophilic substitution

The H has been replaced by the Br

electrophilic addition

Two Br have been added to the double bond

Bromine in the electrophilic substitution reaction replaces a hydrogen atom. This is due to the stability of the aromatic ring which is due to extensive delocalization of π electrons. Even though the reaction in benzene goes through an intermediate where the aromaticity is broken, it is restored after the completion of the reaction. Therefore, electrophilic substitution does not affect the overall stability of the benzene ring. In electrophilic addition the delocalisation is broken and addition is not favourable.

Quick Check 20.3

Although benzene is highly unsaturated yet it does not prefer to undergo addition reactions. Explain.

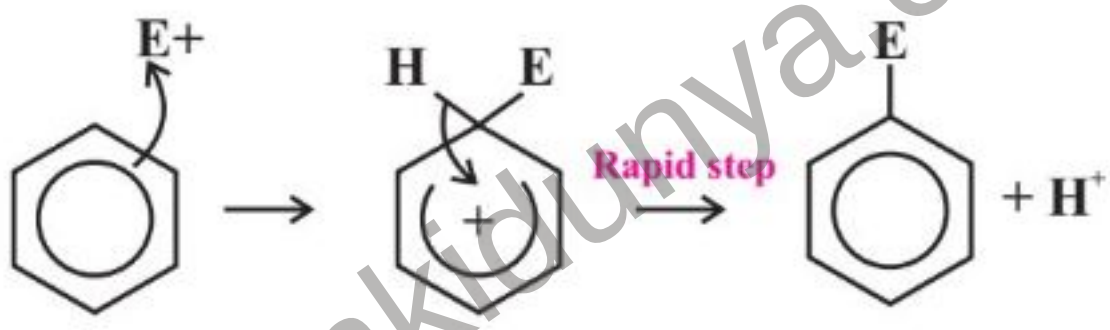
20.3.1 Electrophilic Aromatic Substitution

Regardless of electrophile used, the electrophilic aromatic substitution mechanism can be divided into three main steps.

i. **Generation of electrophile:** The first step of an electrophilic substitution reaction involves the generation of an electrophile. The electrophile can be a positive ion or the positive end of a polar molecule. Typically, electrophiles cannot simply be added to the reaction mixture. The electrophile is produced in situ, by adding appropriate reagents to the reaction mixture.

ii. **Electrophilic attack**: In the second step the π electrons of benzene attack the electrophile**.** This forms a sigma bond between one carbon atom of the benzene ring and the electrophile. This disrupts the aromaticity in the ring as there are now only four π electrons and there is a positive charge spread over the five carbon atoms. Because of the new sigma bond formed, this intermediate is called a **sigma complex.**

iii. **Restoration of aromaticity:** In the 3rd step, the hydrogen on the sp^3-hybridized carbon is removed by a counterion/conjugate base restoring the aromaticity to the ring. This happens by **heterolytic cleavage** of the C-H bond. This means that the electrons in this bond go into the benzene π bonding system, and the d-localisation in the ring is restored



General mechanism of electrophilic substitution

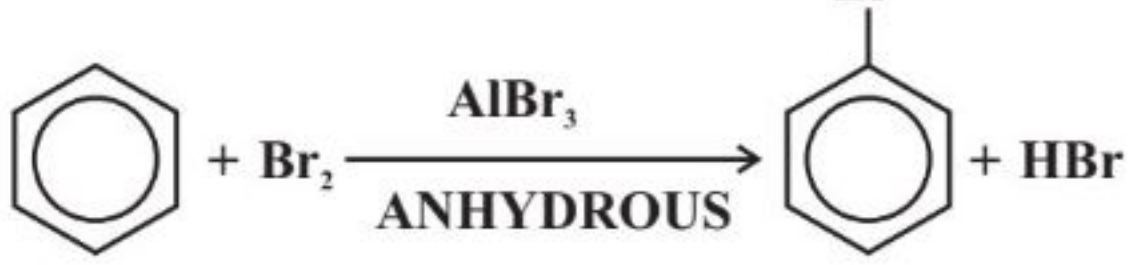
Examples of electrophilic substitution reactions of arenes are given as follows.

Halogenation of Benzene

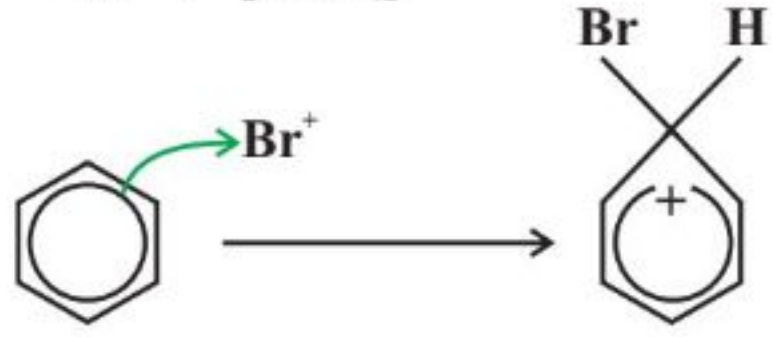
Benzene only reacts with bromine and chlorine in the presence of Lewis acids as they coordinate to the halogens and generate strong electrophilic species.

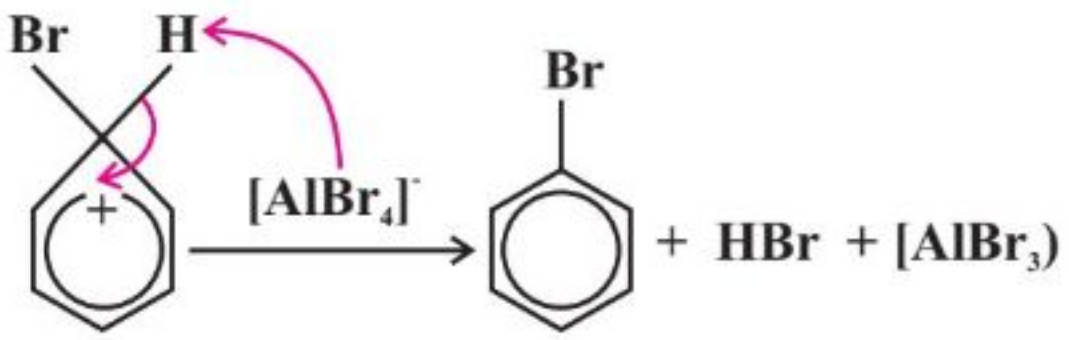
The Lewis acids are usually aluminum chloride ($AlCl_3$), iron chloride ($FeCl_3$) or iron bromide ($FeBr_3$).

This is bromination of benzene, which involves following steps:



Once the electrophile is formed, it follows the same general mechanism as we have discussed earlier.





First, the addition of the electrophile, forming the sigma complex which is then deprotonated by $AlCl_4^-$

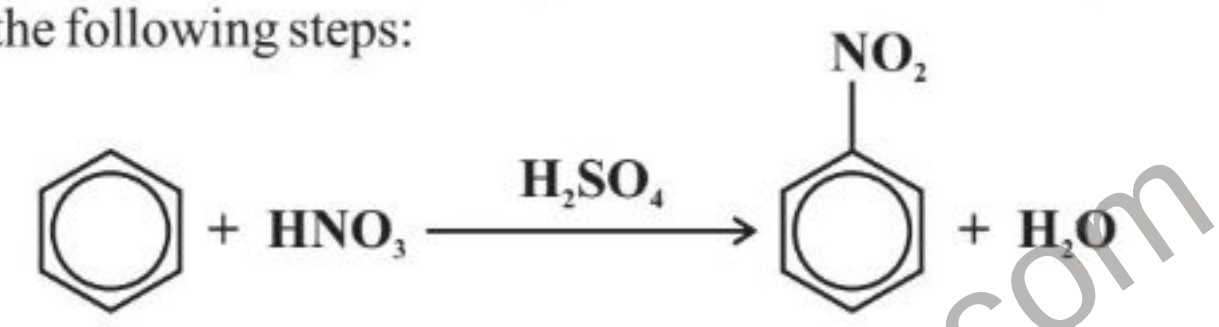
In the same way, $FeCl_3$ is used as the Lewis acid activator for generating Cl^+. The rest of the mechanism is identical to what we saw for the bromination of benzene.

Quick Check 20.4

a) Write mechanism of reaction of benzene with chlorine using $AlCl_3$ as catalyst.

Nitration of Benzene

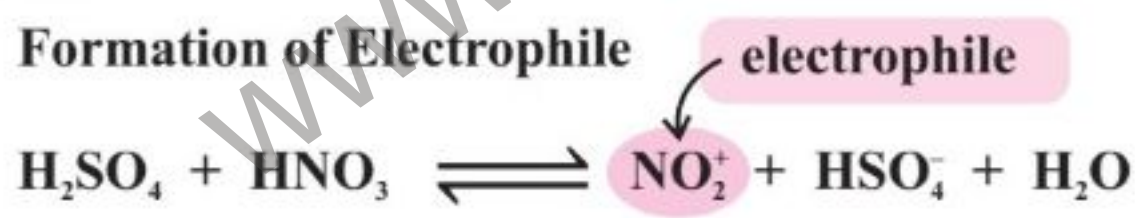
Nitro group is introduced on benzene, using mixture of conc. HNO_3 and conc. H_2SO_4. The mechanism involves the following steps:



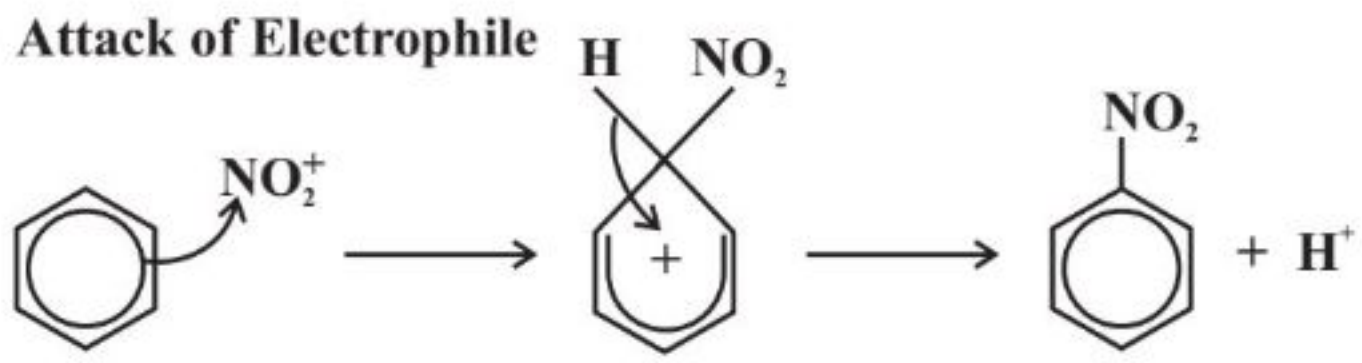
- The electrophile **NO_2^+ ion** is generated by reacting concentrated **nitric acid** (HNO_3) and **concentrated sulphuric acid** (H_2SO_4).
- A pair of electrons from the benzene ring is donated to the NO_2^+ electrophile to form a covalent bond causing a loss in aromaticity
- The C–H bond of the substituted carbon atom breaks and the electrons go back into the benzene π bonding system, restoring its aromaticity

Mechanism:

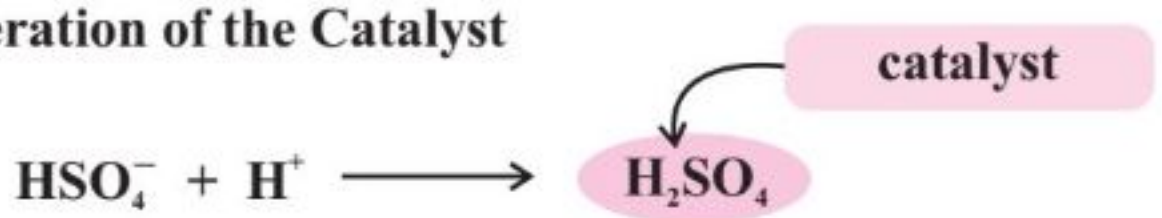
- **Formation of Electrophile**



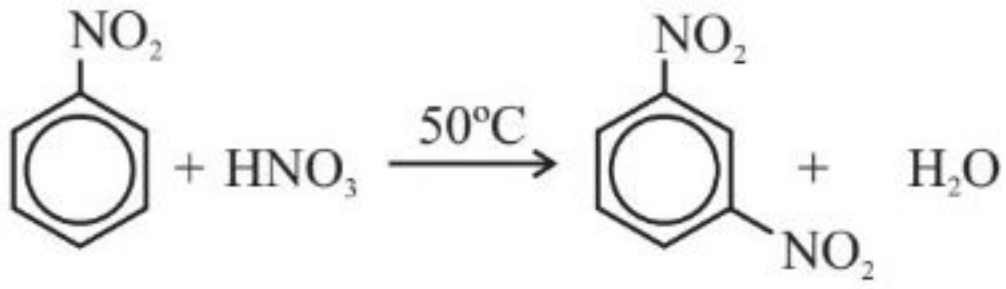
- **Attack of Electrophile**



- **Regeneration of the Catalyst**



Concentrated sulphuric acid acts as a catalyst so is not written in the equations. At higher temperatures there is a greater chance of getting more than one nitro group substituted onto the ring. You will get a certain amount of 1,3-dinitrobenzene formed even at 50°C.



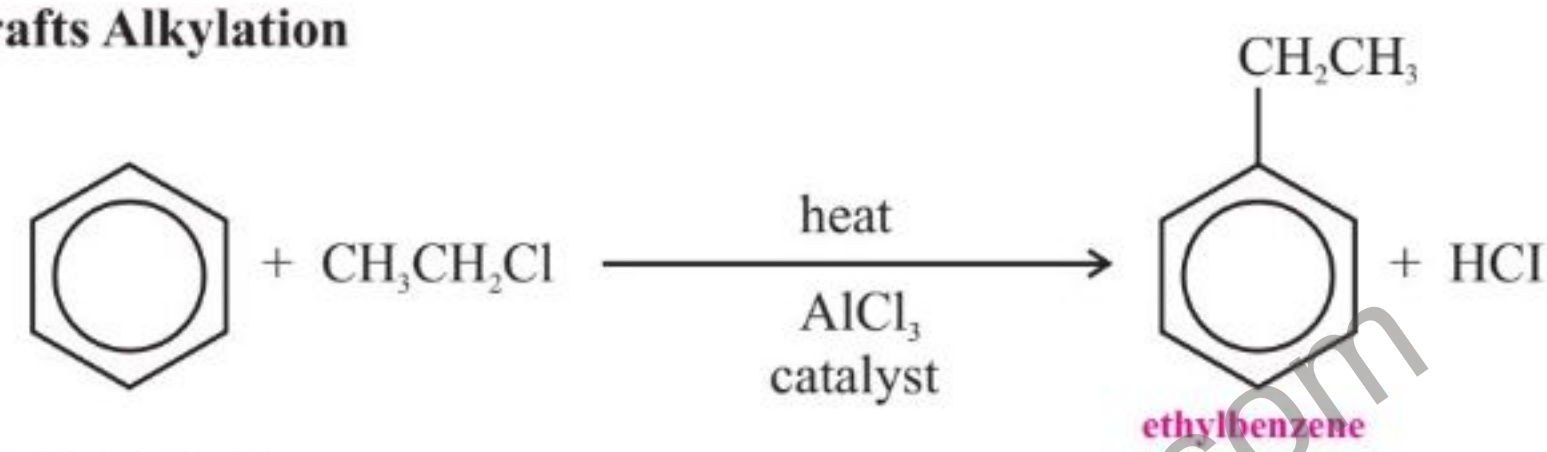
Quick Check 20.5

Show how the electrophile is produced in the nitration of benzene from sulphuric acid and nitric acid. Which of these two acts as an acid and which acts as a base?

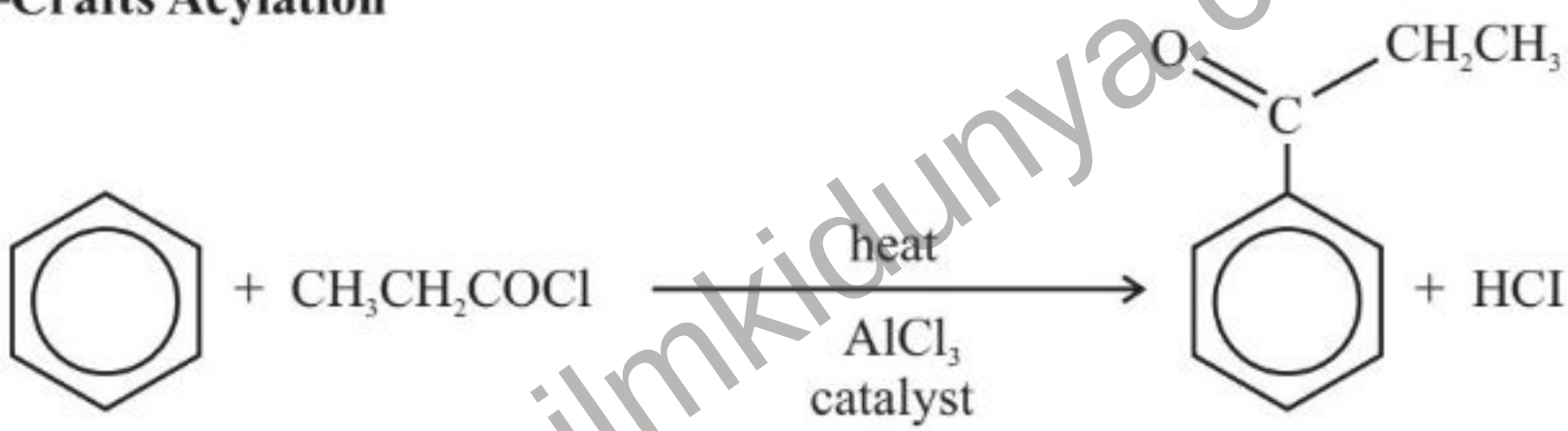
Friedel-Crafts Alkylation and Acylation

In the Friedel-Crafts acylation reaction, an **acyl group** is substituted into the benzene ring in the presence of a Lewis acid catalyst. An acyl group is an alkyl group attached to a carbonyl group, R-C=O. In the Friedel-Crafts alkylation, an **alkyl group** is substituted into the benzene ring.

Friedel–Crafts Alkylation



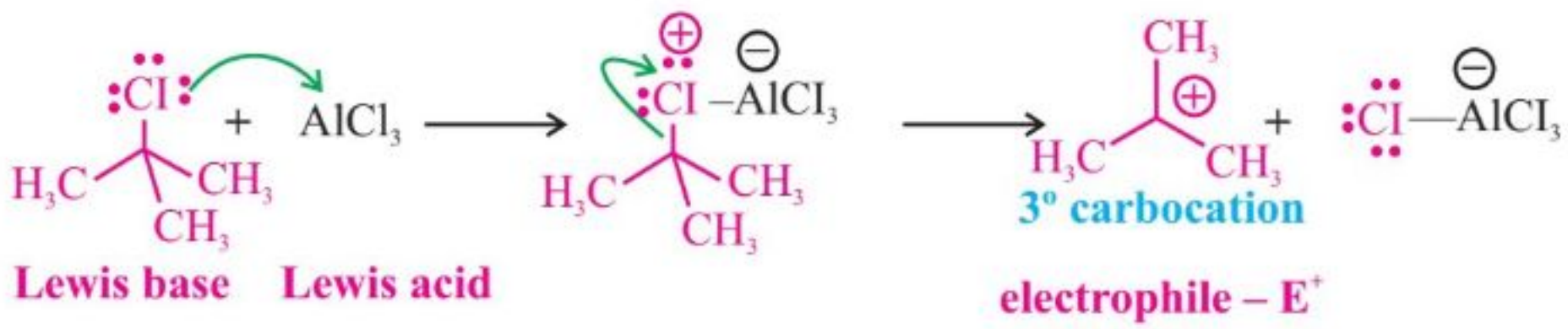
Friedel–Crafts Acylation



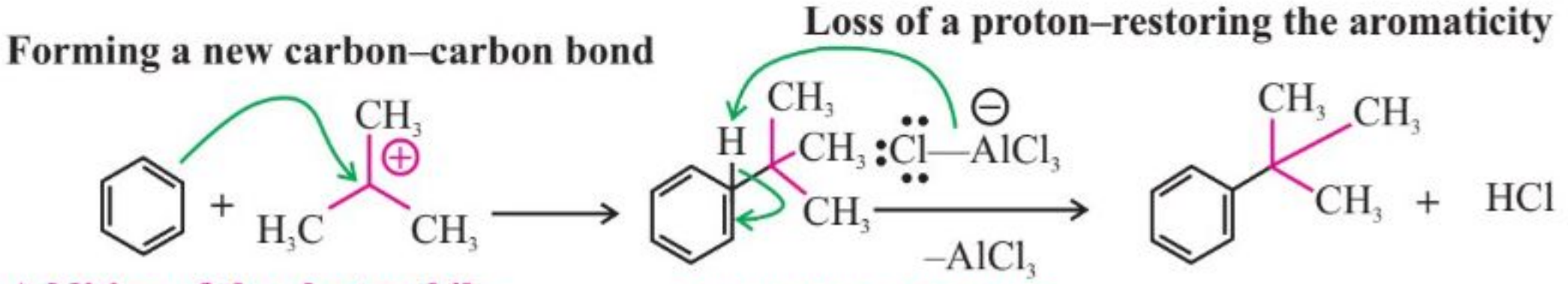
a) Friedel-Crafts Alkylation

The Friedel-Crafts alkylation reaction proceeds via a three-step mechanism.

- The Lewis acid catalyst ($AlCl_3$) undergoes reaction with the alkyl halide, resulting in the formation of a carbocation which acts as an electrophile.



- The π electrons of aromatic ring attack on electrophilic carbocation, forming an arenium ion as an intermediate. The aromaticity of the arene is temporarily lost due to the breakage of the carbon-carbon double bond.
- The deprotonation of the intermediate leads to the reformation of the carbon-carbon double bond, restoring aromaticity to the compound. This proton goes on to form hydrochloric acid, regenerating the $AlCl_3$ catalyst.

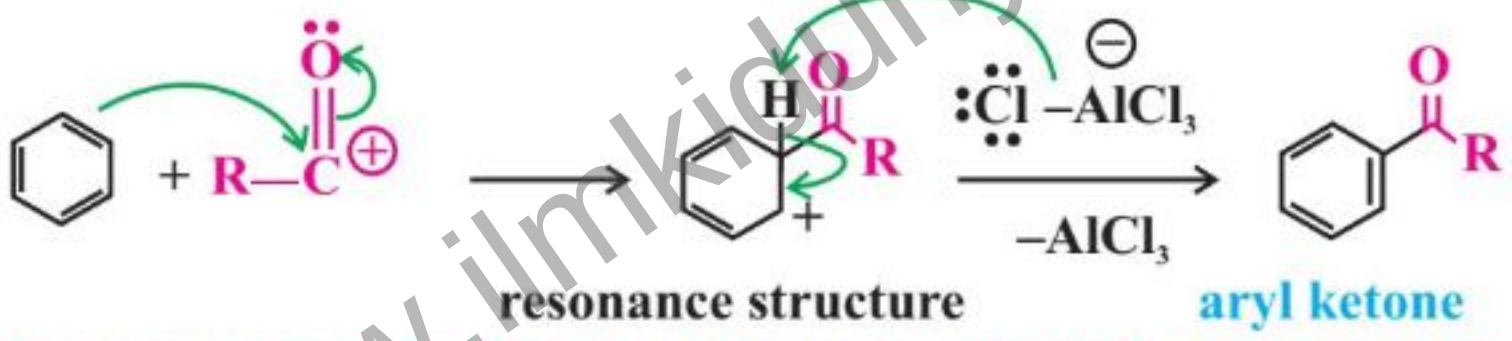


b) Friedel-Crafts Acylation

Friedel-Crafts acylations proceed through a four-step mechanism.

- A reaction occurs between the Lewis acid catalyst ($AlCl_3$) and the acyl halide. A complex is formed and the acyl halide loses a halide ion, forming an acylium ion.

- An electrophilic attack of π electrons of the aromatic ring on the acylium ion (RCO^+) takes place.
- The intermediate complex is now deprotonated, restoring the aromaticity to the ring. This proton attaches itself to a chloride ion, forming HCl. The $AlCl_3$ catalyst is regenerated. Thus, the required acyl benzene product is obtained via the Friedel-Crafts acylation reaction.



Quick Check 20.6

1. Write down reactions of methyl benzene with bromine in the presence of $AlBr_3$.
2. Explain the difference in the reactivity of bromine with benzene and with phenol. Include the type of reaction, the products that form, and any conditions required. Mechanisms for the reactions are not required.
3. Explain the difference in the reactivity of bromine with benzene and with ethyl benzene. Include the type of reaction, the products that form, and any conditions required. Mechanisms for the reactions are not required.
4. Which of 1,1-dimethyethyllbenzene and methyl benzene is easier to form by Friedel-Craft reaction? Explain based on the stability of carbocation.

20.4 ORIENTAION IN ELECTROPHILIC SUBSTITUTION REACTIONS

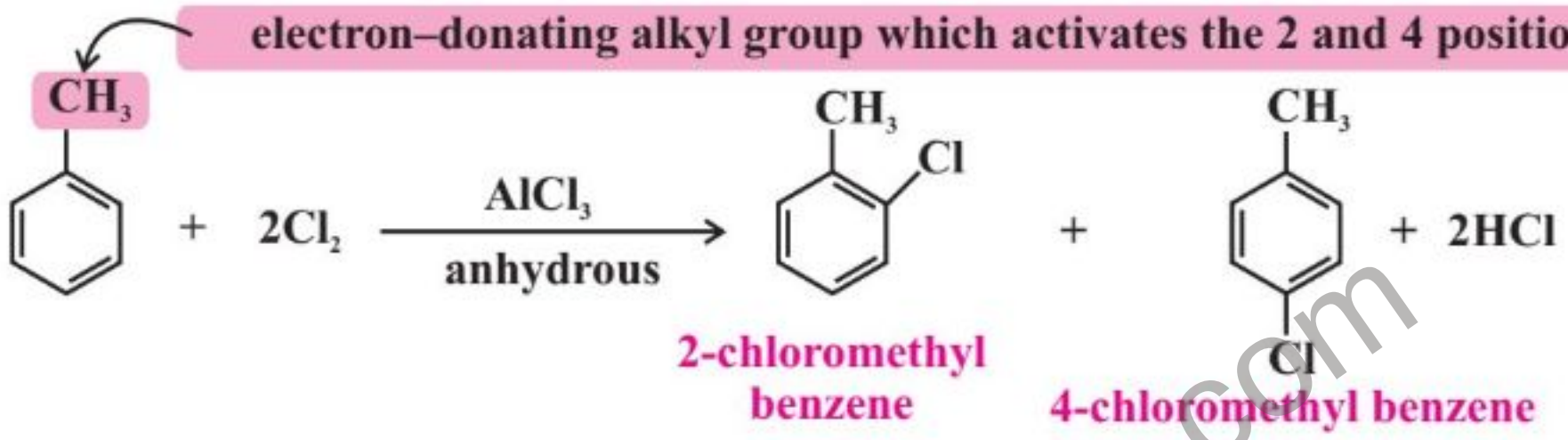
Any group attached with benzene ring affects the electrophilic substitution reaction and determines the orientation of the substitution. There are two ways in which various substituents "**direct**" electrophilic aromatic substitution of incoming electrophile to benzene ring.

Ortho-Para Directing Groups (Activating Groups):

A group that makes the ring more reactive than benzene and influences the incoming electrophile to attach on -ortho and -para positions only, is called as -ortho, -para director. Substituents direct

the reaction to give either the "*ortho*" (1,2) or "*para*" (1,4) product, with a slight preference for "para". In this pattern, *ortho*- and *para*– products dominate, and the *meta*- product is an extremely minor byproduct. Examples of ortho-, *para*– directors are -SR, -R,-OH, -OR, $-NR_2$, -SH. Note that these are groups that have the ability to donate electrons to the benzene ring.

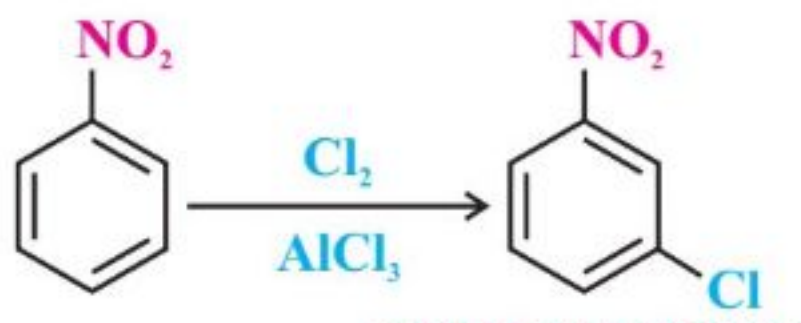
The chlorination in the methyl benzene ring takes place in the presence of **aluminium chloride** (or aluminum bromide if you are using bromine) or iron, and in the **absence of UV light**. The reactions take place at room temperature. Methyl group is 2,4-directing (o-p directing), which means that incoming groups will tend to go into the 2 or 4 positions on the ring. With chlorine, substitution into the ring gives a mixture of 2-chloromethylbenzene and 4-chloromethylbenzene.



With bromine, you would get the equivalent bromine compounds. Like methyl group on benzene ring, OH group is also ring activator so incoming groups will tend to go into the 2, 4 & 6 positions on the ring.

Meta Directing (Deactivating) Groups:

Group that makes the ring less reactive than benzene, and directs the incoming electrophile to attack on meta position only is called as-meta director. Such groups are mostly electron-withdrawing groups, that destabilize the arenium intermediate. These substituents direct the reaction to give primarily the "*meta*" (1,3) product. Major product formed in this case is meta substituted. Examples of *meta*– directors include -CN, C=O, $-NO_2$, $-CO_2$-. Nitrobenzene contains a meta directing group ($-NO_2$), its chlorination occurs at the meta position.



meta-chloronitrobenzene

Quick Check 20.7

a) Explain why phenol can be nitrated using milder conditions than for benzene.
b) How would you prepare 3-chloronitrobenzene from benzene?
c) Which products are expected to form in majority when the following are nitrated with conc. sulphuric acid and nitic acid? Give reactions
i. benzaldehyde ii. chlorobenzene iii. phenol iv. Benzene carboxylic acid

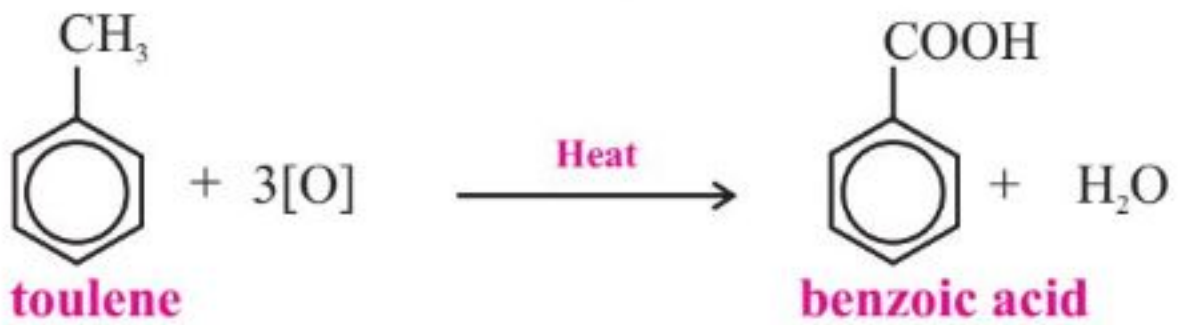
20.4.1 Combustion

When benzene is burnt in excess of air, it is completely oxidized to CO_2 and H_2O. However, this reaction gives a smoky flame which is used as a test for aromatic compounds.

$$2C_6H_6 + 15O_2 \longrightarrow 12CO_2 + 6H_2O$$

20.4.2 Side Chain Oxidation in Benzene

Oxidation reaction that takes place at an alkyl group directly attached to a benzene ring is termed as side-chain oxidation. In this reaction, alkylbenzenes are readily oxidized by alkaline $KMnO_4$ or acidic $K_2Cr_2O_7$ or dilute HNO_3. In these kinds of reaction, the alkyl groups are oxidized to carboxylic acid group, regardless of the size of alkyl group, keeping the benzene ring intact.



Side-chain oxidation of alkylbenzene takes place when there is at least one benzylic hydrogen attached to the carbon. No reaction occurs in the absence of benzylic hydrogen. Thus, these reactions have no effect on tertiary carbons attached to an aromatic ring.

Whatever the length of an alkyl group may be, it gives only on carboxyl group as a product after oxidation. Following example demonstrates the utilization of oxidation reaction in the production of substituted benzoic acid.

Both alkane and benzene are very stable and insusceptible to oxidation but when put together, the benzylic carbon which is directly attached to the benzene ring becomes more reactive and more susceptible to oxidation.

Oxidation of alkylbenzene containing benzylic protons by $KMnO_4$ is used an identification test. Purple colour of $KMnO_4$ solution is discharged, once consumed in the oxidation reaction. Therefore, one can easily differentiate between benzene, benzene containing primary, secondary, and tertiary alkyl groups by chemical test with $KMnO_4$ solution.

20.4.3 Addition Reactions of Benzene

We will examine hydrogenation and halogenation addition reactions of benzene in the following reactions.

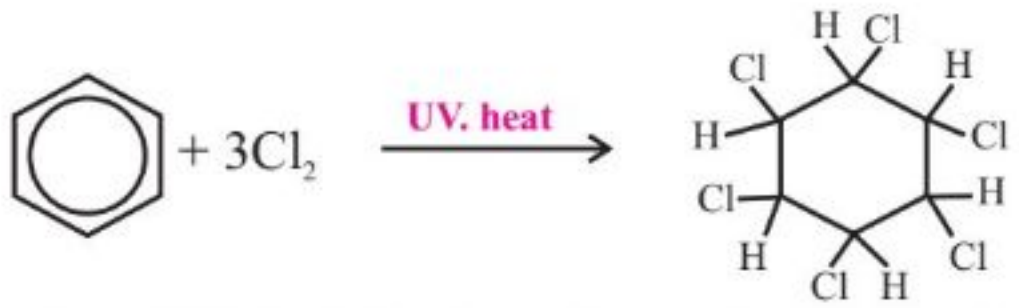
a) Hydrogenation of benzene

The hydrogenation of benzene and other arenes, involves the addition of 1, 2, or 3 moles of hydrogen to the carbons of benzene. Cyclohexane is produced when benzene is completely hydrogenated. Cyclohexane is a useful solvent and a precursor in the production of other chemicals.

These reactions destroy the electron delocalisation in the original benzene ring, because those electrons are being used to form bonds with the new hydrogen atoms. Although the reactions are exothermic overall because of the strength of all the new carbon-hydrogen bonds, there is a high activation barrier to the reaction. The reactions are done using the same finely divided nickel catalyst that is used in hydrogenation of alkenes and at similar temperatures (around 150°C), but a higher pressure is applied.

b) Addition of Halogens

Chlorine and bromine react in the same way. In the absence of a catalyst, UV light and heat are sufficient for complete halogenation. The complete chlorination of benzene is shown below:



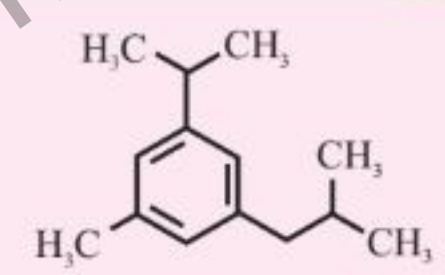
Quick Check 20.8

a) Predict the product formed when:

i. the compound given here is oxidized using acidified $KMnO_4$ or $K_2Cr_2O_7$.

ii. Bromine is added to chlorobenzene in the presence of $AlBr_3$.

iii. Nitrobenzene is reduced in the presence of Ni at high temperature and pressure.



3-Ethyl-5-propyloluene

Exercise

Q1. Multiple Choice Questions:

I. Which of the following is the major product when methyl chloride (CH_3Cl) reacts with methylbenzene in the presence of $AlCl_3$:

a) 1, 2-dimethyl benzene
b) 1,4-dimethyl benzene
c) 1,3-dimethyl benzene
d) both (a) and (b)

II. Bromine reacts more readily with phenol than with benzene. This is because the:

a) benzene ring in phenol is more susceptible to nucleophilic attack

b) benzene ring in phenol is deactivated because the oxygen of the OH group is very electronegative

c) lone pair of electrons on the oxygen atom in phenol overlap with the delocalised electrons in the benzene ring

d) lone pair of electrons on the oxygen atom enable phenol to act as an electrophile

III. Aluminium chloride catalyses the reaction of benzene and ethanoyl chloride. This is because aluminium chloride.

a) has significant covalent character
b) exists as a dimer in non-polar solvents
c) is an electron pair acceptor
d) is rapidly hydrolysed

IV. Benzene is nitrated using a mixture of concentrated nitric and sulphuric acids. The sulphuric acid

a) acts as a solvent for the benzene and the nitric acid
b) protonates the benzene to speed up the reaction
c) protonates the nitric acid which acts as a base
d) reacts with the benzene to form a benzenesulfonic acid intermediate

V. In the reaction of benzene with chloromethane, aluminium chloride is added because it reacts with

a) benzene to produce an electrophile
b) benzene to produce a nucleophile
c) chloromethane to produce a nucleophile
d) chloromethane to produce an electrophile

VI. Methylbenzene reacts with a mixture of concentrated nitric acid and concentrated sulphuric acid.

What is the name of the mechanism for this reaction?

a) electrophilic addition
b) electrophilic substitution
c) nucleophilic addition
d) nucleophilic substitution

VII. X-ray diffraction provides evidence that benzene molecules have:

a) delocalised π-electrons
b) carbon-carbon bonds that are all the same length
c) lower thermodynamic stability than molecules of 1,3,5-cyclohexatriene
d) greater thermodynamic stability than molecules of 1,3,5-cyclohexatriene

VIII. Which statement(s) support(s) the delocalised model for the structure of benzene?

1 All carbon–carbon bonds have the same length.
2 The enthalpy change of hydrogenation of benzene is less exothermic than expected.
3 Bromine reacts with benzene less readily than with cyclohexene.

a) 1, 2 and 3
b) Only 1 and 2
c) Only 2 and 3
d) Only 1

IX. Benzene reacts with an organic reagent in the presence of a halogen carrier to form phenylethanone. Which organic reagent is required?

a) CH_3CH_2OH b) CH_3CHO

c) CH_3COCl d) CH_3COOH

Q2. SHORT ANSWER QUESTIONS

a) Benzene reacts with chlorine in the presence of a halogen carrier, such as $AlCl_3$.

i) Write the equation for the reaction of benzene with chlorine.

ii) How does the halogen carrier allow the reaction to take place?

iii) Outline a mechanism for this reaction. Include curly arrows and relevant dipoles.

iv) State the name of this mechanism.

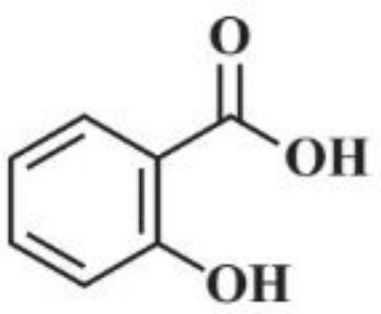
b) Diphenylethanedione is a pale yellow colour, which disappears when it is reduced. The colour results from the arrangement of the delocalised π-bond electrons. Explain what is meant by the term delocalised π-bond electrons.

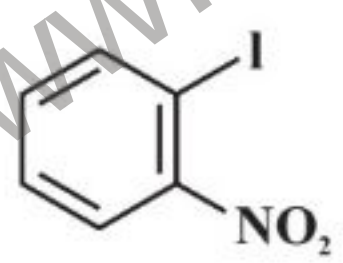
c) An acylium ion has the structure R-C=O where R is any alkyl group. In the conversion of benzene into phenylethanone, $C_6H_5COCH_3$, an acylium ion CH_3CO^+ reacts with a benzene molecule.

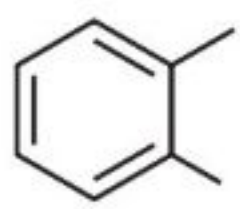
i) Write an equation to show the formation of this acylium ion from ethanoyl chloride and one other substance.

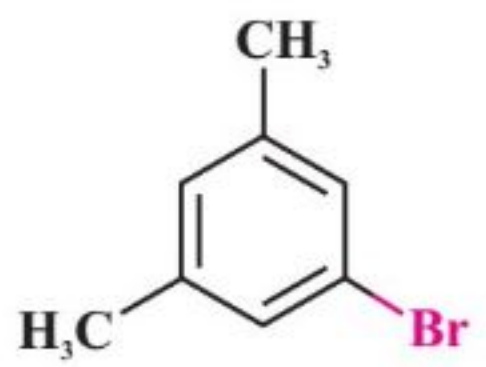
ii) Name and outline the mechanism of the reaction of this acylium ion with benzene.

d) Name the following molecules:









e) Phenol reacts much more readily with bromine than benzene does.

i) Describe, with the aid of a diagram, the bonding in benzene.

ii) Explain why electrophiles, such as bromine, react much more readily with phenol than with benzene.

Q3. CONSTRUCTED RESPONSE QUESTIONS

a) The compound iodine monobromide, IBr, also reacts with benzene in an electrophilic reaction.

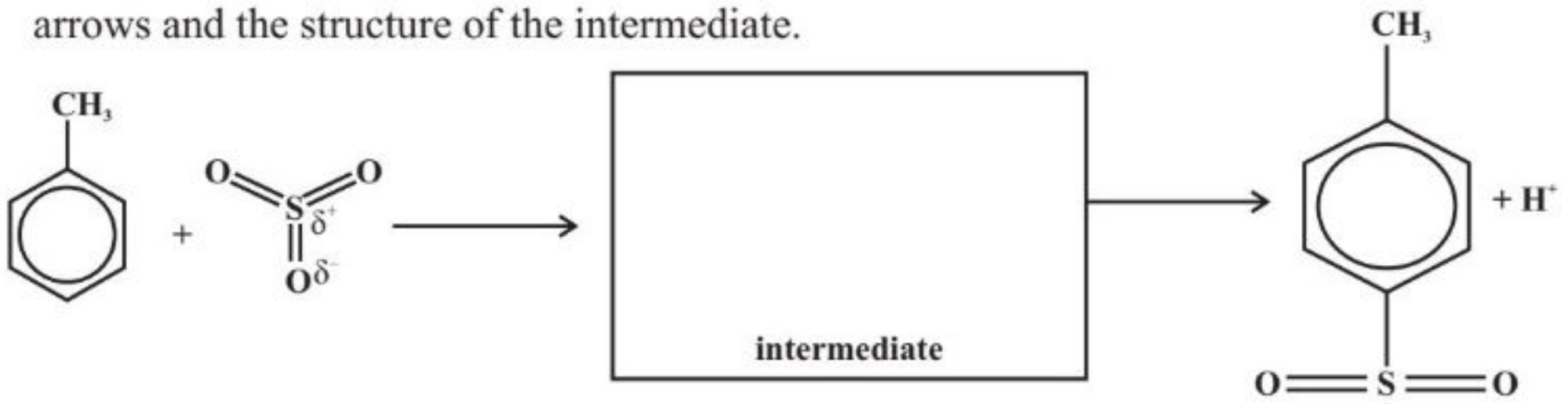
i) Which compound would be the main product of this reaction, iodobenzene or bromobenzene? Explain your answer.

ii) Deduce an equation for the reaction of iodine monobromide with benzene.

b) Methylbenzene reacts with sulphur trioxide, SO_3, to form D, shown below

The electrophile in this reaction is SO_3.

Complete the mechanism for the formation of D. Show curly arrows and the structure of the intermediate.



c) This question is about the chemistry of aromatic compounds.

Benzoic acid can be nitrated by concentrated nitric acid in the presence of concentrated sulphuric acid as a catalyst, as shown in equation below. The organic product of this reaction is 3-nitrobenzoic acid.

benzoic acid — 3-nitrobenzoic acid

i) Outline the mechanism for this nitration of benzoic acid. Show how H_2SO_4 behaves as a catalyst.

ii) A chemist carries out the reaction in Equation above using 4.97 g of benzoic acid.

The chemist obtains 3-nitrobenzoic acid as an impure solid. The chemist purifies the solid to obtain 4.85 g of 3-nitrobenzoic acid.

Describe a method to obtain a pure sample of 3-nitrobenzoic acid from the impure solid, determine the percentage yield and check its purity.

DESCRIPTIVE QUESTIONS

Q4. In contrast to benzene, the reaction of an alkene with bromine does not need a halogen carrier. Compare the different reactivities of benzene and alkenes towards chlorine.

Q5. Many organic reactions use electrophiles as reagents. Explain the role of electrophiles in organic chemistry. Your answer should include one reaction of an aliphatic compound and one reaction of an aromatic compound, including relevant mechanisms.