UNIT 08

HYDROCARBONS

Student Learning Outcomes (SLOs)

- Explain the shape of benzene molecule (molecular orbital aspect).
- Define resonance, resonance energy and the 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 nitronium ion, and predict the major products(s) of the reaction.
- Explain the mechanism of Friedel-Craft 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 formation of a benzoic acid, and predict the major product(s) of the reaction.
- Explain the mechanism of hydrogenation, including the role of 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 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

In previous class we have discussed hydrocarbons in detail. They are compounds having hydrogen and carbon elements only. Broadly, they are classified into aliphatic and aromatic hydrocarbons. The word aliphatic comes from the Greek language "aleiphar" meaning "oil" and was given to hydrocarbons that were obtained by the chemical degradation of fats. All hydrocarbons having no benzene ring are classified as aliphatic hydrocarbons. On the other hand, hydrocarbons having at least one benzene rings are called aromatic hydrocarbons. More recently, the alternative and systematic name of arenes has been used for them. The word arene has a suffix "ar" which means aromatic and "ene" comes from the last three alphabets of benzene, reflecting unsaturation.

Michael Faraday isolated a hydrocarbon from the oily residue that was collected in the gas pipes of London and he called it "bicarburet of hydrogen". In 1834, Eilhardt Mitscherlich of the University of Berlin prepared the same substance by heating benzoic acid with lime. He found that this molecule has empirical formula "CH".

$$C_6H_5COOH + CaO \longrightarrow C_6H_6 + CaCO_3$$

Benzoic acid was obtained from gum benzoin, a resin of balsam tree (Java island of Indonesia) so it got the name benzin which, later on, became benzene.

All compounds related to benzene and toluene are called aromatic hydrocarbons. The word "aroma" is Latin word meaning fragrance. Benzene and toluene are not particularly fragrant compounds themselves; however, their origin comes from pleasant-smelling plant extracts.

Later on, it was investigated that all aromatic compounds are not pleasantsmelling, even some has harmful and unpleasant vapours. They have unusual stability because of benzene ring in them so the name aromatic was used for all those compounds that are stable. All aromatic compounds must have at least one benzene ring.

Warning !

Benzene is a chemical causing cancer (leukemia). People exposed to car exhaust or working in different factories may become victims. There are different rules in the world regarding permissible levels of concentration of benzene in the working space.

8.1 Nomenclature of Benzene

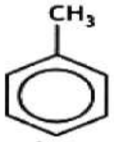
The simplest aromatic compound is benzene itself. There are many aromatic compounds with one or more different substituents. The IUPAC system still retains some common names.

Remember!

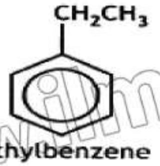
According to IUPAC conventions, all letters in the names of compounds must be written in lowercase, except when they appear at the beginning of a sentence. However, the first letter of element symbols is always uppercase.

Monosubstituted benzenes

They have one substituent attached to benzene ring. The systematic or IUPAC names of some simple monosubstituted aromatic compounds are given.

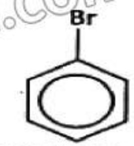


toluene



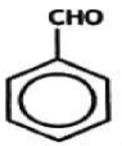
ethylbenzene

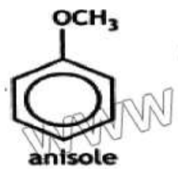
styrene



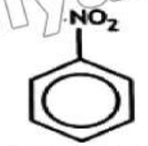
bromobenzene

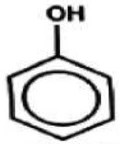
benzoic acid


benzaldehyde


anisole

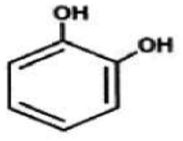

cumene

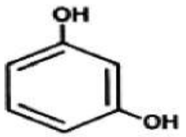

nitrobenzene

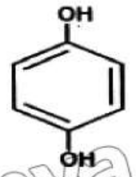

phenol

Disubstituted benzenes

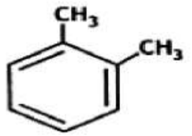
They have two substituents attached to benzene ring and can show three positional isomers. For showing positions of substituents on benzene ring, we may use numbers or Greek words ortho, meta and para. The word "ortho (o)" means straight, "meta (m)" means after and "para (p)" means beyond. The numbers 1,2 are equivalent to ortho, 1,3 equivalent to meta and 1,4 to para.

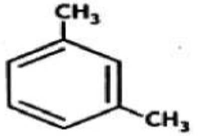

1,2-dihydroxybenzene
(Catechol)

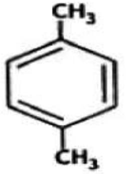

1,3-dihydroxybenzene
(Resorcinol)


1,4-dihydroxybenzene
(Hydroquinone)

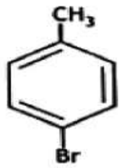
When one of the two substituents on the ring makes a special name to the compound, such as toluene, phenol and aniline, we name the compound as a derivative of that parent molecule. In this case, the special substituent occupies position 1 on the ring position. The IUPAC system retains the common name xylene for the three isomeric dimethylbenzenes.

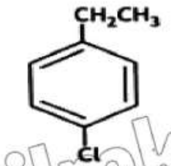

1,2-dimethybenzene
(o-xylene)

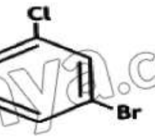

1,3-dimethylbenzene
(m-xylene)


1,4-dimethylbenzene
(p-xylene)

When neither group gives a special name, we treat them in alphabetical order before the word 'benzene'


4-bromotoluene
(p-bromotoluene)

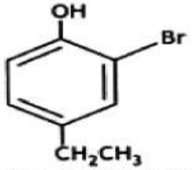

1-chloro-4-ethylbenzene
(p-ethylchlorobenzene)


1-bromo-3-chlorobenzene
(m-chlorobromobenzene)

Polysubstituted Benzenes

When three or more substituents are present on a ring, we specify their locations by numbers. If one of the substituents imparts a special name, the molecule is named as a derivative of that parent molecule. If none of the substituents imparts a special name, we number them to give the smallest set of numbers and list them in alphabetical order before the word 'benzene'. In the following examples, the first compound is a derivative of toluene, and the second is a derivative of phenol. Because there is no special name for the third compound, we number the carbon atoms using the smallest possible set of numbers, then list its three substituents in alphabetical order, followed by the word 'benzene'.

4-bromo-2-nitrotoluene

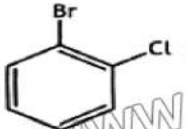


2-bromo-4-ethylphenol

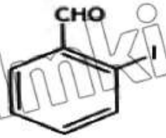
Concept Assessment Exercise 8.1

Name the following aromatic compounds.

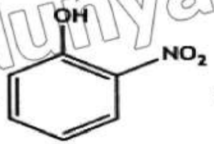
i.



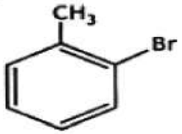
ii.



iii.



iv.



8.2 The Structure of Benzene

After the discovery of benzene in 1835, the structure of benzene molecule puzzled the nineteenth-century chemists for forty years. Elemental analysis proved that benzene has amazingly low hydrogen-to-carbon (H:C) ratio, with molecular formula "C_6H_6" and empirical formula "CH", suggesting high degree of unsaturation. Considering the unsaturated nature of benzene molecule, several chemists proposed different structures for it having carbon-carbon double and triple covalent bonds as shown below.

$$CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH_2$$

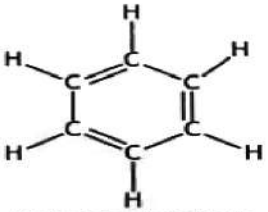
$$HC{\equiv}C{-}CH_2{-}CH_2{-}C{\equiv}CH$$

However, the observed properties of benzene could not align with these structures because they imagined benzene as an open molecule.

Kekul's Structure of Benzene

In 1865, a German chemist named August Kekulé, was sitting near fire on a cold night in his laboratory. He was struggling to determine the structure of benzene molecule. Suddenly, he had a dream and saw atoms dancing *around and* making chains. Ha saw the chains changing into rings and appeared like snakes biting their tails. That image inspired Kekule and he proposed the ring (cyclic) structure of benzene molecule, having six carbon atoms for the first time. He proposed that a benzene is cyclic molecule with six carbon atoms in the ring each bonded to one hydrogen atom.


August Kekule
(1829-96)

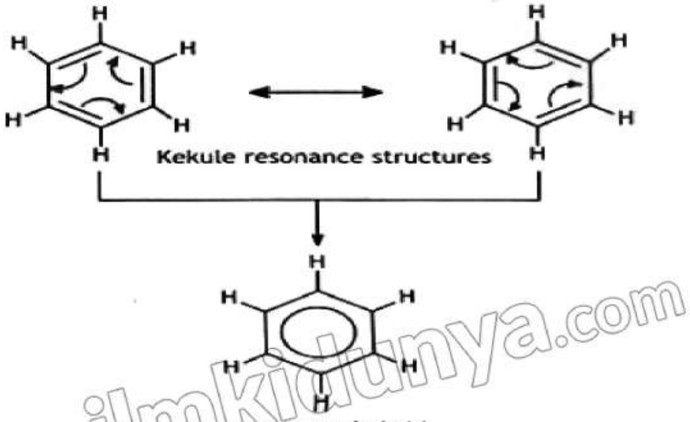


Kekule's structure

Key Information
Kekule's dream serves as an example of how imagination can lead to discoveries in the field of science.

The ring structure of benzene imagined by Kekule was an evolutionary idea in the field of chemistry. This idea led chemists to consider ring structures of different organic molecules. The cyclic structure of benzene molecule could explain the unexpectedly high stability and observed chemical properties of benzene.

Kekule further added that the benzene ring contains three carbon-carbon double bonds which alternate between their position so rapidly that the two structures he suggested cannot be distinguished. The rapid alternation of double bond is because pi (π) electrons are free to move over the six carbon atoms of entire benzene molecule. This implies that Kekule's structures cannot represent the actual structure of benzene. Instead, the real structure of benzene is resonance hybrid of the two Kekule's structures.



Kekule resonance structures

resonance hybrid

Kekule's proposal survived for years as it was consistent with many experimental observations. However, his model was challenged for the following reasons:

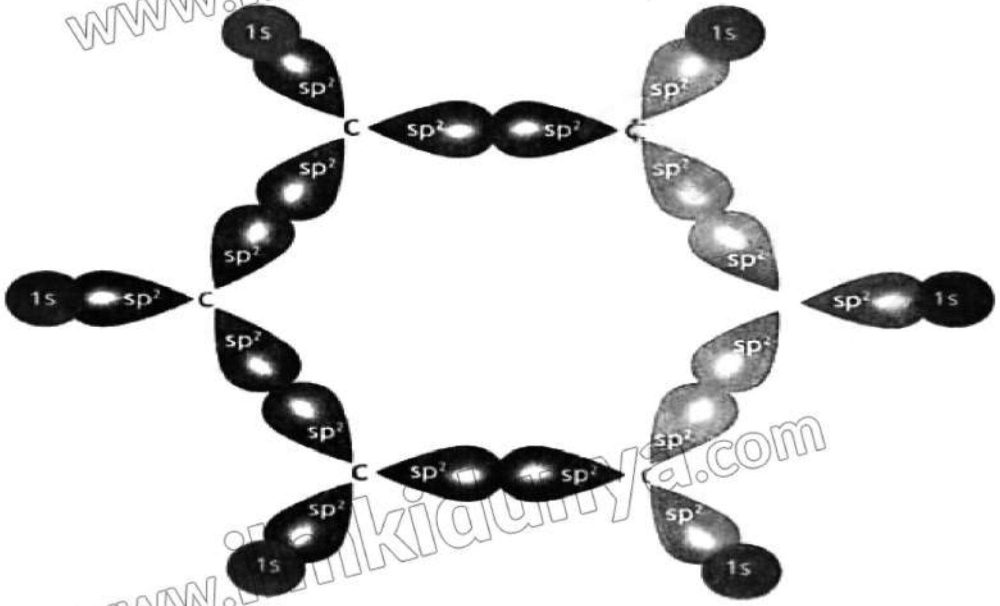
i. Why benzene does not react in a way alkenes do, if it has double bonds like alkenes?
ii. If benzene has three double bonds, why it cannot add three moles of bromine?
iii. Why benzene favours substitution reactions over addition reactions?

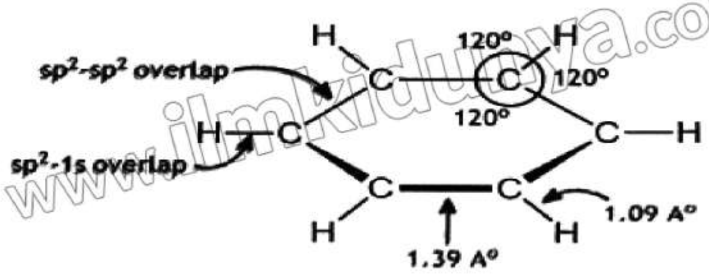
Taking into consideration the criticism against Kekule's structure, different models were tried in order to solve the problem of structure of benzene molecule.

Do You Know?
Resonance is the spreading of electron pairs (lone pair or pi electron pair) across several adjacent atoms in a molecule or ion. Such molecules or ions have more than one Lewis structures because a single Lewis structure cannot show the true picture of distribution of electrons among atoms. Remember that the position of atoms remains unchanged during resonance.

Atomic/Molecular Orbital Model of Benzene

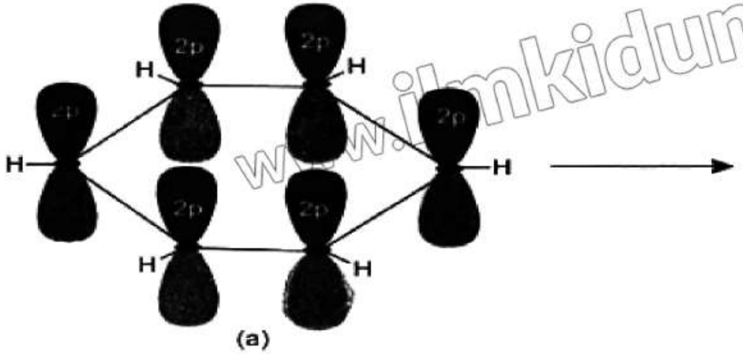
In 1930s, Linus Pauling developed the concept of hybridization and theory of resonance. These two concepts gave the first adequate explanation of the structure of benzene. The carbon skeleton of benzene forms a regular hexagon with C-C-C and H-C-C bond angles of 120°. Each carbon of the ring exhibits sp^2 hybridization forming sigma (σ) bonds to two adjacent carbon atoms, by the overlap of sp^2-sp^2 hybrid orbitals, and one σ bond to hydrogen by, the overlap of sp^2–1s orbitals.



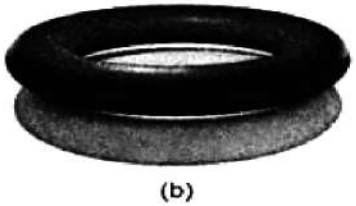


It was determined experimentally that the bond length between carbon atoms in benzene molecule is 1.39 A° which falls in between the bond lengths of a carbon-carbon single bond (1.54 A°) and carbon-carbon double bond (1.30 A°). This also shows that the carbon-carbon bonds are neither double nor single, rather partial double bonds.

Each carbon atom also has a single unhybridized 2p orbital that contains one electron. These six 2p orbitals lie perpendicular to the plane of the ring and overlap to form a continuous pi (π) electron cloud encompassing all six carbon atoms. The electron density of the pi electron (π) system of a benzene ring lies in one torus (a doughnut shaped region) above the plane of the ring and in a second torus below as shown.



(a) The carbon-hydrogen network showing six unhybrid 2p orbitals with one electron each



(b) The pi (π) electron cloud like two torus above and below the plane of the ring.

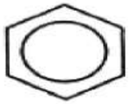
The Resonance Model of Benzene

A molecule that can be represented by more than one Lewis structure show resonance. Resonance is the delocalization of electron pairs across atoms in a molecule. The true structure for such molecule is resonance hybrid of its possible Lewis structures. The different possible Lewis structures for such molecules are called resonance contributing structures or canonical structures.

The actual structure of the benzene molecule is a resonance hybrid, representing an average of all the possible structures.

Interesting Information
The resonance structures are hypothetical so they cannot exist.

Limitations of Kekule's Structure



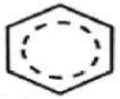
The resonance hybrid is shown by a circle inside the ring. The circle shows six delocalized pi (π) electrons in the six 2p-orbitals on the six carbon atoms of the ring.

Although benzene molecule exists in more than one resonance contributing forms, but we use a single Kekule's structure because of two reasons.

- i. it justifies the tetravalent nature of carbon and electron count in the benzene molecule.
- ii. it easily represents the movement of electrons in reactions mechanisms.

Accurate Structure of Benzene

Johannes Thiele, in 1899, was the first chemist who proposed the concept of partial valence concept for explaining the unexpectedly high stability of benzene molecule.



Thiele structure

Werner Heisenberg described the concept of resonance by applying quantum mechanics. Finally, Linus Pauling developed resonance in 1933 and applied on all organic molecules.

Interesting Information

Chemists of nineteenth century faced the challenge of determination of structure of benzene molecule, but ultimately addressed with the advent of quantum mechanics. In 1931, Linus Pauling was the first chemist who explained the concept of resonance. He concluded that the benzene molecule is resonance hybrid of many Lewis structures. His findings led to a suitable explanation for high stability of benzene molecule. The concept of resonance integrated the structure of benzene molecule with its observational data.

Concept Assessment Exercise 8.2

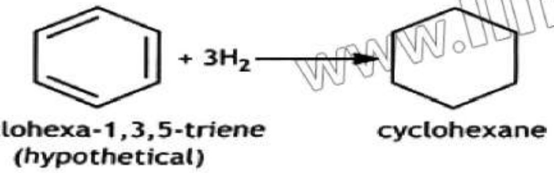
- Draw the two Kekule structures of benzene. How did Kekule switch to closed structure of benzene molecule, although other chemists tried open structure for it?
- Define resonance in benzene. Why is benzene exceptionally stable than alkenes?

8.2.1 Resonance and Resonance Energy of Benzene

The difference in energy between the benzene molecule and hypothetical 1,3,4-cyclohexatriene is called resonance energy or delocalization energy. This energy indicated the extra stability of the benzene molecule due to the delocalization of the π-electron cloud over the six carbon atoms. To calculate the resonance energy of benzene, we compare the enthalpies of hydrogenation of cyclohexene, 1,2,3-cyclohexatriene (hypothetical) and benzene.

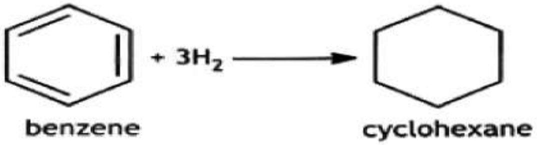
$\Delta H = -120$kJ/mol (experimental)

Based on the above experimental data, a molecule with three double bonds should theoretically release three times the heat of hydrogenation of cyclohexene.



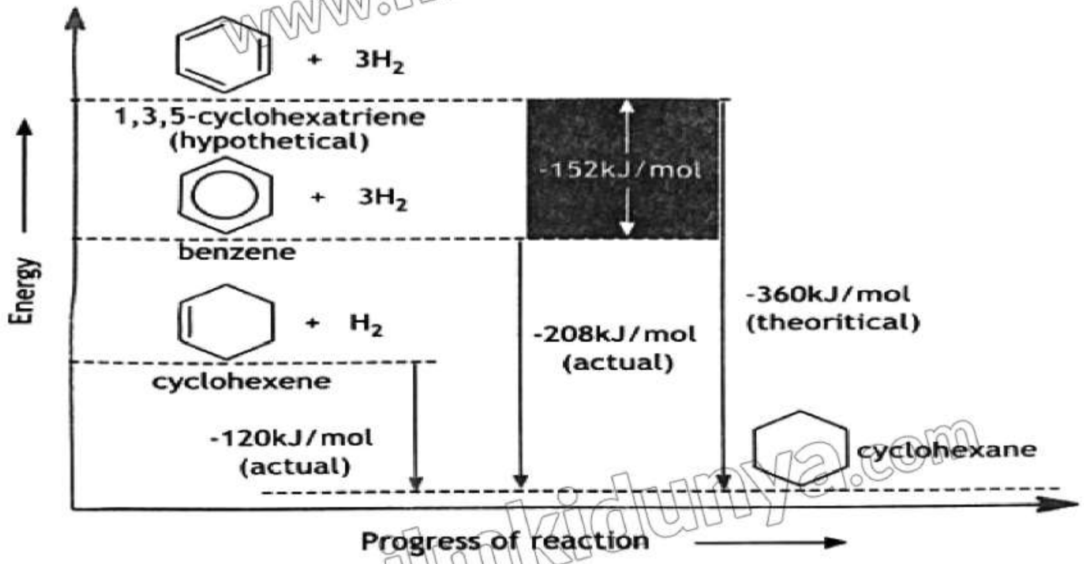
$\Delta H = 3 \times -120\text{kJ/mol} = -360\text{ kJ/mol}$ (calculated)

By contrast, benzene is reduced only very slowly to cyclohexane under these conditions. It is reduced more rapidly when heated under very high pressures of hydrogen.



$\Delta H = -208\text{ kJ/mol}$ (actual value)

The enthalpy of hydrogenation per double bond varies somewhat with the degree of substitution of the double bond; for cyclohexene, $\Delta H = -120\text{ kJ mol}^{-1}$. If we consider benzene to be 1,3,5-cyclohexatriene, a hypothetical compound with alternating single and double bonds, we might expect its enthalpy of hydrogenation to be $3 \times -120 = -360\text{ kJ mol}^{-1}$. Instead, the enthalpy of hydrogenation of benzene is only -208 kJ mol^{-1}. The difference of 152 kJ mol^{-1} between the expected value and the experimentally observed value is the resonance energy of benzene.



8.3 Reactivity of Benzene

Benzene has highly stable delocalized pi (π) electrons ring which remains intact in most reactions. Benzene shows different types of reactions such as addition reactions, oxidation reactions and electrophilic substitution reactions. We will study all these reactions one by one.

8.3.1 Electrophilic Aromatic Substitution Reactions

Electrophilic aromatic substitution reactions involve the attack of electrophile on the high electron density of the delocalized pi-(π) electron ring of benzene molecule. Electrophilic aromatic substitution reactions involve three steps:

- Attack of π-electrons of benzene ring on electrofphile, followed by partial breaking of the aromatic ring.
- Formation of an intermediate called the arenium ion.
- Elimination of hydrogen ion (H^+) from the intermediate, reforming the aromatic ring.

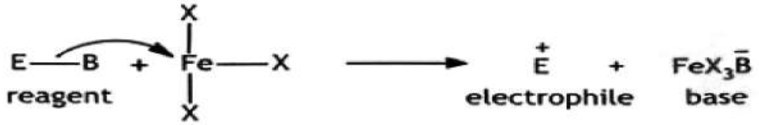
In electrophilic aromatic substitution reactions of benzene molecule, an electrophile attacks the benzene molecule and partially breaks the delocalized π-electron ring. The electrophile replaces a hydrogen atom on benzene molecule. The delocalized π-electron system restores as soon as electrophile replaces the hydrogen atom of the benzene molecule. This justifies the significant stability of benzene molecule due to delocalized π-electron ring.

Key Information
The delocalized pi (π) electron system in benzene molecule is far more stable than the localized pi (π) bonds in alkenes. This is why the benzene molecule always requires a catalyst for electrophilic substitution reactions of benzene.

The general mechanism of electrophilic aromatic substitution reactions involves three steps:

i. Generation of the electrophile.

An electrophile is generated first from a suitable reagent with the help of a Lewis acid catalyst, like FeX_3.

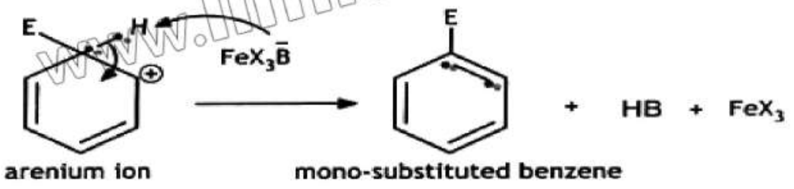


ii. Reaction of electrophile with benzene.

The pi (π) electrons of benzene molecule attack on electrophile to make a cation intermediate called arenium ion. In this intermediate the aromatic ring is partially broken.

iii. Removal of hydrogen by a base.

A Lewis base takes the hydrogen from the arenium ion, resulting in the formation of a mono-substituted benzene. This restores the delocalized π-electron ring of benzene molecule.

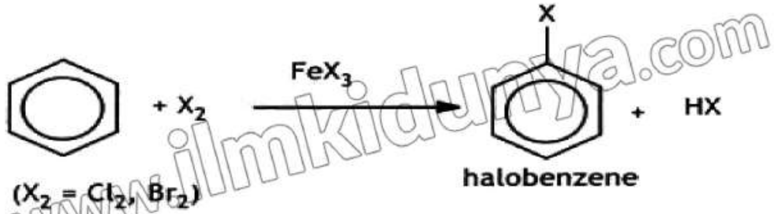


Some important electrophilic aromatic substitution reactions of benzene are given here.

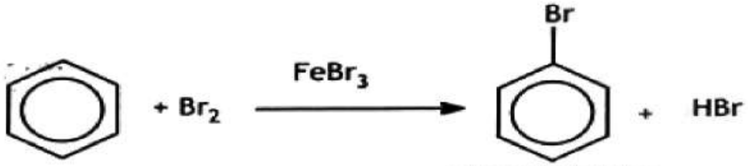
Halogenation

Halogenation is a reaction in which a halogen molecule reacts with benzene molecule, resulting in substitution of a hydrogen atom on the benzene ring with a halogen atom. This reaction takes place in the presence of a catalyst, typically iron (III) halide.

General Reaction:



For example, when a benzene molecule reacts with bromine in the presence of the catalyst iron (III) bromide ($FeBr_3$), bromobenzene is formed.



bromobenzene

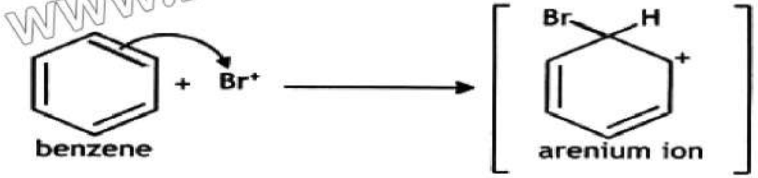
Mechanism of Bromination of Benzene:

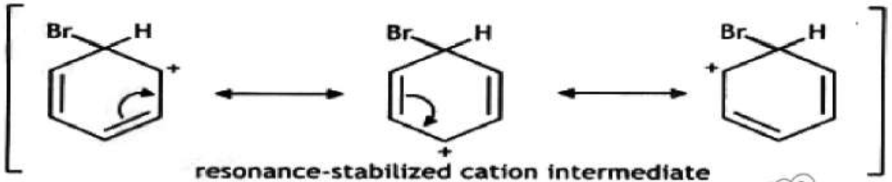
In this reaction, the bromine molecule (Br_2) acts as a Lewis base because it donates a pair of electrons. On the other hand, iron(III) bromide ($FeBr_3$) acts as a Lewis acid as it accepts an electron pair.

Step 1: Generation of Electrophile.

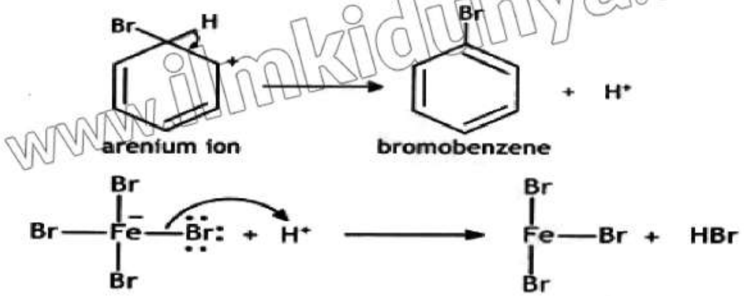
The Br^+ cation (bromonium ion) attacks on benzene ring to form an intermediate called arenium ion. Remember that the curly arrows show the movement of a pair of electrons.

Step 2: Generation of Arenium Ion/Sigma (δ) Complex.

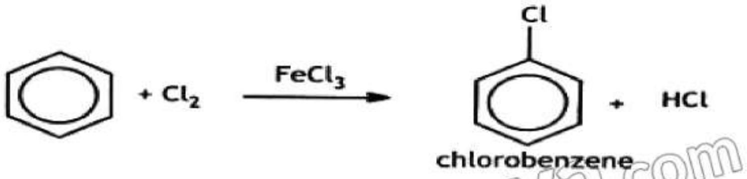




Step 3: Deprotonation/Regeneration of Catalyst.



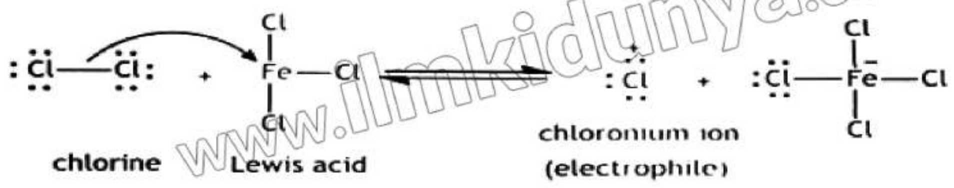
A similar reaction happens when chlorine gas is bubbled through benzene at room temperature in the presence of a catalyst, such as aluminium chloride. The products of this electrophilic substitution are chlorobenzene and hydrogen chloride.



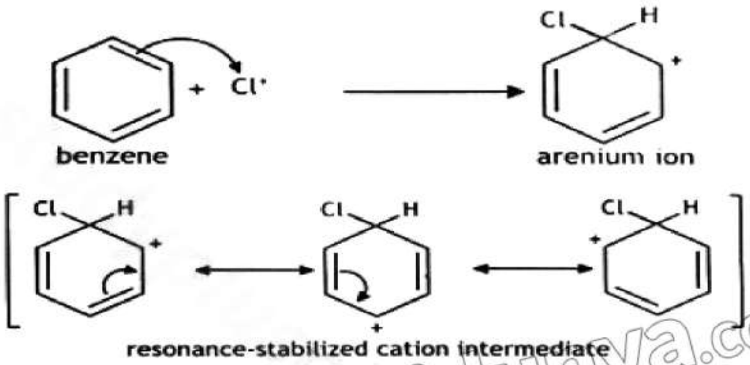
Mechanism of Chlorination of Benzene.

It follows the same pattern as bromination of benzene as shown.

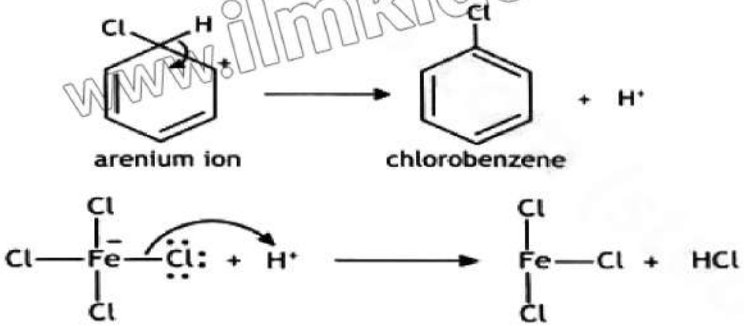
Step 1:



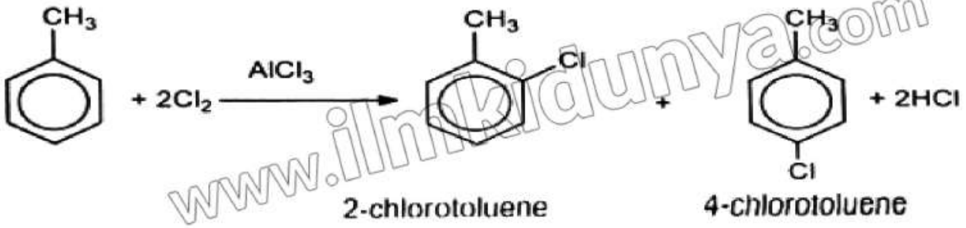
Step 2:



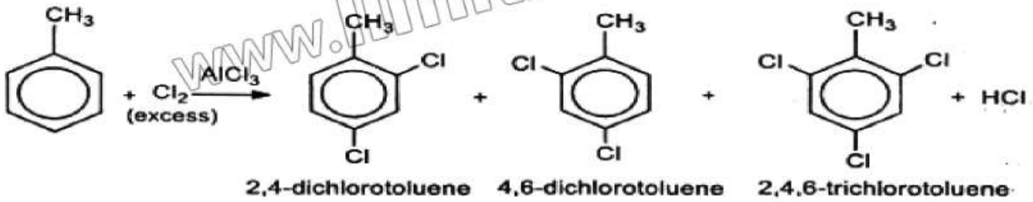
Step 3:



Halogenation of methylbenzene or other alkylarenes involved electrophilic attack at positions 2 or 4. The alkyl substituents are ring activating and increase electron cloud at position 2 and 4 in benzene ring. Similarly, hydroxyl group and amino groups also activate the benzene ring by pumping electrons in it through p-orbitals bridge. When methylbenzene is reacted with chlorine gas, using an anhydrous aluminium chloride catalyst, two products can be formed.

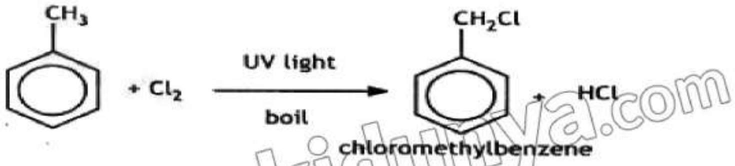


If excess chlorine gas is used, we get a mixture of 2,4-dichlorotoluene, 2,6- dichlorotoluene and 2,4,6-trichlorotoluene.

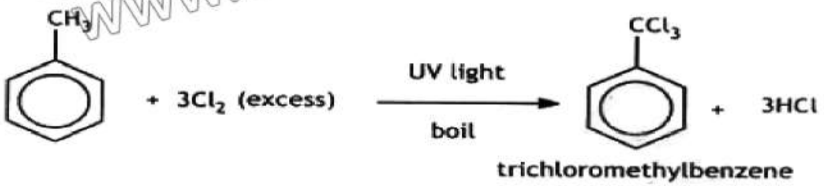


Side Chain Halogenation

When chlorine will react with alkyl side chain of alkylbenzene in the presence of ultraviolet (UV) light or strong sunlight. This reaction follows free-radical substitution mechanism. When chlorine gas is passed over boiling methylbenzene in the presence of UV light, the following reaction takes place.



Remember that there is no substitution into the benzene ring under these conditions. In excess of chlorine, eventually all three of the hydrogen atoms on the methyl side-chain will be replaced by chlorine atoms.



Nitration

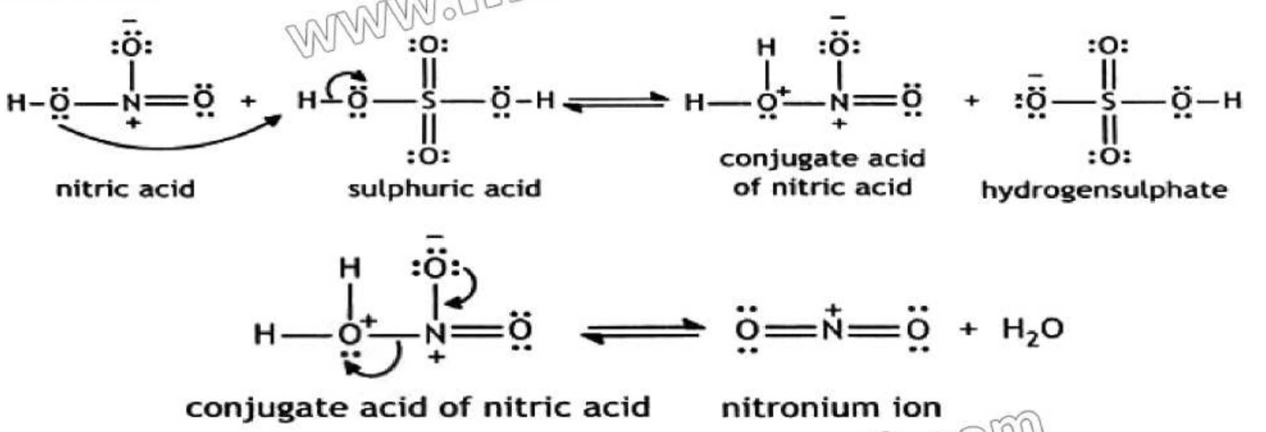
The nitration of benzene is another example of electrophilic substitution. Nitration refers to the introduction of nitro group(—NO_2) in benzene molecule. In this reaction the electrophile is the nitryl cation or nitronium ion (NO_2^+). This is made from a mixture of concentrated nitric acid and concentrated sulfuric acid.

This 'nitrating mixture' is refluxed with benzene at between 25 °C and 60 °C to make nitrobenzene.

Mechanism

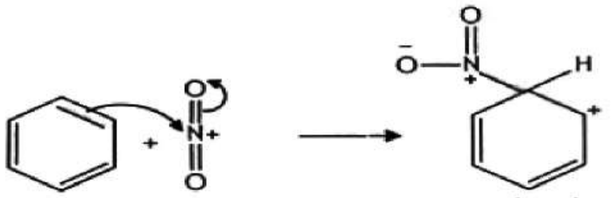
Step 1: Generation of Nitronium ion.

In this step, the electrophile nitronium ion (NO_2^+) is generated, when nitric acid reacts with sulphuric acid.



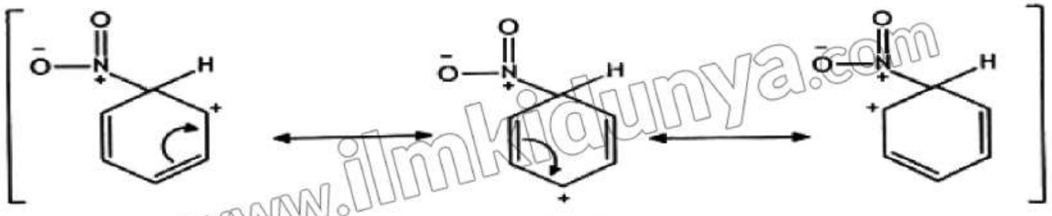
Step 2: Formation of Arenium ion (Sigma Complex)

In this step, the electrophile (NO_2^+) attacks the high electron density of pi (π) bonding system of benzene. A pair of electrons from the benzene ring is donated to the nitrogen atom of nitronium ion (NO_2^+) forming covalent bond. Resultantly, the delocalized pi (π) electron ring of benzene molecule is broken giving rise to an unstable intermediate called arenium ion.



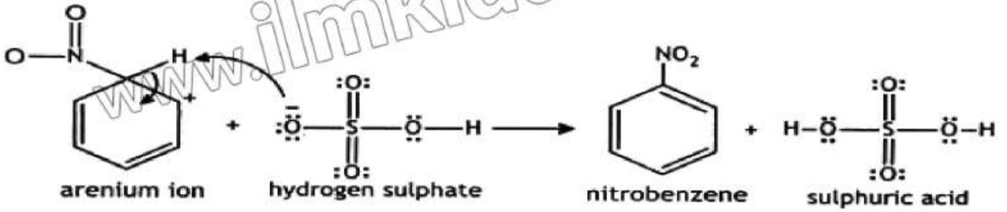
arenium ion
(resonance stabilized)

The arenium ion has four pi (π) electrons and a positive charge delocalized over five carbon atoms. It undergoes resonance stabilization as follows:



arenium ion
(resonance stabilized)

Step 3: Deprotonation of Arenium ion/Regeneration of Catalyst.



Finally, the delocalized pi (π) electrons ring of benzene molecule is restored when two electrons are donated to the ring from heterolytic cleavage of C—H bond, leaving hydrogen ion behind. In this way the stability of benzene ring is retained.

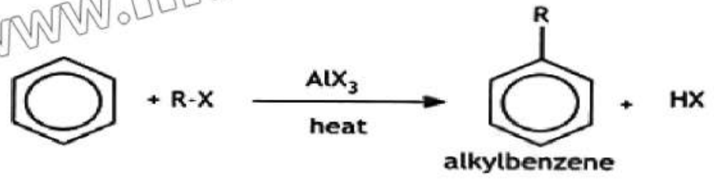
Friedel–Crafts reaction

In 1877 the French chemist Charles Friedel and his co-worker (an American chemist James Crafts) discovered that when benzene is heated with a alkyl halide and acyl halide in presence of aluminium chloride, alkylbenzene and phenylketon are obtained respectively. They studied the following two reactions.

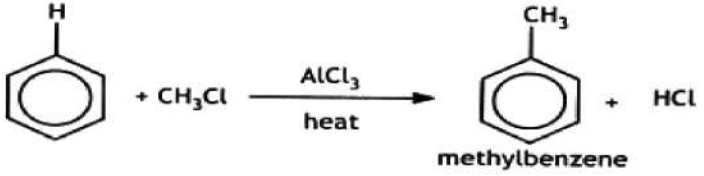
(i) Alkylation

The introduction of alkyl group in benzene ring when it is heated with chloroalkane in the presence of aluminium chloride (Lewis acid) is called Fridel-Craft alkylation. The aluminium chloride acts as catalyst in this reaction.

General Reaction:



Example:



Mechanism:

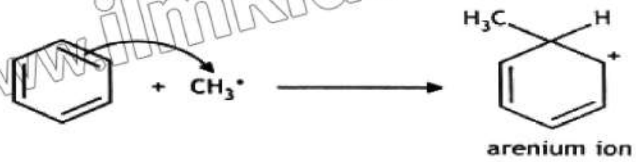
Step 1: Generation of Electrophile (CH_3^+).

In this step, the electrophile is generated which is methyl cation in this reaction.

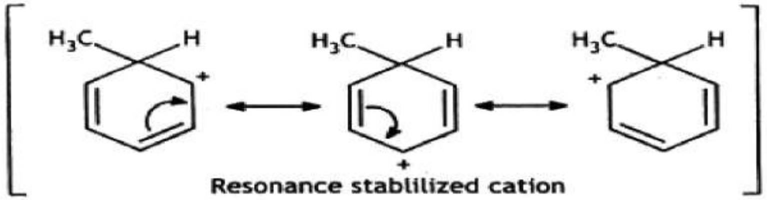
$$CH_3-Cl: + AlCl_3 \longrightarrow CH_3^+ + AlCl_4^-$$

Step 2: Formation of Arenium ion.

This step involves the attack of electrophile (CH_3^+) on benzene ring, rupturing the ring and gives arenium ion.

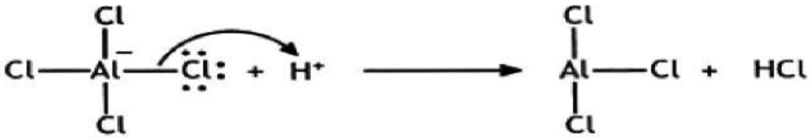


The arenium ion undergoes resonance stabilization as follows:



Step 3: Deprotonation of Arenium ion/Regeneration of Catalyst.

In this step, the pi electron cloud of benzene molecule is restored by loss of hydrogen ion and catalyst is regenerated.



The aluminium chloride is regenerated at the end of reaction, so it acts as catalyst.

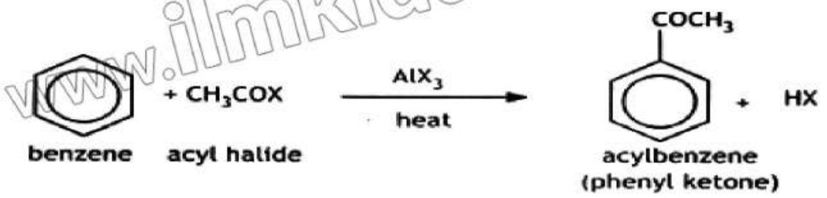
Concept Assessment Exercise 8.3

- How does chloroethane react with benzene molecule? Name the electrophile and end product of this reaction.
- Which two roles are being played by aluminium chloride ($AlCl_3$) in Friedel-Craft alkylation?

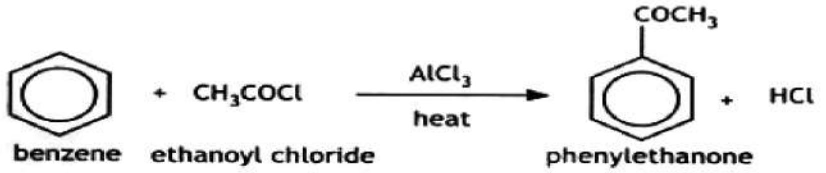
ii. Acylation

The reaction in which acyl group is introduced in benzene ring when acyl halide is reacted with benzene in presence of catalyst, aluminium trihalide (AlX_3) is called acylation. The product obtained in this reaction is phenylethanone (phenylacetone).

General Reaction:



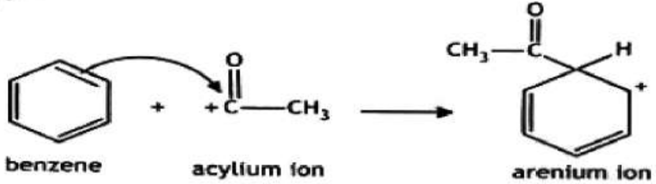
Example:



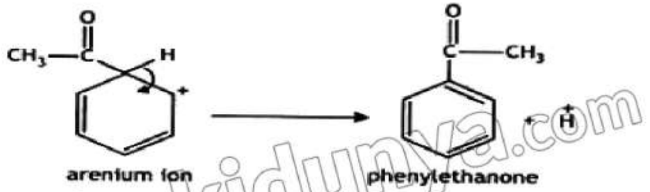
Mechanism:

Step 1: In this step, an electrophile called acylium ion (acyl cation) is generated.

Step 2: Then acyl cation reacts with benzene to form the intermediate arenium ion.



Step 3: The final step involves rearrangement where the benzene pi (π) electron ring is restored forming phenylethanone. The hydrogen ion eliminated reacts with tetrachloroaluminate(III) to regenerate aluminium chloride ($AlCl_3$).



$$[AlCl_4]^- + \overset{+}{H} \longrightarrow AlCl_3 + HCl$$

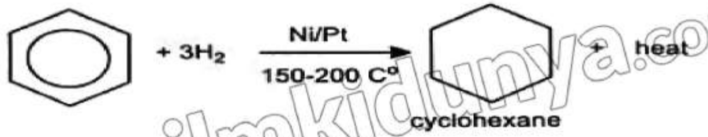
8.3.2 Addition Reaction

Benzene has a delocalized π-electron cloud, which typically allows for addition reactions. However, under normal conditions, benzene does not undergo addition reactions as readily as alkenes. This is because the π-electron cloud in benzene is part of a highly stable conjugated system known as an aromatic ring. The delocalized π-electrons in the aromatic ring of benzene circulate continuously across all six carbon atoms, making them less available for chemical reactions. Breaking this stable aromatic system requires harsh or vigorous conditions, such as high temperature, high pressure, or strong reagents.

The aluminium chloride ($AlCl_3$) carries halogen with itself in Friedel-Craft reaction, so it is called halogen carrier.

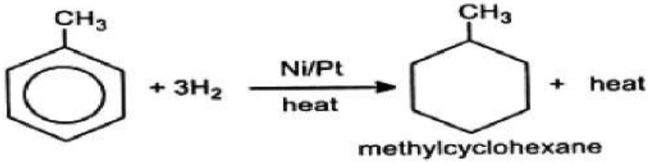
Hydrogenation

Hydrogenation is the addition of hydrogen molecules across the carbon atoms of benzene molecule, converting it into cyclohexane. This reaction takes place in the presence of catalysts, like nickel (Ni), platinum (Pt) or palladium (Pd) at temperature 150-200 C° and 20-30 atm pressure.



Role of Catalyst: The catalyst used provides surface area to hydrogen molecules breaking them into individual hydrogen atoms. The catalyst interacts with benzene molecule making it more reactive by weakening its pi (π) electron system. Six hydrogen atoms add to the six carbon atoms of benzene molecule to give cyclohexane, breaking the aromatic ring. The cyclohexane molecule releases from the catalyst surface and the catalyst is ready for more reactions.

Similarly, methylbenzene is hydrogenated to methylcyclohexane under the same reaction conditions.



Difference Between Addition Reactions and Electrophilic Substitution Reactions

The key difference between addition reactions and electrophilic aromatic substitution reactions is what happens to the intermediate (a positively charged ion) formed in the first step of their mechanisms when an electrophile attacks. Remember from grade 11 that the halogenation of an alkene is a two-step process: first, a bridged halonium ion intermediate is formed, and

The unsaturation in benzene seems that it shows addition reactions readily like alkenes, but benzene is quite reluctant to undergo addition reactions. Unlike alkenes, it requires rather harsh conditions to show addition reactions.

then in the second step, a halide ion attacks the positively charged intermediate, giving a saturated product.

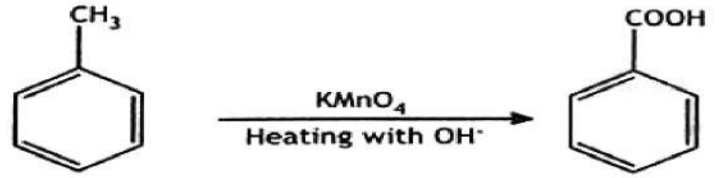
In contrast, the electrophilic aromatic substitution reaction of benzene involves the formation of a cation intermediate (arenium ion) in the first step. In the second step, the cation is stabilized by the loss of a hydrogen ion, rather than by the attack of a nucleophile (anion). This process results in a nucleophile substituting a hydrogen atom in the benzene molecule, leading to the formation of a substituted product.

8.3.3 Oxidation Reactions

Benzene can show oxidation reactions as other hydrocarbons do. However, unlike alkenes and alkynes, benzene and alkanes are quite resistant to oxidation by general oxidizing agents. However, they can be oxidized under certain conditions. In alkylbenzenes, the aliphatic side chain is more likely to be oxidized than the aromatic ring, although this requires prolonged heating.

The presence of the benzene ring in an alkylarene, such as methylbenzene, has significant influence of side chain reactions. For example, alkanes are not usually oxidized by a oxidizing agent such as potassium manganate(VII), but the methyl side-chain of methylbenzene is oxidized by hot alkaline or hot acidic potassium manganate(VII) to produce benzoic acid. This is because the benzene ring alkylarenes makes the alkyl side-chain more reactive.

In alkylbenzenes, the oxidation reactions can involve both aromatic ring and side alkyl chain of alkylarenes, depending upon the conditions used. Oxidation of benzene ring requires more aggressive conditions while alkyl side-chain can be oxidized under a bit gentle conditions. The carbon of alkyl side-chain closest to the benzene ring is oxidized to carboxylic acid group. In this topic, we will limit ourselves to the oxidation of the side chain on the benzene ring, resulting in benzoic acid.

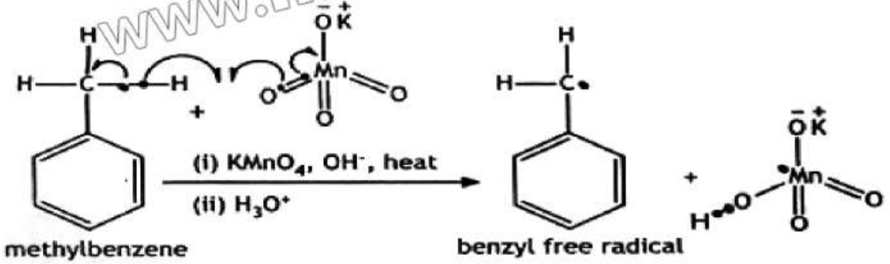


methylbenzene benzoic acid

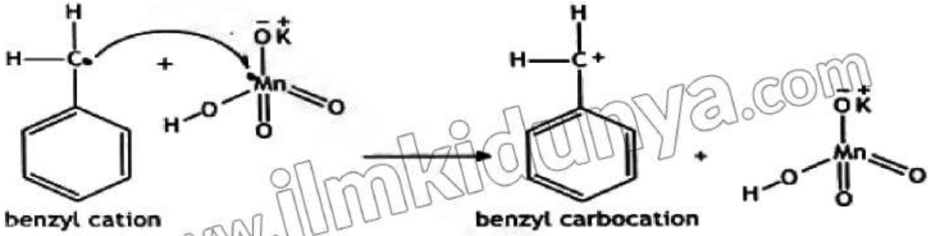
1-ethyl-3-methylbenzene benzene-1,3-dioic acid

Mechanism involves the following three steps:

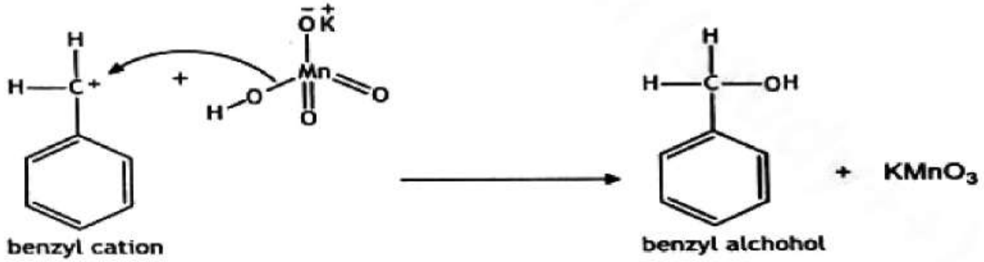
i. Hot alkaline potassium manganate (VII) abstracts a benzylic hydrogen atom as a free radical from the methyl side chain of methylbenzene, oxidizing it and leaving behind a benzyl radical.



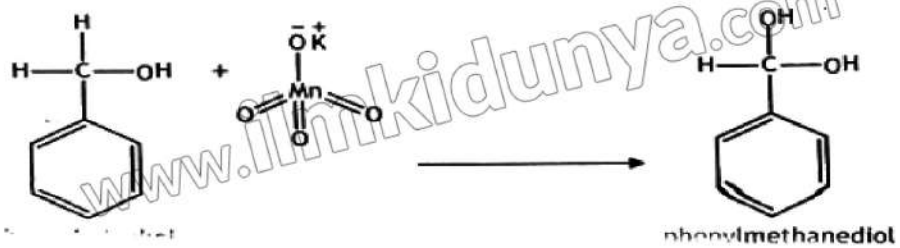
The benzyl free radical changes to benzyl cation after reacting with the odd-electron intermediate of potassium manganate (VII).



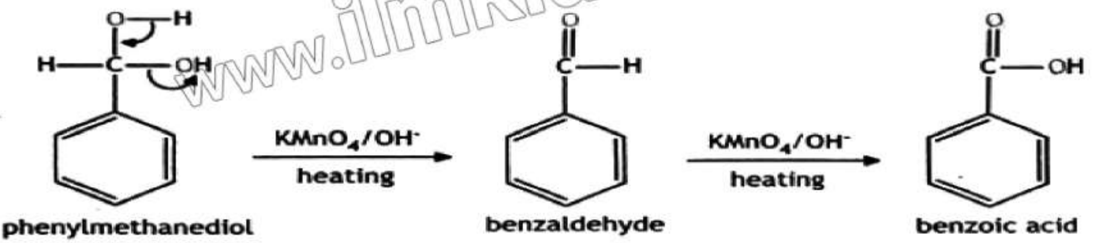
The benzyl cation abstracts hydroxyl group (-OH) from the potassium hydrogenmanganate, which is unstable.



In the next step, the alkaline potassium manganate (VII) further oxidizes benzylic carbon to give diol, as in the previous step.



Phenylmethanediol is oxidized by the same oxidizing agent to benzaldehyde which further oxidizes to benzoic acid.



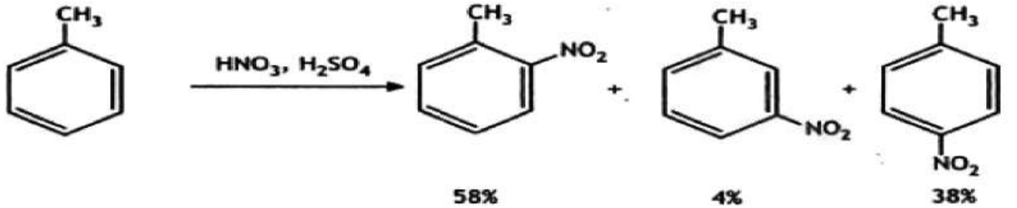
In these reactions, the first carbon of the side chain is oxidized always. In alkyls bigger than methyl, all carbon atoms next to the first one give rise to carbon dioxide formation.

8.4 Electrophilic aromatic substitution in substituted arenes

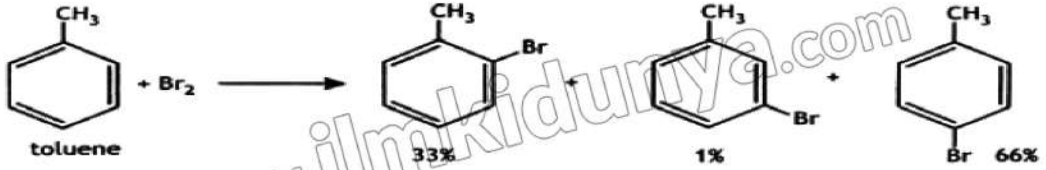
We have already studied that benzene molecule can undergo electrophilic aromatic substitution reactions, forming only one mono-substituted benzene. The substituent attacks any carbon in the benzene ring because all the six carbon atoms are equivalent.

When a second electrophile reacts with a monosubstituted benzene ring, it forms three different disubstituted benzene isomers. This occurs because the benzene ring offers three possible positions (carbons) where the second substituent can attach relative to the first. The position of the second electrophile in each of these isomeric disubstituted benzene molecules varies in relation to the position of the first substituent on the ring.

For example, methylbenzene reacts with nitric acid and sulfuric acids, forming three disubstituted benzene isomers with the ratio given.



If this reaction is carried out in a random way, the distribution of the three isomers formed would be 40:40:20. It indicates that we obtain two parts of 2-nitromethylbenzene, two parts of 3-nitromethylbenzene and one part of 4-nitromethylbenzene. Other mono-substituted benzene compounds can also undergo such random aromatic substitution reactions as given below.



In the light of the above data, it is concluded that

i. *the orientation* of the incoming group is determined by the nature of the substituent already bonded to the ring, rather than the nature of the incoming electrophile.

ii. Some substituents direct the incoming electrophile to the 2-position (ortho position) and 4-position (para position), while others guide it to the 3-position (meta position).

There are three possible positions on the benzene ring where a second group (electrophile) can attack. The position of this attack is determined by the nature of the substituents already bonded to the benzene ring. Based on this, substituents are categorized into two classes.

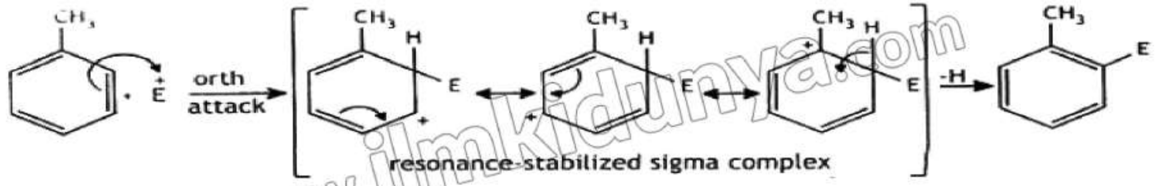
(a) Ring-Activating or Ortho/Para Directing Substituents

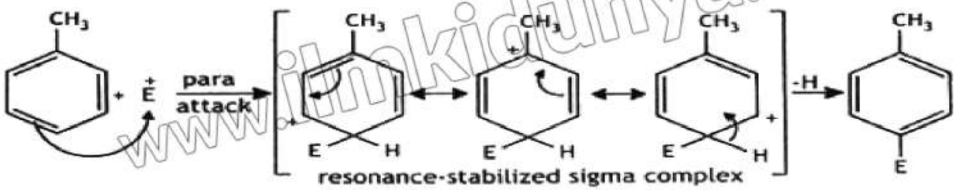
Substituents that increase the reactivity of benzene ring compared to single benzene molecule are called ring-activating substituents. These substituents are capable of donating electrons to the benzene ring through electron-donating resonance effect, increasing electron cloud relatively on all carbon atoms (positions) in benzene ring. This makes benzene molecule more reactive toward the incoming electrophile compared to single benzene molecule itself.

The ring-activating substituents are also called ortho/para directing substituents because they direct the incoming electrophile to the 2- and 4-positions (ortho-para positions). These substituents increase electron cloud at carbon-2 and carbon-4 compared to single benzene molecule. Due to higher electron cloud at carbon-2 and carbon-4 and lower electron cloud at carbon-3 (meta position), the next electrophile will attack ortho and para positions of the benzene molecule.

To explain the 2,4-directing effect of electron-donating substituents we need to focus on the electron distribution pattern in the arenium ion involved in electrophilic aromatic substitution reactions of benzene. Consider the arenium intermediate (sigma complex) formed in electrophilic attack on toluene.

Key Information
The halogen groups are ring-deactivating by electron-withdrawing inductive effect, but ortho-para directing by electron-donating resonance effect. The resonance effect dominates the electron-withdrawing inductive effect, so halogen groups are ortho-para directing groups.

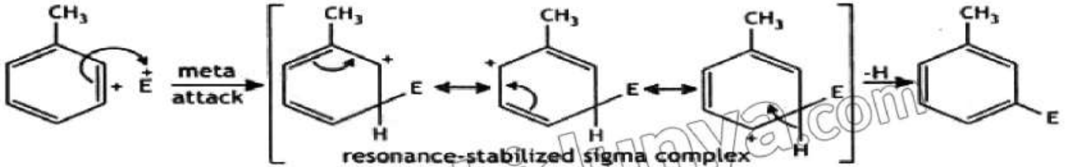




Both in ortho and para attack, a resonance structure is formed possessing positive charge on the carbon directly connected to the substituent. This resonance structure is the most stable one among all because its positive charge is stabilized more than that resulting from the meta attack. Such substituents are ring-activating and ortho para directing.

Inductive effect of substituents in benzene molecule diminishes with distance.

Electron-donating substituents will be more effective at these positions to stabilize the intermediate cation, by spreading out its charge.



On the other hand, in meta attack, none of the three arenium ions has positive charge on the carbon atom directly bonded to the substituent, making alky substituents less effective at this position.

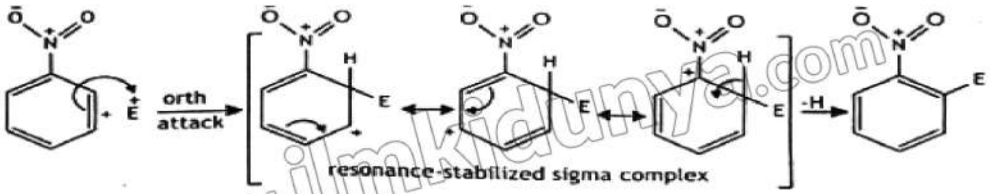
Examples of 2 and 4 directing substituents include alkyl group (-R), hydroxyl group (-OH), amino group (-NH_2), alkoxy group (-OR) and halo group (-X) etc.

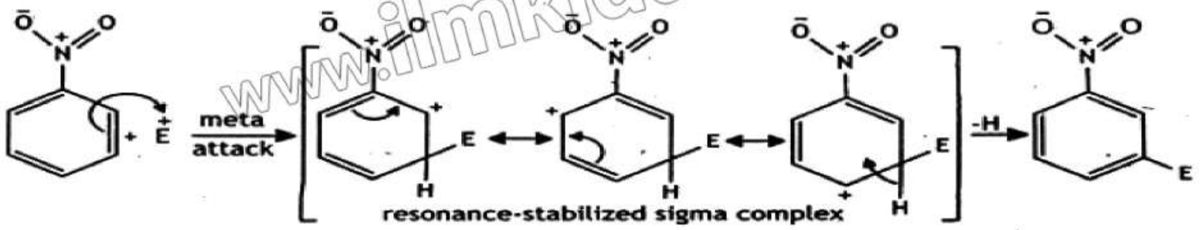
Key Information
All halo group (-X) are ortho and para directing due to resonance effect but deactivating due to inductive effect.

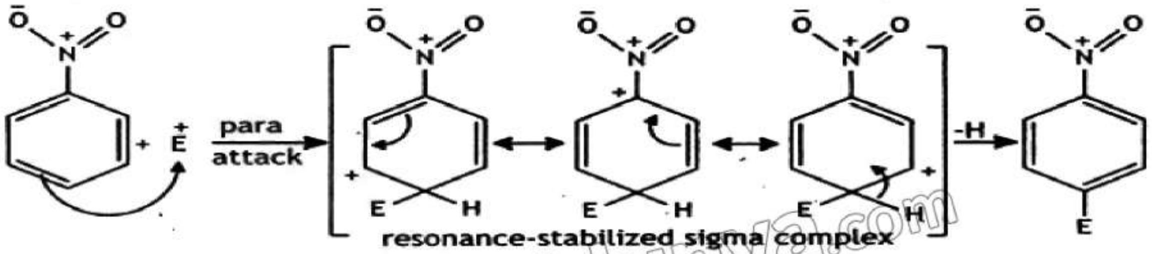
(b) Ring-Deactivating or Meta-Directing Substituents

On the other hand, some substituents direct the incoming electrophile to the carbon-3 (meta position). These substituents withdraw electrons from the benzene ring through inductive effect, making overall benzene ring electron deficient and less reactive. Such substituents possess a partial or full positive charge on the atom directly connected to the benzene ring.

To explain 3-directing (meta-directing) effect of electron-withdrawing substituents, we need to focus on the electron distribution pattern in the arenium ion involved in electrophilic aromatic substitution reactions of benzene. Consider the arenium intermediate formed in nitration of benzene.







In light of this explanation, electron-withdrawing (meta) substituents destabilize the arenium ions of ortho and para attack more than the arenium ion of meta attack. This is because the positive Therefore, such substituents invite electrophiles at meta position and are called meta-directing substituents.

Examples of 3-directing groups: $-NO_2$, -CHO, -COOH etc

Key Information
The substituents that direct the incoming electrophile at ortho/para position are called ortha/para directing groups while those inviting electrophile at meta position are called meta directing groups.

Concept Assessment Exercise 8.4

- Why is aldehyde group (-CHO) termed as 3-directing substituent?
- How a 2 and 4-directing substituents release electrons to benzene ring?

KEY POINTS

- Benzene was discovered by Michael Faraday.
- The name aromatic comes from the word "aroma" meaning fragrance. Benzene was obtained from benzoic acid which, in turn, was extracted form the gum of benzoin, a resin of balsam tree.
- It was found that all aromatic compounds do not give pleasant fragrance.
- All aromatic compounds contain at least one benzene ring so aromatic compounds were declared the benzene ring containing compounds.

- **The x-ray diffraction technique proved that the molecular formula of benzene molecule is C_6H_6 which suggests low hydrogen-to-carbon ratio (H:C).**
- **The molecular formula of benzene also proposes high unsaturation in its molecule, so it shows addition reactions.**
- **Benzene molecule, however, shows addition reactions less readily than alkenes which means that benzene is highly stable.**
- **The remarkable stability of benzene molecule is due to delocalization of pi (π) electron cloud in the ring.**
- **The delocalization of pi (π) electron cloud on unhybrid p-orbitals bridge on six carbon atoms of benzene ring is called resonance.**
- **Resonance gives extra stability and lower energy to benzene ring compared to hypothetical 1,2,3-cyclohexatrience molecule that has localized pi (π) bonds.**
- **Benzene has no defined structure like water because it has no pi (π) bond at fixed position. Rather, its pi (π) bonds are circulating across benzene ring continuously.**
- **There are many structures that contribute to understanding actual structure of benzene. These structures are called resonance contributors.**
- **Kekule, after 40 years struggle, in 1864 saw a daydream, watching a snake biting its tail. He was the first to propose that benzene has ring structure. Before Kekule, all chemists thought benzene to be having open structure.**
- **Kekule, however, failed in understanding that benzene has equal carbon-carbon bond lengths and bond strengths.**
- **A German chemist, Johannes Thiele, in 1899, presented the idea of partial double bonds between carbon atoms in benzene showing delocalized pi (π) bonds.**
- **The carbon-carbon bonds in benzene are neither single nor double, rather in between (partial double bonds).**
- **Benzene shows substitution reactions like alkanes and addition reactions like alkenes.**
- **The exceptional high stability of benzene is attributed to resonance.**
- **Resonance is the delocalization of pi (π) electron cloud in benzene ring on the unhybrid p-orbital bridge of six carbon atoms resulting in continuous circulation of pi (π) electron cloud.**
- **Benzene shows addition reactions under vigorous conditions like hydrogenation in the presence of nickel catalyst to give cyclohexane.**
- **Alkylbenzene undergoes oxidation of side alkyl chain in potassium manganate(VII) and produces carboxylic acid.**
- **Benzene can show electrophilic substitution reactions involving breakage of pi (π) electron ring forming an intermediate (arenium ion). After very short interval, the pi (π) electron ring is restored and give rise to substituted benzene.**
- **The attack of second electrophile on benzene ring is dictated by the substituent already attached to the ring.**
- **If the substituent bonded to the ring is electron donating, it means it activates the ring paving the way for the next electrophile to attack carbon 2 and 4 (ortho/para directing).**
- **In case, the group already bonded to the ring is electron-withdrawing, it deactivates the ring, removing electron cloud from carbon-2 and 4, relatively making electron cloud greater at position 3 on the ring.**

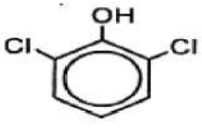
References for Further Information

- Chemistry by Brain Ratcliff, Helen Eccles, John Raffan, John Nicholson, David Johnson and John Newman.
- Chemistry by George Facer
- Chemistry-The molecular nature of matter and change by Silberberg.
- Chemistry by Peter Cann and Peter Hughes.
- Chemistry by Blackman, Bottle, Schmid, Mocerino and Wille.
- Chemistry by Cliff Curtis, Jason Murgatroyd and Divid Scott.
- Chemistry by Christopher Talbot, Richard Harwood and Christopher Coates.

EXERCISE

1. Multiple Choice Questions (MCQs)

i. The IUPAC name of the following compound is



a) 1,3-dichlorophenol
b) 2,6-dichlorophenol
c) 2-hydroxy-1,3-dichlorobenzene
d) 1,5-dichlorophenol

ii. The type of intermolecular forces in benzene are
a) Dipole-dipole forces
b) London dispersion forces
c) hydrogen bonding
d) ion-dipole forces

iii. Which one of the following carbon atom in monosubstituted benzene ring is called meta carbon?
a) carbon 1 b) carbon 2 c) carbon 3 d. carbon 4

iv. The unsaturated nature of benzene can be justified by
a) Hydrogenation
b) nitration
c) alkylation
d) oxidation

v. Which one of the following challenges was faced by Kekule's structure of benzene?
a) benzene is immiscible with water
b) benzene is hexagonal
b) benzene is less reactive than alkenes
d) benzene is planar

vi. Benzene molecule has
a) three double bonds
b) hexagonal planar ring
b) sp^3 hybridization
d) three single bonds

vii. The C-C-C bond angle in benzene molecule is
a) 180° b) 120° c) 90° d) 109.5°

viii. Delocalization of pi (π) electrons in benzene molecule is because
a) each carbon is sp^2 hybridized
b) it is hexagonal
c) it is unsaturated
d) it has 5 unhybrid 2p orbitals

ix. The electrophile used in bromination of benzene molecule is
a) bromide ion
b) bromonium ion
c) aluminium bromide
d) bromine molecule

x. The electrophile used in Friedel-Craft acylation is
a) arenium ion b) acylium ion c) hydrogen ion d) nitronium ion

xi. Aromatic hydrocarbons are found in the extracts of many plants. Their common characteristic is that they have
a) pleasant smell b) benzene unit
c) coloured compounds d) pleasant taste

xii. Which one of the following compounds can easily be nitrated?
a) Benzene b) phenol
c) nitrobenzene d) benzaldehyde

xiii. The most reactive compound, in terms of addition reactions, among the following is:
a) propene b) ethyne c) propane d) benzene

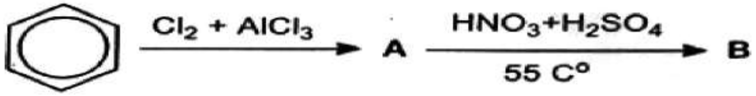
2. Short Answer Questions

i. Cyclohexene decolourizes bromine water whereas benzene cannot, why?

ii. Consider the synthesis of 3-chlorobenzoic acid from methylbenzene given:

b) Name the intermediate A.
c) Write down the reagents and conditions for reaction 1 and reaction 2.

iii. Predict the products and their structural formulae of the following chemical reactions of benzene.



iv. In Friedel-Craft acylation of benzene, the aluminium chloride ($AlCl_3$) acts as Lewis acid. Justify the statement.

v. Explain the difference between halogenation of benzene when reacted with
a. Cl_2 and $AlCl_3$ b. Cl_2 and UV light

vi. Explain how is arenium ion formed in electrophilic substitution reactions of benzene?

vii. State the difference between substitution reactions of alkanes and benzene.

viii. Explain the structure on benzene with the help of atomic orbital treatment.

ix. How can unhybrid 2p-orbitals of benzene adopt a doughnut shape? Show diagram.

3. Long Answer Questions

i. **Benzene reacts with bromine.**
   - a. Write the balanced chemical equation.
   - b. Name the catalyst used.
   - c. What is the visual observation during this reaction?

ii. **Benzene also reacts halogenoalkanes.**
   - a. Name the catalyst used.
   - b. Using 2-bromopropane, write the formula of electrophile formed.
   - c. Name the product of this reaction.
   - d. Write down curly arrows mechanism for this reaction showing all the three steps, i.e generation of electrophile, formation of carbocation and the final product.

iii. **The exceptional stability of benzene molecule is due to resonance in it.**
   - a. Why benzene has delocalized carbon-carbon double bond?
   - b. Why benzene has energy lower than hypothetical cyclohexa-1,3,5-trien?
   - c. The carbon-carbon bonds are partial double bonds. Comment.

iv. **Benzene is more stable compounds than expected by chemists.**
   - a. Explain the stability of benzene molecule with reference to resonance energy.
   - b. Draw the diagram showing resonance energy.

v. **The electrophilic attack on a mono-substituted benzene is governed by the substituent already attached to benzene ring.**
   - a. Define meta-directing substituents. Give two examples.
   - b. Explain the ortho/para and meta-directing effects of different substituents referring to different electron distribution pattern in arenium ion.

vi. **A nitrobenzene undergoes nitration much more slowly than benzene. Explain why this happens and predict how the rate would change if a methoxy group were present instead.**

vii. **Toluene undergoes bromination in the presence of $FeBr_3$. Predict the major product(s) and justify the position(s) of substitution.**

viii. **Chlorobenzene is treated with nitric acid and sulfuric acid. Explain which position the NO_2 group is most likely to occupy and why, considering both resonance and inductive effects of Cl.**

ix. **You are asked to synthesize 4-nitrotoluene from benzene in the fewest steps possible. What steps would you take, and in what order? Justify your sequence based on directing effects.**

x. **Design a synthesis for m-bromonitrobenzene starting from benzene.**