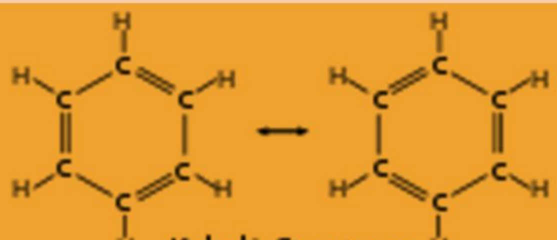
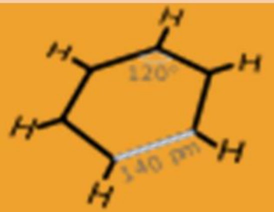
BENZENE AND AROMATICITY

C_6H_6

Benzene
Molecular formula

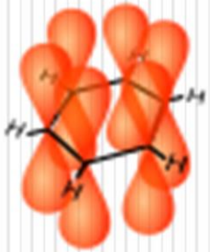


Kekulé Structures
(Isomers)



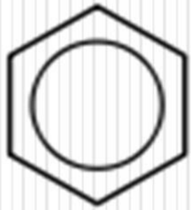
Planar Hexagon
Bond Length 140 pm

Sigma Bonds
sp^2Hybridized orbitals



6 p_z orbitals

delocalized pi
system



Benzene ring
Simplified depiction

Prof. D. K. Kadam

Learning Outcomes

Upon completion of this unit the student shall be able to understand

1. the structure of benzene.
2. Hukel’s Rule for Aromaticity
3. resonance in benzene
4. Electrophilic Aromatic Substitution Reactions like Halogenation, Nitration, Sulphonation, Friedel Crafts Alkylation, Friedel Crafts Acylation,
5. Orientation and reactivity in mono substituted benzene.
6. Mechanism of nueleophilic aromatic substitution

UNIT I 10 Hours

CONTENTS

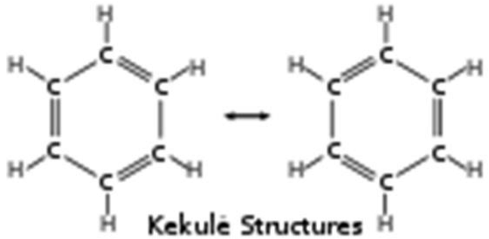
- Introduction and Structure: Evidences for derivation
- Orbital Picture
- Hukel's Rule,
- Resonance in benzene and derivatives.
- Aromaticity
- Mechanism of electrophilic aromatic substitution:
  - Halogenation,
  - Nitration,
  - Sulphonation
  - Friedel Crafts Alkylation
  - Friedel Crafts Acylation,
- Orientation and reactivity in monosubstituted benzene.
- Structure and uses of DDT, Saccharin, BHC and Chloramine

Benzene

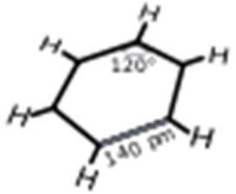
Cyclohexa-1,3,5-triene

C_6H_6

Benzene
Molecular formula

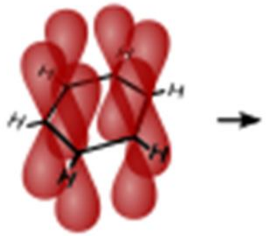


Kekulé Structures
(Isomers)

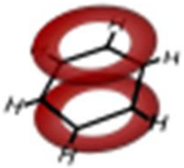


Planar Hexagon
Bond Length 140 pm

Sigma Bonds
sp^3Hybridized orbitals



6 p_z orbitals



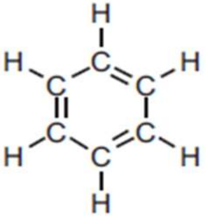
delocalized pi system

Benzene ring
Simplified depiction

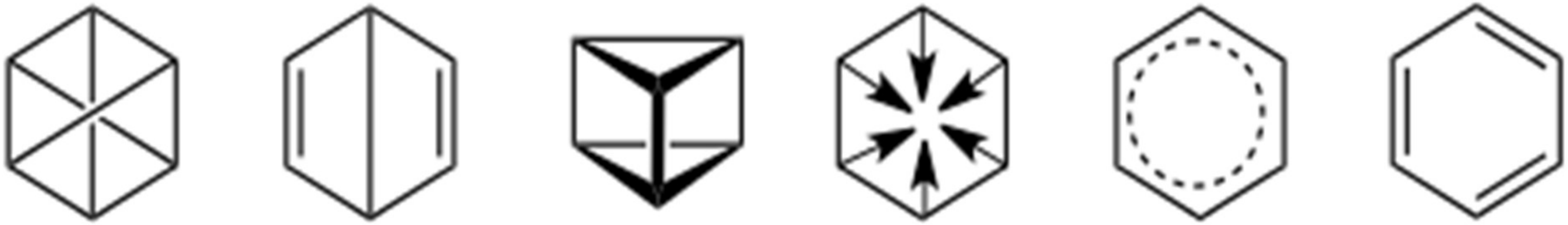
Molar mass	78.11 g·mol^{-1}
Appearance	White solid crystals/ flakes when freezed else low density liquid
Odour	Strong odour
Melting point	5.5 °C
Boiling point	80.1 °C
Density	876.50 kg/m^3
Hazard	potential occupational carcinogen, flammable
Uses	As a petrol additive, benzene increases the octane rating and reduces knocking

BENZENE

Introduction: Structure

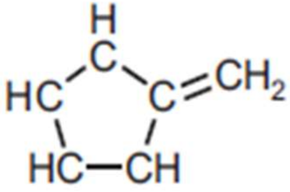


- **Benzene** is an important organic chemical compound with the **chemical formula C_6H_6**.
- Its molecule is composed of **6 carbon atoms** joined in **a ring**, with **1 hydrogen atom attached to each carbon atom**.
- Because its molecules contain only carbon and hydrogen atoms, benzene is classed as a hydrocarbon.
- Historic benzene formulae (from left to right) by

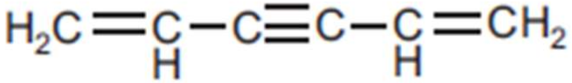


Claus (1867), Dewar (1867), Ladenburg (1869), Armstrong (1887), Thiele (1899) and Kekulé (1865).

Thiele and Kekulé's structures are used today



$H_3C-C\equiv C-C\equiv C-CH_3$



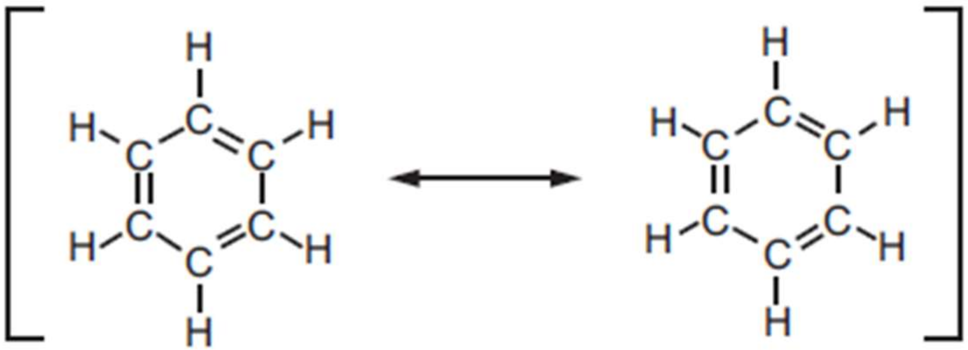
$H_2C=\underset{H}{C}-C\equiv C-\underset{H}{C}=CH_2$

Other proposed structures

Structure of Benzene:

Kekule's formula or structure I of benzene is most accepted because the satisfactory answers it offers to various substitution products as compared with other proposed structures.

Kekule proposed two structures having **alternate single and double bonds** in a ring of six carbon atoms, each having one hydrogen attached.

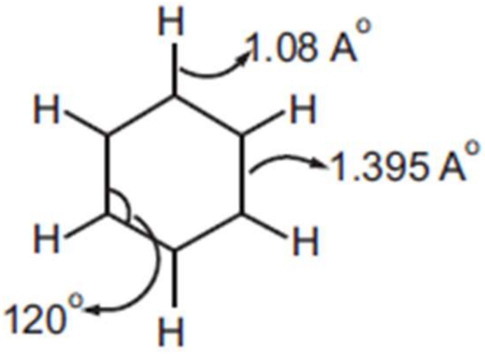


Further, since benzene has alternate **single** and **double** bonds, **two different C-C bond distances** should be there………..**[(C-C) - 1.53** Å and **(C=C) -1.33** Å**].**

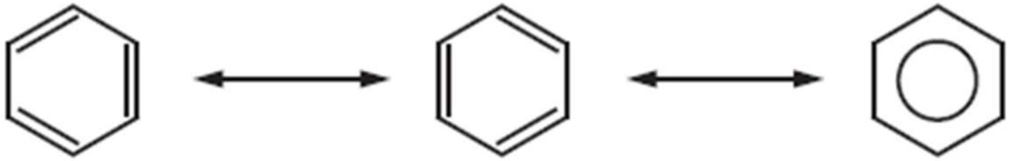
Actual C-C bond length in benzene has been found to be **1.39** Å for all six C-C bonds.

In short it can be said that- "**Benzene is a regular hexagon with identical angles 120°C with molecular formula C_6H_6.**

All six C-C bonds have same length i.e., 1.395 A, which is intermediate of $sp^2 - sp^2$ single bonds 1.46 Å and double bond length 1.33 A "

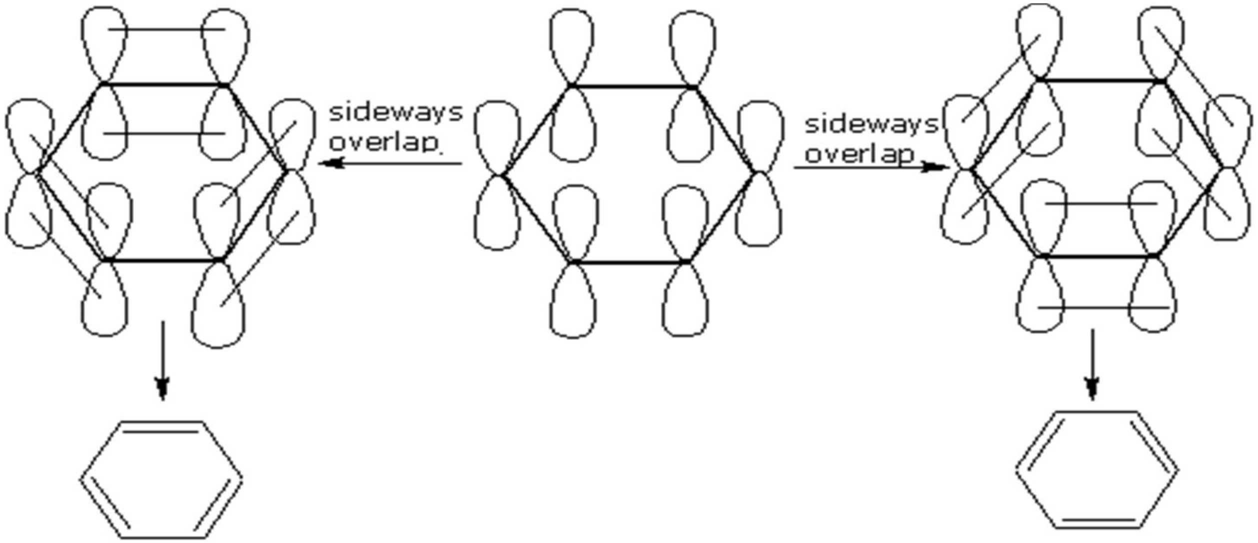


Therefore, the structures of benzene can be shown as below; Benzene is an average of the first two structures. The C-C bond is neither a double nor a single bond, but is something in between


Ia Ib Ic

Orbital picture of Benzene:

Kekule’s structure of benzene suggests that each carbon atom should be triagonal and therefore sp^2 hybridised. This means that each C atom has a 2p orbital and because the benzene molecule is planner and axes of all six 2p orbitals of benzene are parallel, these 2p orbitals can overlap the bonding π molecular orbitals of lowest energy as shown below.

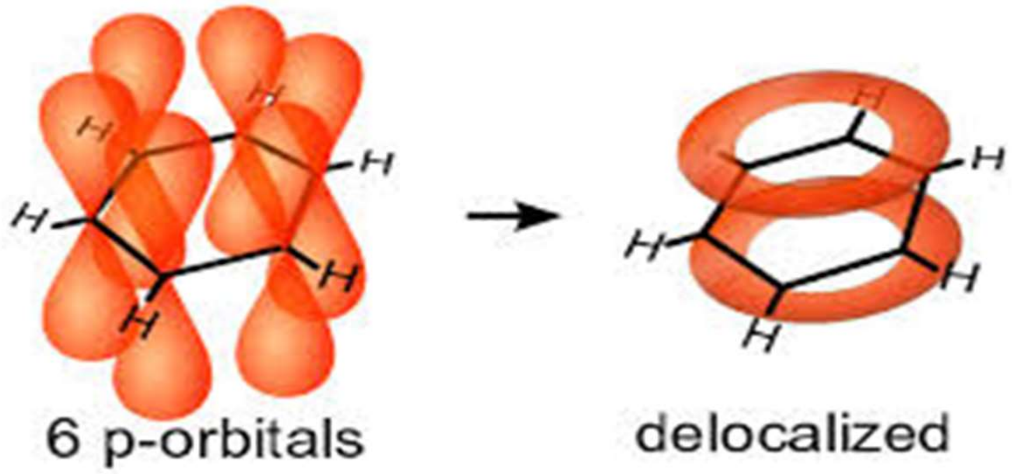


Orbital overlap picture of benzene

(a) Each carbon of benzene has a p orbital.

(b) The overlap of the p-orbitals forms a cloud of electrons above and below the plane of the benzene ring.

(c) The electrostatic potential map for benzene shows that all the carbon–carbon bonds have the same electron density



Stability of Benzene: Resonance Energy:

Chemical reactivity of any compound is measured in terms of its standard heats of formation ΔH°_{f} .

Benzene is a cyclohexatriene (cyclic)

The ΔH°_{f} for a double bond is 28.6 kcal/mol, so it is expected to have 28.6 × 3 = 85.8 kcal/mol (theoretical)

[As cyclohexene has Δ Hf = 28.6 kcal/mol;

cyclohexadiene has ΔHf = 55.4 kcal/mol.]

However, in practical (reality) it is only 49.8 kJ/mol.

85.8-49.8 = 36 less energy

Therefore, benzene is stable by 36 kcal/mol, or it contains 36 kcal/mol, less energy.

This energy difference of 36 kcal/mol is called empirical resonance energy (RE) of benzene.

RE is the energy by which benzene is stabilized and it is therefore, an energy that benzene doesn't have.

Let us understand more about what is resonance and aromaticity.

Concept of Resonance and Aromaticity:

Sometimes, multiple chemical structures in which electrons are shared between just two atoms can be used to represent a single molecule. In these cases no single such structure is correct, and the molecule exhibits special stability.

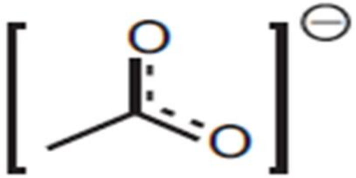
This phenomenon imparts special chemical properties, especially, for certain cyclic systems. The reasons lie in the following two concepts.

Resonance:

Consider the following representations of an acetate anion:

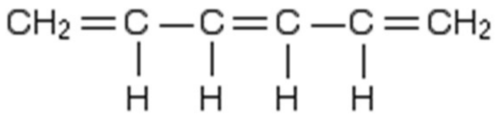
Fig. 9.6: Resonance structures of the acetate anion

When two chemical structures involving electrons shared between just two atoms may be drawn that represent a molecule, the molecule's true structure is intermediate between them. The contribution from multiple hypothetical structures to the true structure of a molecule is called **resonance**. The two structures are called **resonance structures** and the intermediate is called a **resonance hybrid**. Resonance often results in the presence of electrons which cannot be assigned to a single atom or bond; the electrons are said to be **delocalized.** A resonance hybrid is always more stable than the resonance structures (canonical forms) that contribute to it, a phenomenon known as **resonance stabilization**.

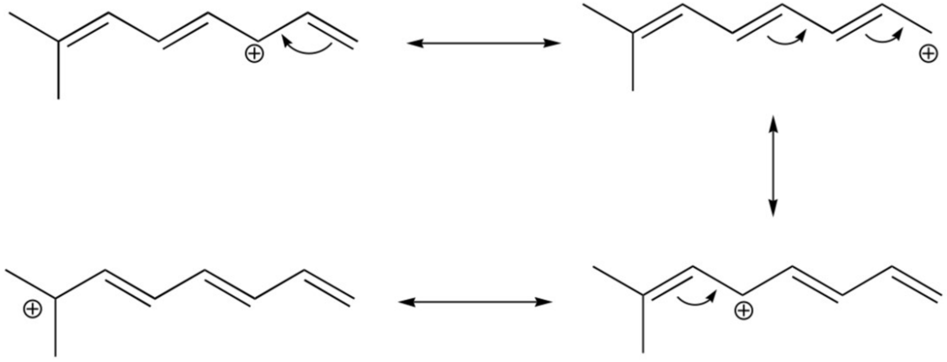


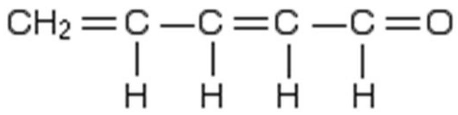
Aromaticity:

A **conjugated system** is a chemical system or structure bearing a series of alternating single and double bonds, meaning there is a p orbital on each atom. Owing to resonance, in a conjugated system of alternating bonds, the double and single bonds are able to switch places, producing an overall more stable structure. Conjugated systems can also exist in cyclic molecules. A conjugated cyclic system which is stabilized by resonance is called an **aromatic** system. The classic example of an aromatic system involves a six-membered ring.

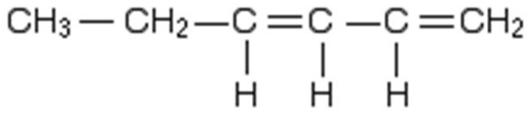


$$CH_2{=}\underset{H}{\underset{|}{C}}-\underset{H}{\underset{|}{C}}{=}\underset{H}{\underset{|}{C}}-\underset{H}{\underset{|}{C}}{=}CH_2$$

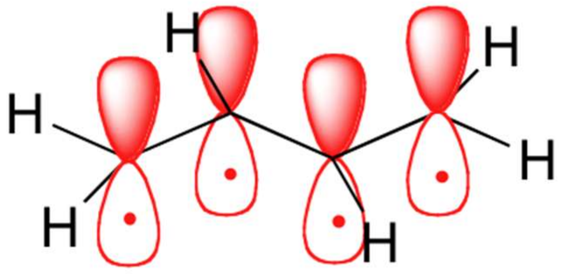


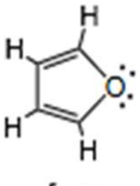


$$CH_2{=}\underset{H}{\underset{|}{C}}-\underset{H}{\underset{|}{C}}{=}\underset{H}{\underset{|}{C}}-\underset{H}{\underset{|}{C}}{=}O$$

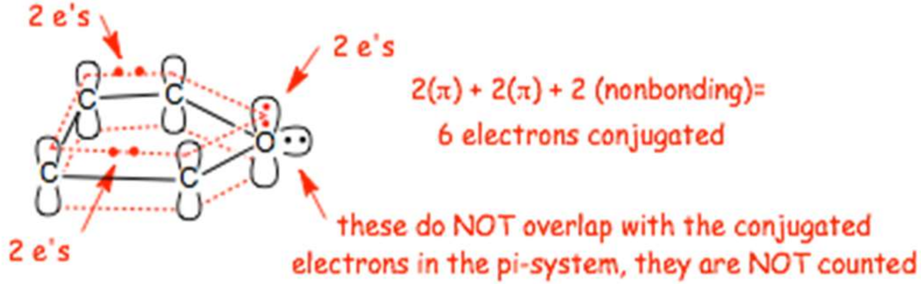


$$CH_3-CH_2-\underset{H}{\underset{|}{C}}{=}\underset{H}{\underset{|}{C}}-\underset{H}{\underset{|}{C}}{=}CH_2$$





furan



2(π) + 2(π) + 2 (nonbonding)=
6 electrons conjugated

these do NOT overlap with the conjugated electrons in the pi-system, they are NOT counted

RESONANCE IN BENZENE AND ITS DERIVATIVES

There are two possible chemical structures for a conjugated six-membered ring.

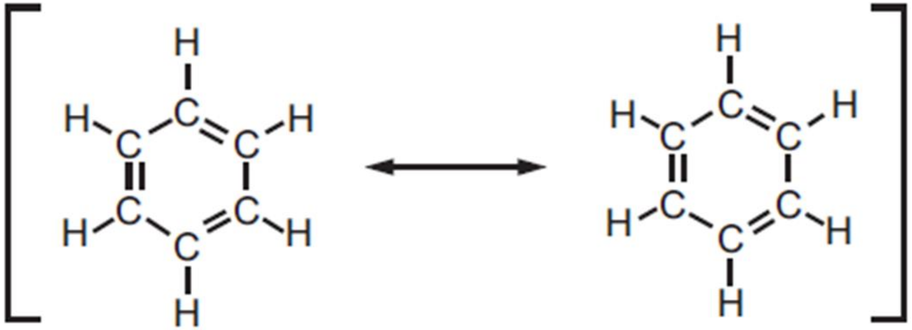


Fig. 9.8: Resonance structures of benzene

Fig. 9.9: Benzene

A conjugated six-membered ring is called **benzene**.

Benzene and other aromatic compounds exhibit a chemistry very different from ordinary, non-aromatic hydrocarbons. To distinguish between them, non-aromatic compounds are labelled **aliphatic**. Benzene and other aromatic compounds can have substituents. When benzene itself is a substituent, it is called a **phenyl group**.

AROMATICITY AND HŰCKEL'S (4n + 2) RULE

Benzene is unusually stable and this stability seems to be correlated with the overlap of its carbon 2p orbitals to form π molecular orbital. Ehrlich Hűckel proposed criteria for this sort of stability, which are called aromaticity.

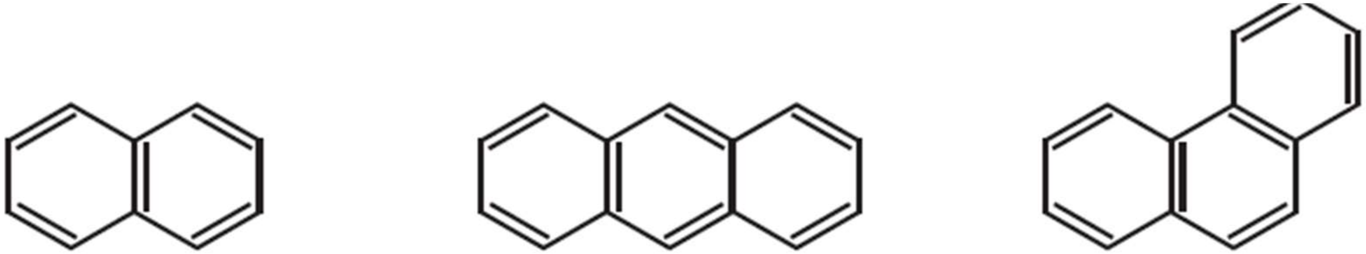
A compound is said to be aromatic when it meets **all** the following criteria:

1. Aromatic compound consists of one or more rings that have a cyclic arrangement of p orbitals. Thus, aromaticity is a property of certain cyclic compounds.
2. Every atom of an aromatic ring has a p orbital.
3. Aromatic rings are planar.
4. Cyclic arrangement of p orbitals in an aromatic compounds must contain (4n + 2π) electrons, where n is any positive integer (0, 1, 2 …) in other words an aromatic ring must contain 2, 6, 10, 14 … π electrons.

These are collectively called Hűckel 4n + 2 rule or simply 4n + 2 rule.

benzene i.e., 4n + 2 = 6 when n = 1 which shows that aromatic compound takes 4n + 2 electrons to fill exactly the bonding orbitals of π electrons system therefore criteria of 4. Each double bond contributes two π electrons.

Let’s see some examples and understand, if they are aromatic, *e.g.* Benzene has 6 π electrons n = 1; naphthalene has 10 π electrons. n = 2; phenanthrene and anthracene have 14 π electrons …. n = 3.



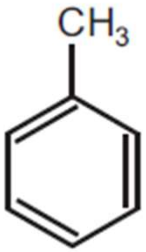
Naphthalene **Anthracene** **Phenanthrene**

Fig. 9.10: Aromatic benzene derivatives

Aromaticity is defined as ability to sustain induced ring current by a flat or nearly flat cyclic system with 4n + 2 π delocalized π electrons. (n = 0, 1, 2, 3 … n).

Some more examples:

1.



The ring is toluene, like the ring in benzene it is a continuous planar cycle of 6π electrons. Hence, the ring in toluene is aromatic.

2. 1, 3, 5-Hexatriene

   $CH_2=CH-CH=CH-CH=CH_2$

   Although 1, 3, 5-hexatriene contains six π electrons, it is not aromatic, as it fails in the criterion 1 for aromaticity, as it is not cyclic. Aromatic species must be cyclic.

To summarize **Aromatic characteristics**:

The characteristic properties of aromatic compounds are:

- Low ΔH of hydrogenation.
- Undergo electrophilic substitution reactions.
- Resistant to addition reactions like alkenes/alkynes etc. are
- Flat molecules.
- They contain (4n + 2π) electrons - (Hűckel's 4n + 2 rule).

Aromatic systems have special chemical and physical properties:

1. Though unsaturated, they undergo electrophilic substitution reactions rather than addition reactions.
2. They are resistant to $KMnO_4$ or HNO_3 oxidation
3. They exhibit unusual thermal stability
    - Low Δ H
    - Low Δ of combustion
4. Unique nuclear magnetic resonance properties.

Reactivity of Benzene:

Sr. No.	Reagent	Cyclohexatriene gives	Benzene gives
1.	$KMnO_4$ (cold, dil, aq.)	Rapid oxidation	No reaction
2.	Br_2/CCl_4	Rapid addition	No reaction
3.	HI	Rapid addition	No reaction
4.	H_2/Ni	Rapid hydrogenation	Slow hydrogenation

In place of addition benzene readily undergoes a new set of reactions involving **electrophilic aromatic substitution.** e.g.,

Nitration:

$$C_6H_6 + HNO_3 \xrightarrow{H_2SO_4} C_6H_5NO_2 + H_2O$$

In place of addition benzene readily undergoes a new set of reactions involving **electrophilic aromatic substitution.** e.g.,

Nitration:

$$C_6H_6 + HNO_3 \xrightarrow{H_2SO_4} C_6H_5NO_2 + H_2O$$

Halogenation:

$$C_6H_6 + Cl_2 \xrightarrow{Fe/FeCl_3} C_6H_5Cl + HCl$$

$$C_6H_6 + Br_2 \xrightarrow{Fe/FeBr_3} C_6H_5Br + HBr$$

Sulphonation:

$$C_6H_6 + H_2SO_4 \xrightarrow{SO_3^-} C_6H_5SO_3H + H_2O$$

Friedel Craft's Alkylation:

$$C_6H_6 + RCl \xrightarrow{AlCl_3} C_6H_5R + HCl$$

Friedel Craft's Acylation:

$$C_6H_6 - RCOCl \xrightarrow{AlCl_3} C_6H_5COR + HCl$$

In all the above reactions, it is evident that C_6H_6 resists additions in which benzene ring system is destroyed, whereas it readily undergoes substitution reactions in which ring system is preserved.

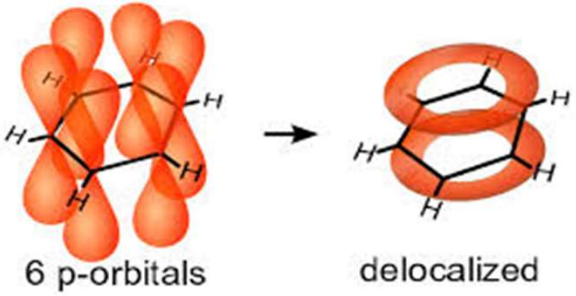
ELECTROPHILIC AROMATIC SUBSTITUTION

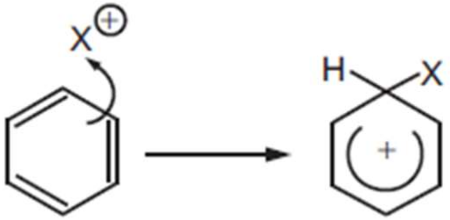
Electron clouds below and above the aromatic ring shield it from the nucleophilic attack, but it is prone to electrophilic attack.

Because of the delocalised electrons exposed above and below the plane of the rest of the molecule, benzene is obviously going to be highly attractive to electrophiles -species which seek the electron rich areas in other molecules. The electrophile will either be a positive ion, or the slightly positive end of a polar molecule.

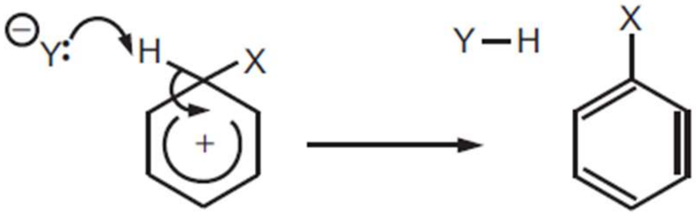
Step 1: Formation of C+ ion

First an electrophile, X$^+$ attacks benzene to form an intermediate C$^+$ ion (Benzonium ion or σ complex), the rate limiting step.





Step 2: Abstraction of H$^+$



The energetics of the reaction:

This initial input of energy is simply the activation energy for the reaction. In this case, it is going to be high (something around 150 kJ mol^{-1}), and this means that benzene's reactions tend to be slow.

1. Nitration:

The electrophilic substitution reaction between benzene and nitric acid: The facts

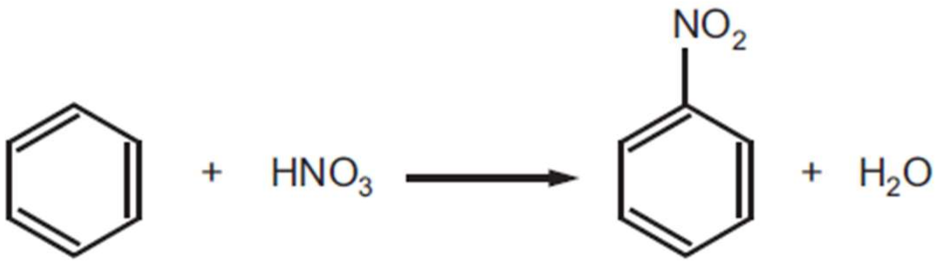
(Displacement of H (Ar-H) by NO_2^+ group.)

Various Nitrating agents:

1. HNO_3
2. HNO_3/H_2SO_4
3. Fuming HNO_3 in conc. H_2SO_4
4. Fuming HNO_3 in fuming H_2SO_4
5. $RCOONO_2$ (Acyl Nitrates)
6. Nitronium salts
7. N_2O_5 Nitronium pentoxide in CCl_4

$$C_6H_6 + HNO_3 \longrightarrow C_6H_5NO_2 + H_2O$$

or:

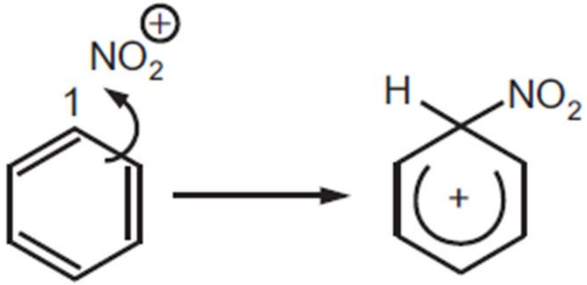


The formation of the electrophile:

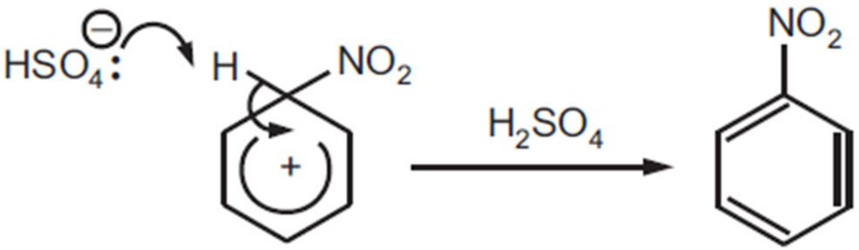
$$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^{\oplus} + 2HSO_4^{\ominus} + H_3O^{\oplus}$$

Mechanism:

Step 1:



Step 2:



2. Halogenation

The electrophilic substitution reaction between benzene and halogens (chlorine or bromine): The facts [Displacement of H (Ar-H) by X^+ (halonium ion)].

Benzene reacts with chlorine or bromine in an electrophilic substitution reaction, but only in the presence of a catalyst. The catalyst is either aluminium chloride (or aluminium bromide for reaction of benzene with bromine) or iron.

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

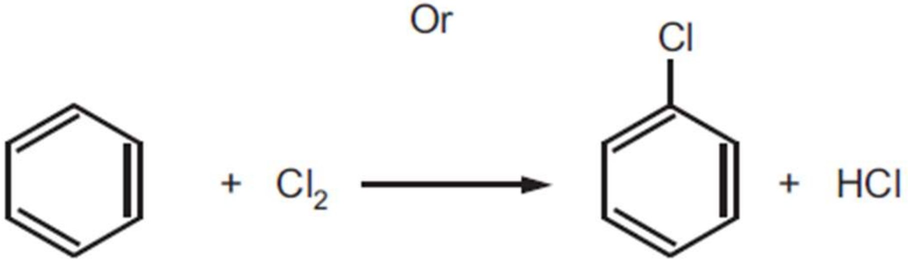
$$2Fe + 3Br_2 \longrightarrow 2FeBr_3$$

The reaction with chlorine:

The reaction between benzene and chlorine in the presence of either aluminium chloride or iron gives chlorobenzene.

$$C_6H_6 + Cl_2 \longrightarrow C_6H_5Cl + HCl$$

Or

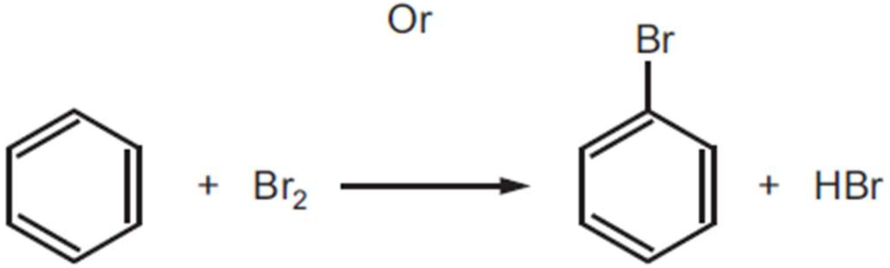


The reaction with bromine:

The reaction between benzene and bromine in the presence of either aluminium bromide or iron gives bromobenzene. Iron is usually used because it is cheaper and more readily available.

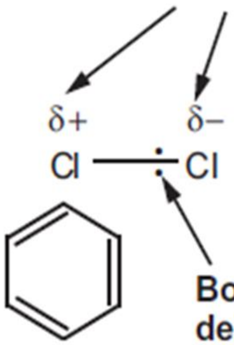
$$C_6H_6 + Br_2 \longrightarrow C_6H_5Br + HBr$$

Or



The formation of the electrophile:

We are going to explore the reaction using chlorine and aluminium chloride. If you want one of the other combinations, all you have to do is to replace each Cl by Br, or Al by Fe.

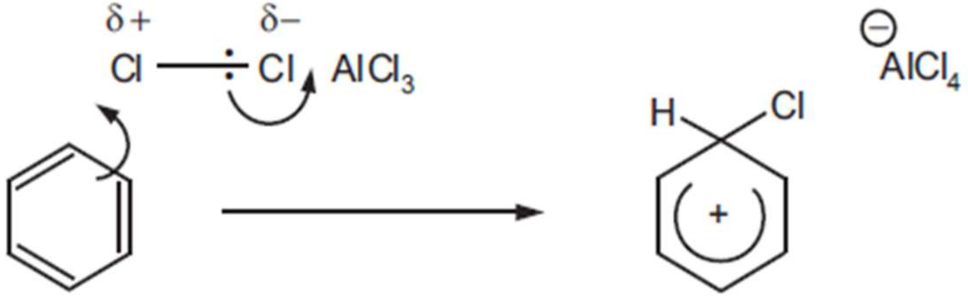


Chlorine molecule becomes polarised

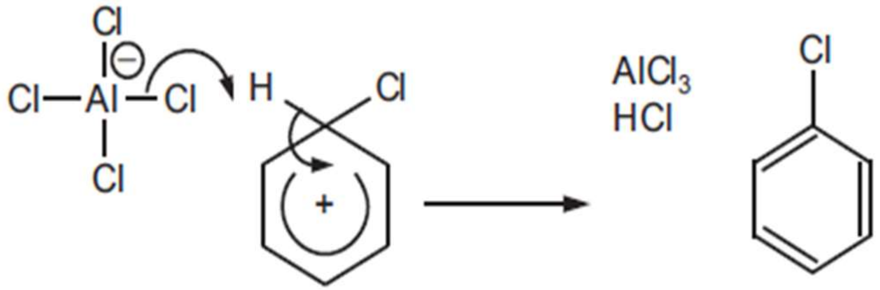
Bonding electrons repelled by the nearby delocalised electrons in benzene

Mechanism:

Step 1:



Step 2:



The hydrogen is removed by the $AlCl_4^-$ ion which was formed in the first stage. The aluminium chloride catalyst is re-generated in this second stage.

3. Sulphonation

The electrophilic substitution reaction between benzene and sulphuric acid: The facts [Displacement of H (Ar-H) by SO_3^+ (sulfuryl group)].

There are two equivalent ways of sulphonating benzene:

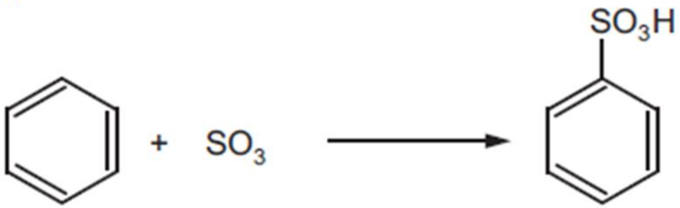
- Heat benzene under reflux with concentrated sulphuric acid for several hours or
- Warm benzene under reflux at 40°C with fuming sulphuric acid for 20 to 30 minutes.

$$C_6H_6 + H_2SO_4 \longrightarrow C_6H_5SO_3H + H_2O$$

Or:

… equation (1)

The product is benzenesulphonic acid. The electrophile is actually sulphur trioxide, SO_3, and you may find the equation for the sulphonation reaction written as this also:



… equation (2)

The formation of the electrophile:

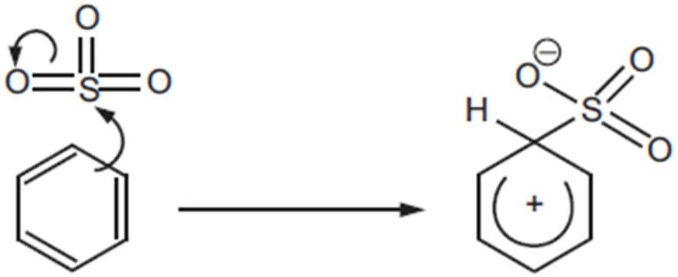
The sulphur trioxide electrophile arises in one of two ways depending on which sort of acid you are using. Concentrated sulphuric acid contains traces of SO_3 due to slight dissociation of the acid.

$$H_2SO_4 \rightleftharpoons H_2O + SO_3$$

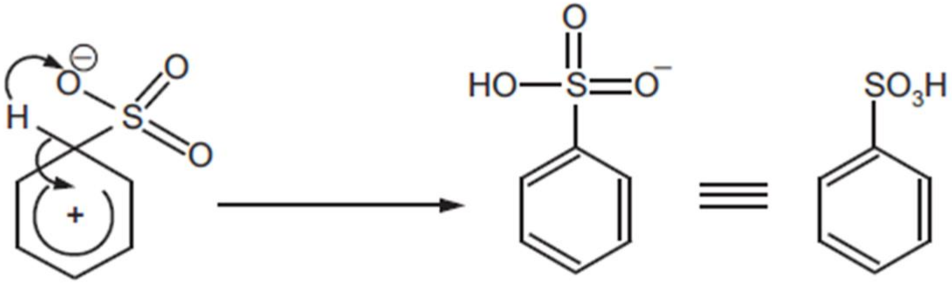
Fuming sulphuric acid, $H_2S_2O_7$, as a solution of SO_3 in sulphuric acid and so is a much richer source of the SO_3.

Mechanism

Step 1:



Step 2:



4. Freidal Craft's Alkylation:

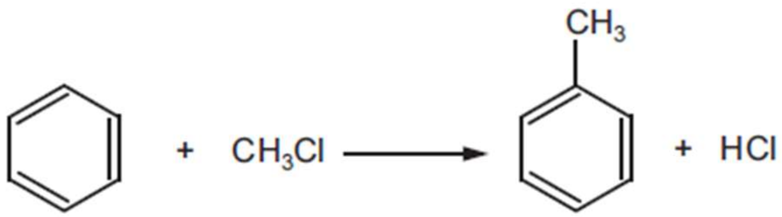
The electrophilic substitution reaction between benzene and alkyl chloride: The facts (Displacement of H (Ar-H) by R^+ group.)

Benzene is treated with a chloroalkane (for example, chloromethane or chloroethane) in the presence of aluminium chloride as a catalyst. As an example, we will look at substituting a methyl group, but any other alkyl group could be used in the same way.

Substituting a methyl group gives methylbenzene - also commonly known as toluene.

$$C_6H_6 + CH_3Cl \longrightarrow C_6H_5CH_3 + HCl$$

or better:



Aluminium chloride is acting as a catalyst. It is a Lewis acid.

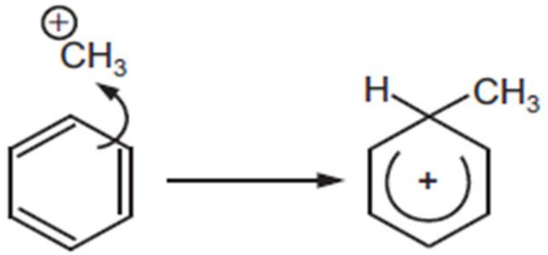
The formation of the electrophile:

The electrophile is CH_3^+. It is formed by reaction between the chloromethane and the aluminium chloride catalyst.

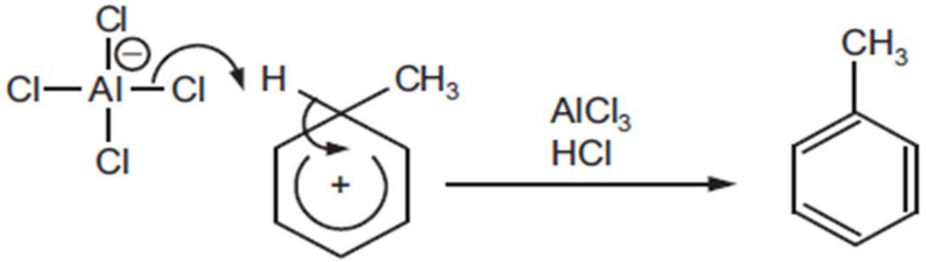
$$CH_3Cl + AlCl_3 \longrightarrow \overset{\oplus}{C}H_3 + AlCl_4^{\ominus}$$

Mechanism:

Step 1:



Step 2:



5. Friedel Craft's Acylation:

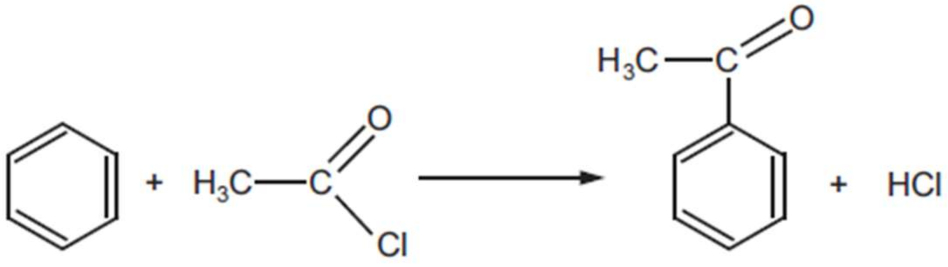
The electrophilic substitution reaction between benzene and an alkanoyl chloride:

The facts (Displacement of H (Ar-H) by RCO^+ group.) (RCO^+ = acylium ion)

Benzene is treated with a mixture of ethanoyl chloride, CH_3COCl, and aluminium chloride as the catalyst. A ketone called phenylethanone is formed.

$$C_6H_6 + CH_3COCl \longrightarrow C_6H_5COCH_3 + HCl$$

or better:



The aluminium chloride isn't written into these equations because it is acting as a catalyst. If you wanted to include it, you could write $AlCl_3$ over the top of the arrow.

The formation of the electrophile:

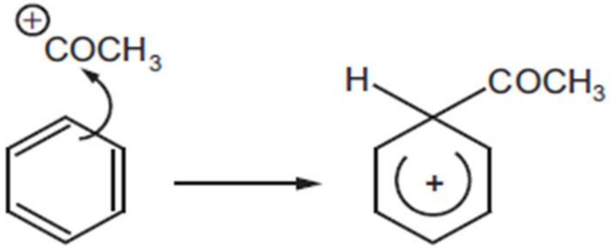
The electrophile is CH_3CO^+. It is formed by reaction between the ethanoyl chloride and the aluminium chloride catalyst.

$$CH_3COCl + AlCl_3 \longrightarrow CH_3CO^+_3 + AlCl_4^{\ominus}$$

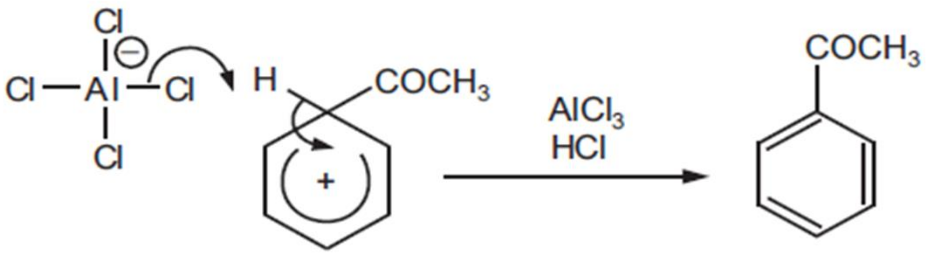
The electrophilic substitution mechanism:

Mechanism:

Step 1:

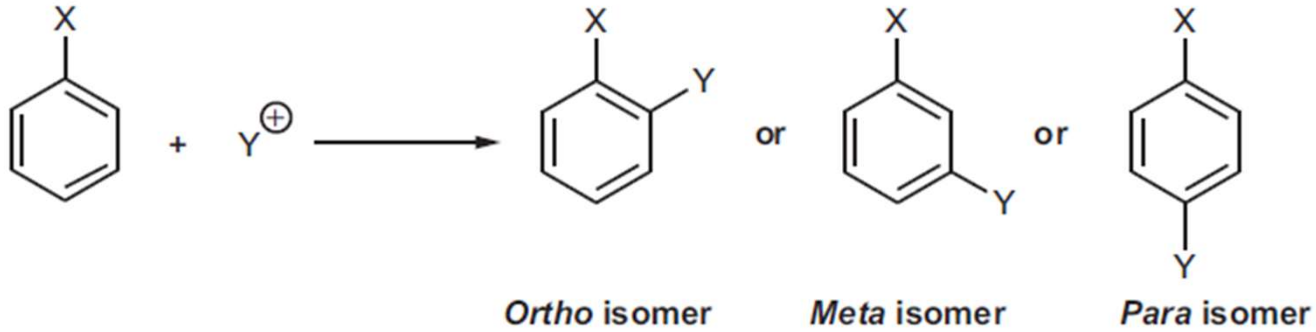


Step 2:



ORIENTATION AND
REACTIVITY IN MONOSUBSTITUTED BENZENE

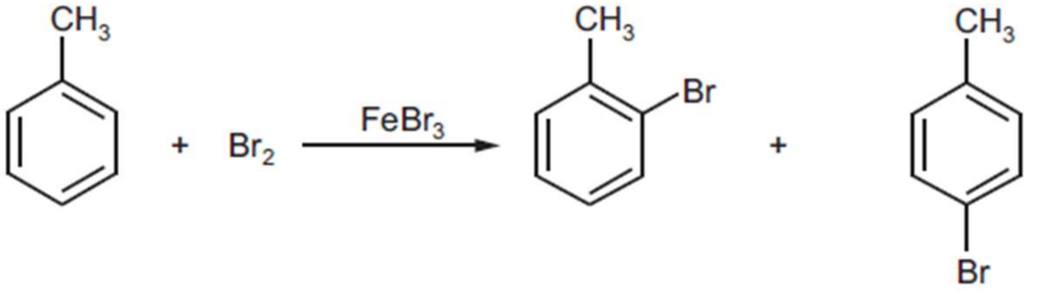
The Effect of substituents on orientation:



The substituent already attached to the benzene ring determines the location of the new substituent. There are two possibilities: A substituent will direct an incoming substituent either to the *ortho and para* positions, or it will direct an incoming substituent to the meta position. All activating substituents and the weakly deactivating halogens are ***ortho, para* directors**, and all substituents that are more deactivating than the halogens are ***meta* directors**.

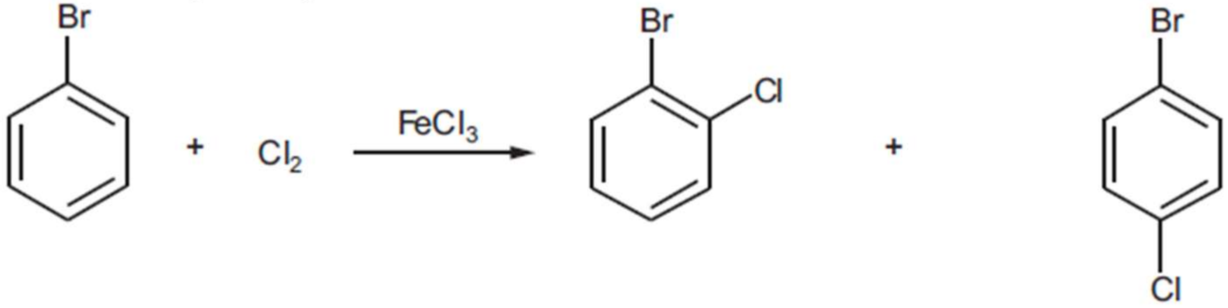
Thus the substituents are divided into three groups

1. All activating substituents direct an incoming electrophile to the *ortho* and *para* positions.



Toluene **o-Bromotoluene** **p-Bromotoluene**

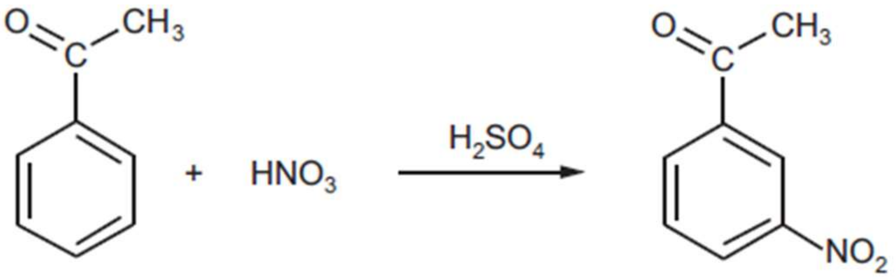
2. The weakly deactivating halogens also direct an incoming electrophile to the *ortho*- and *para*- positions.



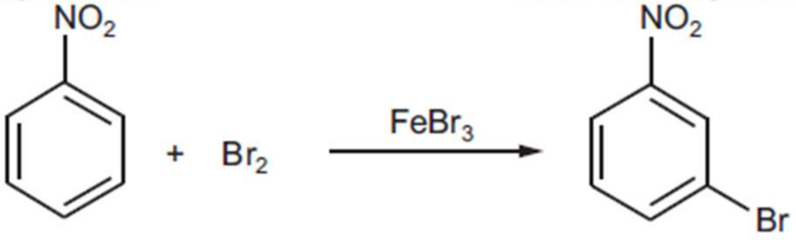
Bromobenzene **o-Chlorobromobenzene** **p-Chlorobromobenzene**

3. All moderately deactivating and strongly deactivating substituents direct an incoming electrophile to the meta position.

3. All moderately deactivating and strongly deactivating substituents direct an incoming electrophile to the meta position.



Acetophenone **m-Niroacetophenone**

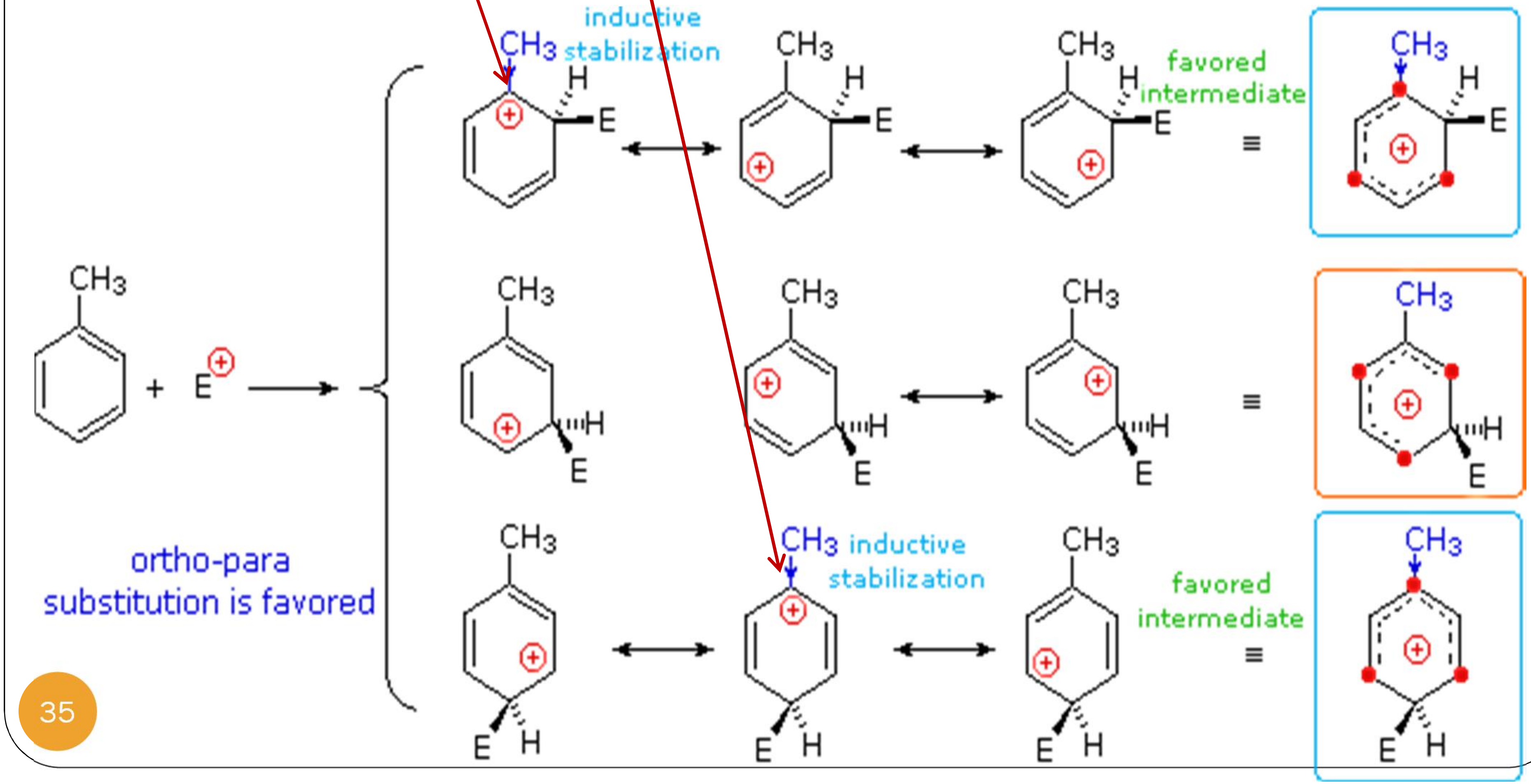


Nitrobenzene ***m*-Bromonitrobenzene**

To understand why a substituent directs an incoming electrophile to a particular position, we must look at the stability of the carbocation intermediate that is formed in the rate-determining step. When a substituted benzene undergoes an electrophilic substitution reaction, three different carbocation intermediates can be formed: an *ortho*-substituted carbocation, a *meta*-substituted carbocation, and a *para*-substituted carbocation.

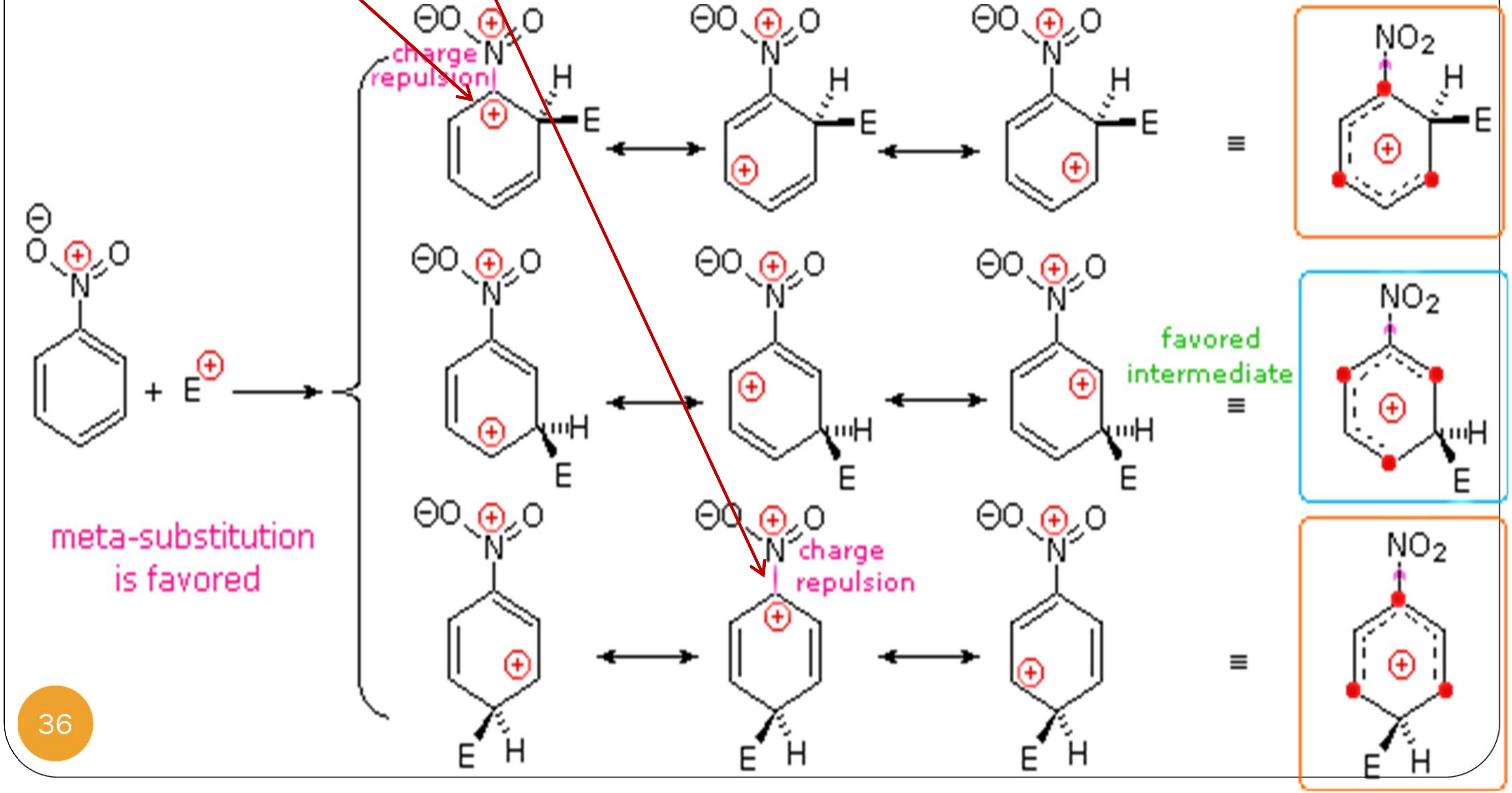
Activating Groups- *o-* or *p-* directors

In the case of alkyl substituents, charge stabilization is greatest when the **alkyl group is bonded to one of the positively charged carbons** of the benzenonium intermediate. **This happens only for *ortho* and *para* electrophilic attack,** so such substituents favor formation of those products. Interestingly, primary alkyl substituents, especially methyl, provide greater stabilization of an adjacent charge than do more substituted groups (note the greater reactivity of toluene compared with *tert*-butylbenzene).



Dectivating Groups- *m-* directors

Nitro (NO_2), sulfonic acid (SO_3H) and carbonyl (C=O) substituents have a full or partial positive charge on the atom bonded to the aromatic ring. Structures in which **like-charges are close to each other are destabilized by charge repulsion**, so these substituents **inhibit *ortho* and *para* substitution** more than ***meta*** substitution. Consequently, ***meta*-products predominate** when electrophilic substitution is forced to occur.



Halogen (X), OR and NR_2 substituents all exert a destabilizing inductive effect on an adjacent positive charge, due to the high electronegativity of the substituent atoms. By itself, this would favour meta-substitution; however, **all these substituent atoms have non-bonding valence electron pairs which serve to stabilize an adjacent positive charge by pi-bonding, with resulting delocalization of charge**. Consequently, all these substituents **direct substitution to *ortho* and *para* sites**. The balance between inductive electron withdrawal and p-π conjugation is such that the nitrogen and oxygen substituents have an overall stabilizing influence on the benzenonium intermediate and increase the rate of substitution markedly; whereas halogen substituents have an overall destabilizing influence.

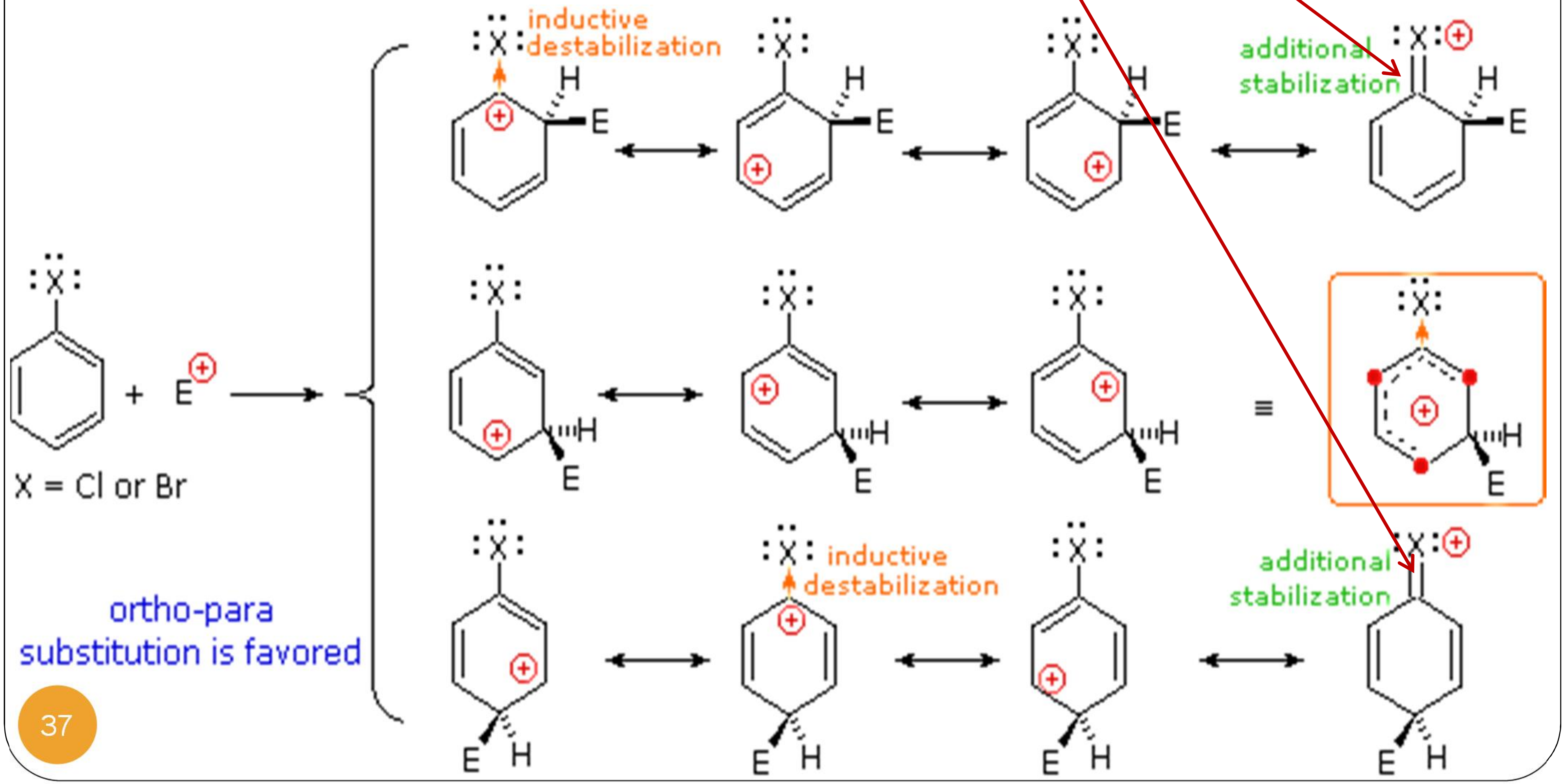
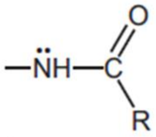
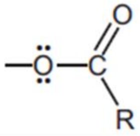
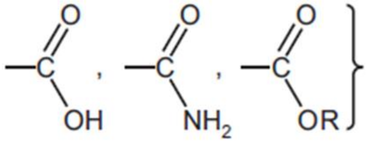
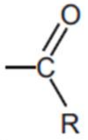


Table: Classification of substituents with respect to their directive effects on orientation of substitution *vis-a-vis* their activating or deactivating effects on benzene ring

Substituent group	Name of group	Directing effect	Activating or deactivating
$-\ddot{N}H_2$, $-\ddot{N}R_2$	amino	*ortho*, *para* directors	activating substituents
$-\ddot{O}H$	hydroxy		
$-\ddot{O}R$	alkoxy		
	acylamino		
$-R$	alkyl		
	acyloxy		
	phenyl		
$-\ddot{F}:$, $-\ddot{B}r:$, $-\ddot{C}l:$, $-\ddot{I}:$	halogens		deactivating substituents
	carboxy, carboxamido, carboalkoxy	*meta* directors	
	acyl		
$-SO_3H$	sulfonic acid		
$-CN$	cyano		
$-NO_2$	nitro		

Orientation and Reactivity Effects of Ring Substituents

Activating Substituents ortho & para-Orientation		Deactivating Substituents meta-Orientation		Deactivating Substituents ortho & para-Orientation
$–O^{(-)}$	$–NH_2$	$–NO_2$	$–CO_2H$	$–F$
$–OH$	$–NR_2$	$–NR_3^{(+)}$	$–CO_2R$	$–Cl$
$–OR$	$–NHCOCH_3$	$–PR_3^{(+)}$	$–CONH_2$	$–Br$
$–OC_6H_5$	$–R$	$–SR_2^{(+)}$	$–CHO$	$–I$
$–OCOCH_3$	$–C_6H_5$	$–SO_3H$	$–COR$	$–CH_2Cl$
		$–SO_2R$	$–CN$	$–CH=CHNO_2$

NUCLEOPHILIC AROMATIC SUBSTITUTION

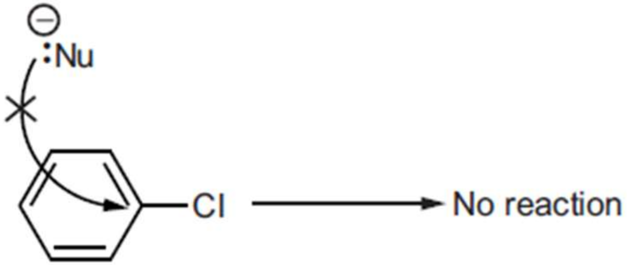
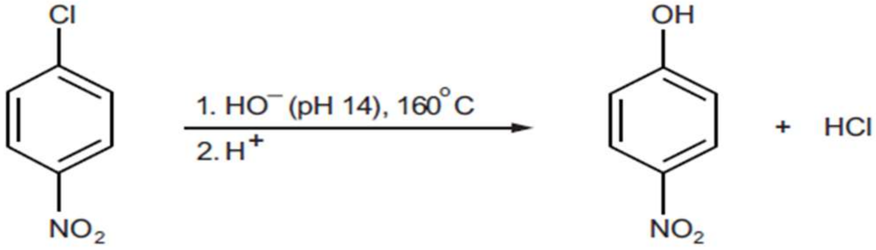
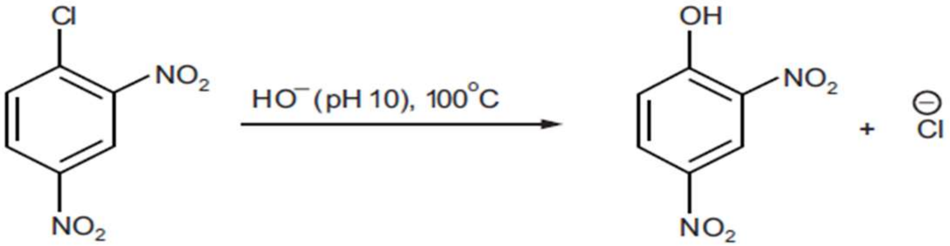


Fig. 9.12: Reason for disfavoured nucleophilic substitution by benzene derivatives under normal conditions

If, however, the aryl halide has one or more substituents that strongly withdraw electrons from the ring by resonance, **nucleophilic aromatic substitution** reactions can occur without using extreme conditions.





Nucleophilic aromatic substitution by addition-elimination:

Nucleophilic aromatic substitution takes place by a two-step reaction known as an **SNAr reaction** (substitution nucleophilic aromatic). In the first step, the nucleophile attacks the carbon bearing the leaving group from a trajectory that is nearly perpendicular to the aromatic ring. (The leaving groups cannot be displaced from sp^2 carbon atoms by back-side attack.) Nucleophilic attack forms a resonance-stabilized carbanion intermediate called a *Meisenheimer complex*. In the second step of the reaction, the leaving group departs, reestablishing the aromaticity of the ring.

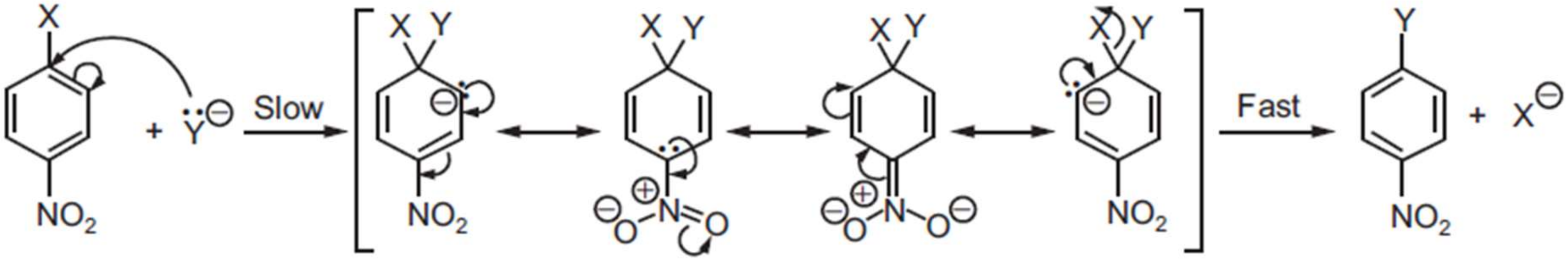
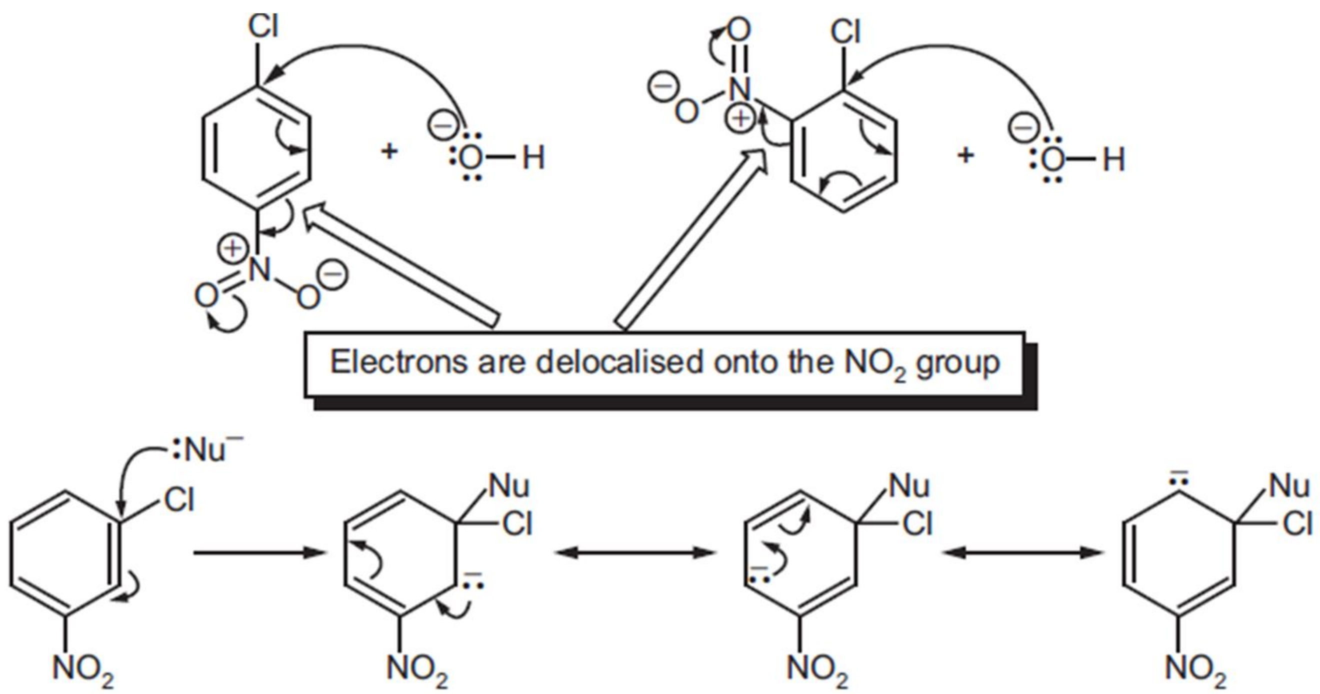


Fig. 9.13: General mechanism for nucleophilic aromatic substitution

In a nucleophilic aromatic substitution reaction, the incoming nucleophile must be a stronger base than the substituent that is being replaced, because the weaker of the two bases will be the one eliminated from the intermediate.

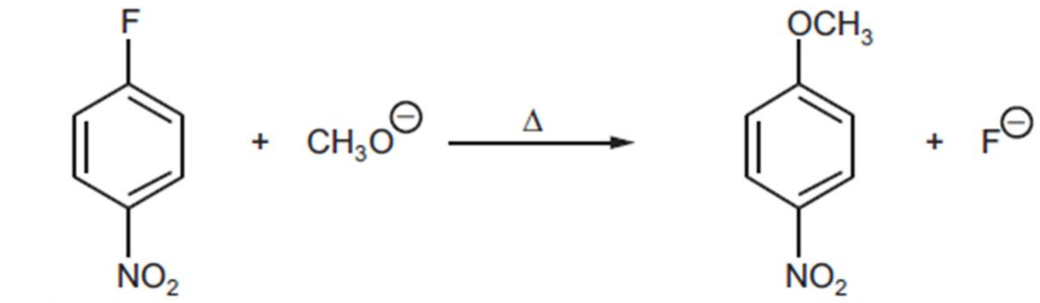
The electron-withdrawing substituent must be *ortho* or *para* to the site of nucleophilic attack because the electrons of the attacking nucleophile can be delocalized on to the substituent only if the substituent is in one of those positions.



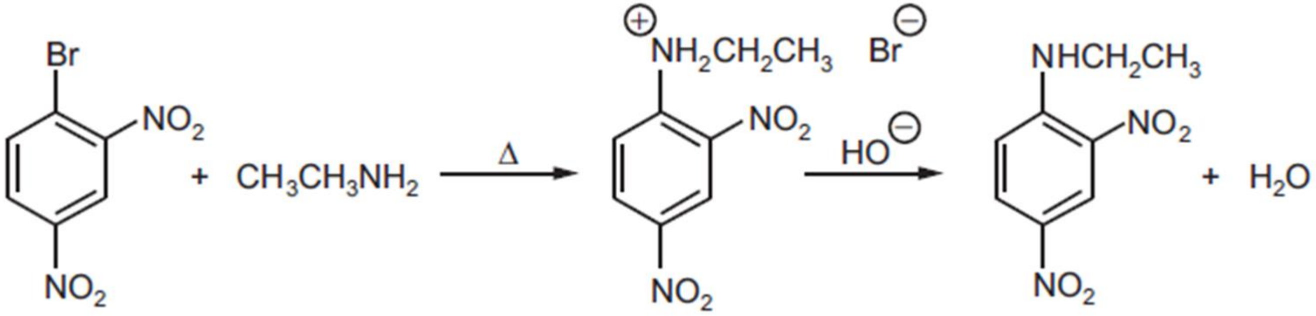
The negative charge is never delocalized on the NO_2 group **If it is *meta***

Fig. 9.14: Mechanism of nucleophilic aromatic substitution: Nucleophilic aromatic substitution by an addition elimination mechanism occurs only with aryl halides that contain electron-withdrawing substituents at the *ortho* or *para* positions and not the meta position.

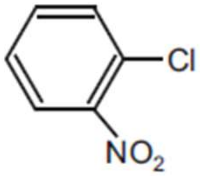
A variety of substituents can be placed on a benzene ring by means of nucleophilic aromatic substitution reactions. The only requirement is that the incoming group be a stronger base than the group that is being replaced.



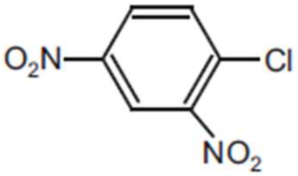
p-Fluoronitrobenzene **p-Nitroanisole**



1-Bromo-2,4-dinitrobenzene **N-Ethyl-2,4-dinitroaniline**



A



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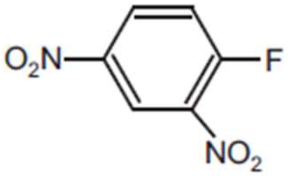
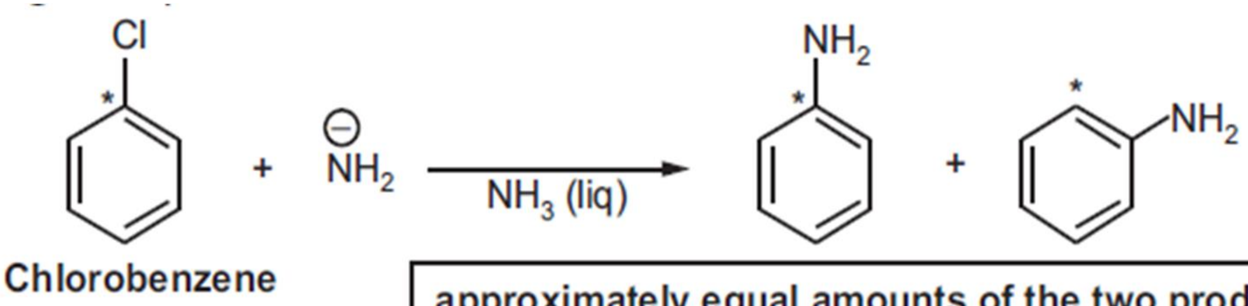


C

Increasing reactivity

REACTIONS INVOLVING BENZYNE INTERMEDIATE

An aryl halide such as chlorobenzene can undergo a nucleophilic substitution reaction in the presence of a very strong base such liquid ammonia, soda amide or sodium hydride. There are two surprising features about this reaction: The aryl halide does not have to contain an electron withdrawing group, and the incoming substituent does not always end up on the carbon vacated by the leaving group. For example, when chlorobenzene with the carbon to which the chlorine is attached isotopically labeled with is treated with amide ion in liquid ammonia, aniline is obtained as the product.



approximately equal amounts of the two products are obtained

Fig. 9.15: The involvement of benzyne intermediate during nucleophilic aromatic substitution

Elimination and Addition:

These are the only products formed. Anilines with the amino group two or three carbons removed from the labeled carbon are not formed.

The fact that the two products are formed in approximately equal amounts indicates that the reaction takes place by a mechanism that forms an intermediate in which the two carbons to which the amino group is attached in the product are equivalent. The mechanism that accounts for the experimental observations involves the formation of a **benzyne intermediate**. Benzyne has a triple bond between two adjacent carbon atoms of benzene. In the first step of the mechanism, the strong base removes a proton from the position *ortho* to the halogen. The resulting anion expels the halide ion, thereby forming benzyne.

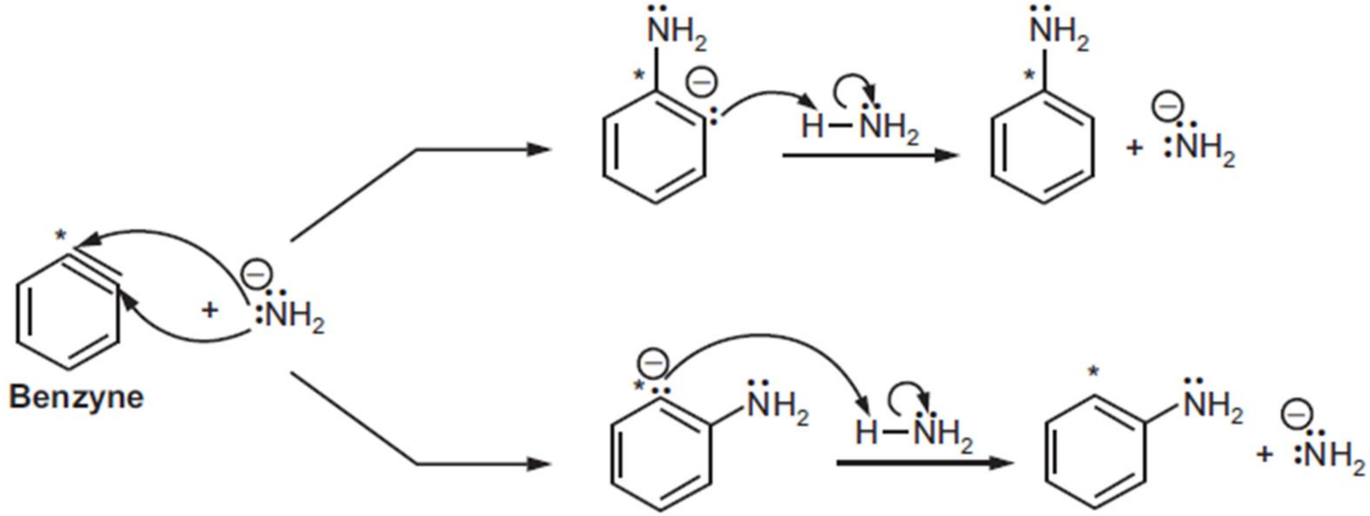
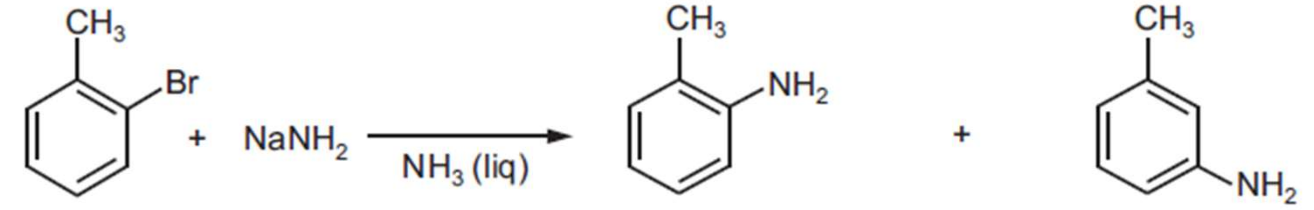


Fig. 9.16: The addition of the nucleophile (NH_2^-) to the benzyne intermediate at same (direct) or adjecant (cine) carbons

The incoming nucleophile can attack either of the carbons of the “triple bond” of benzyne. Protonation of the resulting anion forms the substitution product. The overall reaction is an elimination–addition reaction: **Benzyne** is formed in an elimination reaction and immediately undergoes an addition reaction.

Substitution at the carbon that was attached to the leaving group is called **direct substitution**. Substitution at the adjacent carbon is called **cine substitution** (*cine* comes from *kinesis*, which is Greek word for "movement"). In the following reaction, *o*-toluidine is the direct-substitution product; *m*-toluidine is the *cine*-substitution product.



***o*-Bromotoluene** ***o*-Toluidine** **direct-substitution product** ***m*-Toluidine** ***cine*-substitution product**

As you might expect, the triple bond in benzyne is unusual. Each carbon of the six-membered ring is sp^2 hybridized and as a result, the σ bond and two π bonds of the triple bond are formed with the following orbitals.

- The σ bond is formed by overlap of two sp^2 hybrid orbitals.
- One π bond is formed by overlap of two p orbitals perpendicular to the plane of the molecule.
- The second π bond is formed by overlap of two sp^2 hybrid orbitals.

Thus, the second π bond of **Benzyne** differs from all other π bonds seen thus far, because it is formed by the side-by-side overlap of sp^2 hybrid orbitals, not p orbitals. This π bond, located in the plane of the molecule, is extremely weak.

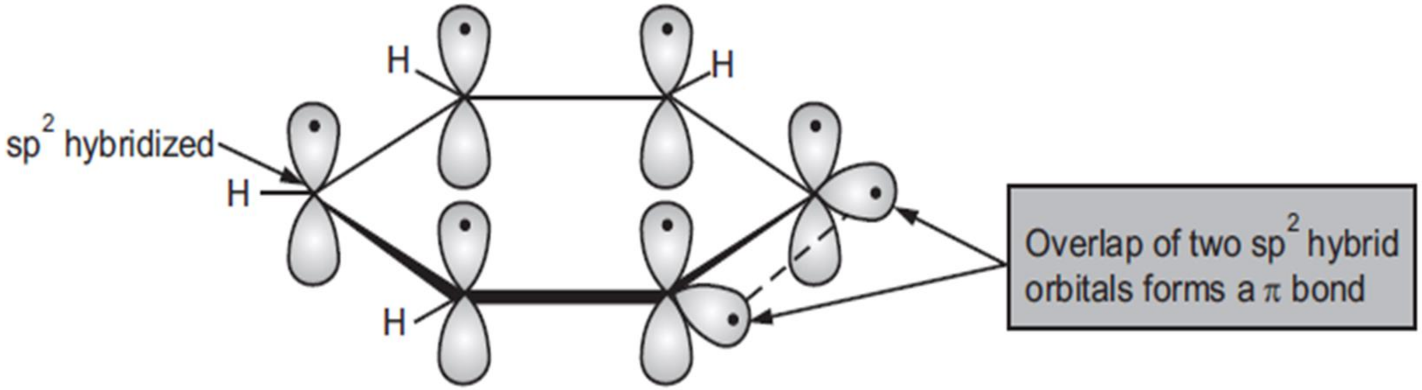


Fig. 9.17: The molecular orbital picture of the I Benzyne ntermediate

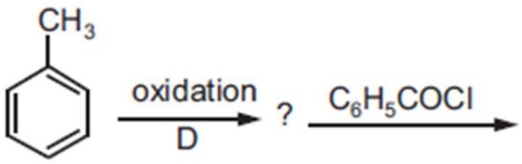
Benzyne is an extremely reactive species. In a molecule with a triple bond, the two *sp* hybridized carbons and the atoms attached to these carbons are linear because the bond angles are 180°. Four linear atoms cannot be incorporated into a six-membered ring, so the system in benzyne is distorted.

QUESTION BANK

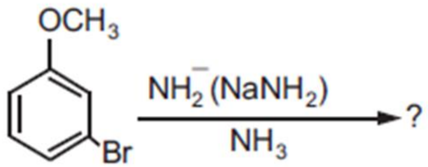
1. Comment on the structure of benzene in details.
2. Comment on the stability of benzene. What is stabilization by resonance?
3. Discuss the concepts of resonance and aromaticity with suitable examples. What is meant by Hűckel’s (4n + 2) rule and what is the criteria for aromaticity? What is its basis? Explain with suitable examples.
4. Discuss the reactivity of benzene, the various electrophilic aromatic substitution reactions predominantly undergone by benzene with the reaction
5. Discuss the orientation of electrophilic substitution in monosubstituted benzene, explaining the exact reasons for *ortho, para* and *meta* directing effects of various substituents.
6. Discuss the Nucleophilic Aromatic Substitution (SNAr) reactions of benzene derivatives and explain its mechanisms. Discuss the normal addition – elimination mechanism as well as the the elimination-addition mechanism involving the benzyne intermediate.
7. Complete the following:

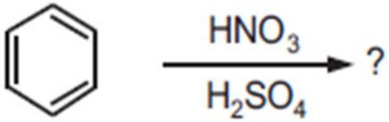
(a) **Toluene** $\xrightarrow{HNO_3,\ H_2SO_4}$

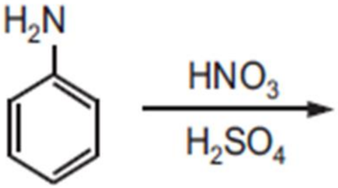
(b)



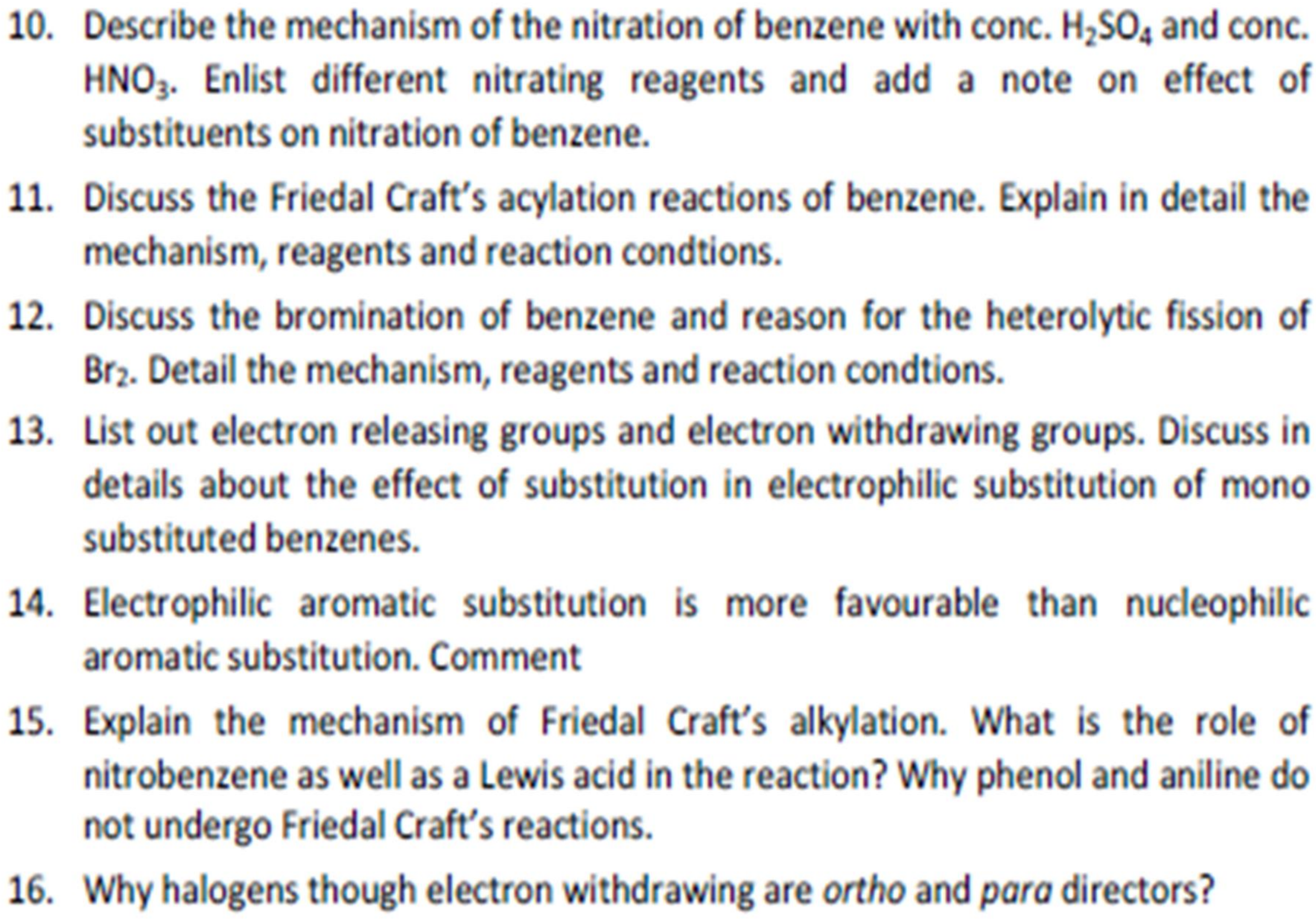
(c)



(d) 

(e) 

8. Is benzene saturated or unsaturated? Explain properly. Comment on the bond character, bond strength and bond length of benzene.
9. Discuss the criteria for aromaticity. Are the following compounds aromatic? Explain why:
   - (i) 1,3-Cyclopentadiene
   - (ii) Pyrrole
   - (iii) Cycloheptatrienyl cation
   - (iv) Thiophene
   - (v) Pyridine
   - (vi) Benzene
   - (vii) Naphthelene
   - (viii) Anthracene
   - (ix) Phenanthrene



10. Describe the mechanism of the nitration of benzene with conc. H_2SO_4 and conc. HNO_3. Enlist different nitrating reagents and add a note on effect of substituents on nitration of benzene.
11. Discuss the Friedal Craft's acylation reactions of benzene. Explain in detail the mechanism, reagents and reaction condtions.
12. Discuss the bromination of benzene and reason for the heterolytic fission of Br_2. Detail the mechanism, reagents and reaction condtions.
13. List out electron releasing groups and electron withdrawing groups. Discuss in details about the effect of substitution in electrophilic substitution of mono substituted benzenes.
14. Electrophilic aromatic substitution is more favourable than nucleophilic aromatic substitution. Comment
15. Explain the mechanism of Friedal Craft's alkylation. What is the role of nitrobenzene as well as a Lewis acid in the reaction? Why phenol and aniline do not undergo Friedal Craft's reactions.
16. Why halogens though electron withdrawing are *ortho* and *para* directors?

17. How will you prepare 4-nitrobenzophenone? Explain with proper reaction conditions.

18. Starting with simple benzene write equations and reactions conditions to prepare:
    - (i) Phenol
    - (ii) Benzoic acid
    - (iii) Benzophenone
    - (iv) Benzaldehyde
    - (v) Acetophenone
    - (vi) Aniline
    - (vii) Toluene
    - (viii) Iodobenzene

19. Explain what is diazotization and Sandmeyer's reaction. How shall you prepare aniline from the following:
    - (i) Phenol
    - (ii) Chorobenzene
    - (iii) Iodobenzene

(iv) Bromobenzene

(v) Benzene

(vi) Benzonitrile.

Give the reaction equations, reagents and reaction conditions for each.

20. Predict the products of the following.

n-Butylbenzene reacted with hot $\xrightarrow{KMNO_4}$?

Nitrobenzene + Benzoyl chloride $\xrightarrow{AlCl_3}$

Phenol + Carbon dioxide $\xrightarrow{NaOH}$?

o-Nitrophenol + Dimethyl sulfate $\xrightarrow{NaOH}$?

21. Starting from benzene or toluene and suitable organic /inorganic regents how will you prepare the following.

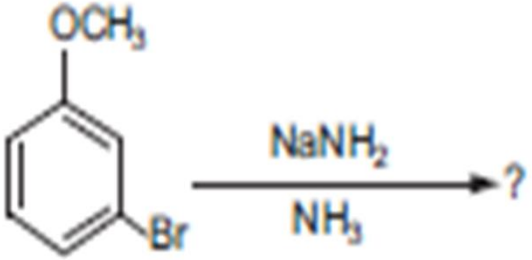
- *m*-Chlorobenzoic acid
- *m*-Nitroanline
- *p*-Toluidine
- *m*-Bromotoluene

- 2,4-Dinitrobenzoic acid
- Sulfacetamide
- Phenol
- Benzaldehyde
- N-N-Dimethylaniline
- Salicylic acid
- *p*-Bromoanline
- Ethyl *p*-nitrobenzoate

22. Complete the following reactions.

(a)

(c)



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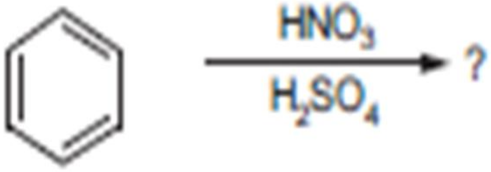

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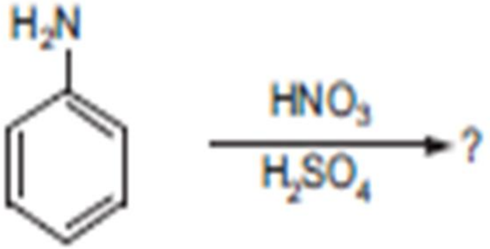

THANK YOU