

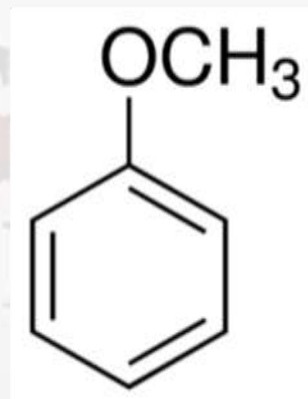
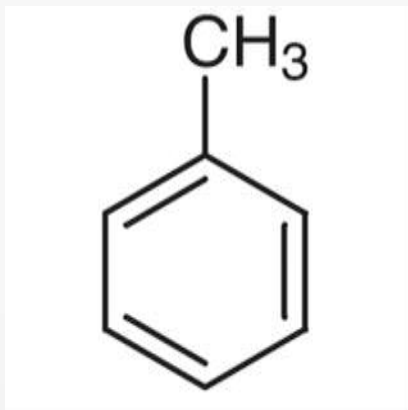
Chemistry-II

UNIT I

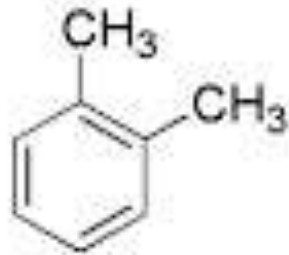
Benzene and its Derivatives

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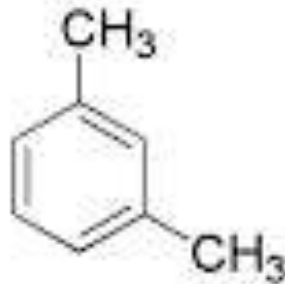
- Benzene and its homologs constitute the most important class of **ARENES** (aromatic hydrocarbons)
- They are frequently called by the common names which are accepted by IUPAC
- The homologs of benzene having a single alkyl group are named as alkyl benzene
- Ex. Methyl benzene (**Toluene**) Methoxy benzene (**Anisole**)



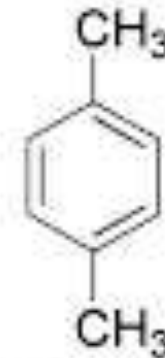
- Dimethyl benzenes (xylene)



ortho-xylene
(1,2-dimethylbenzene)



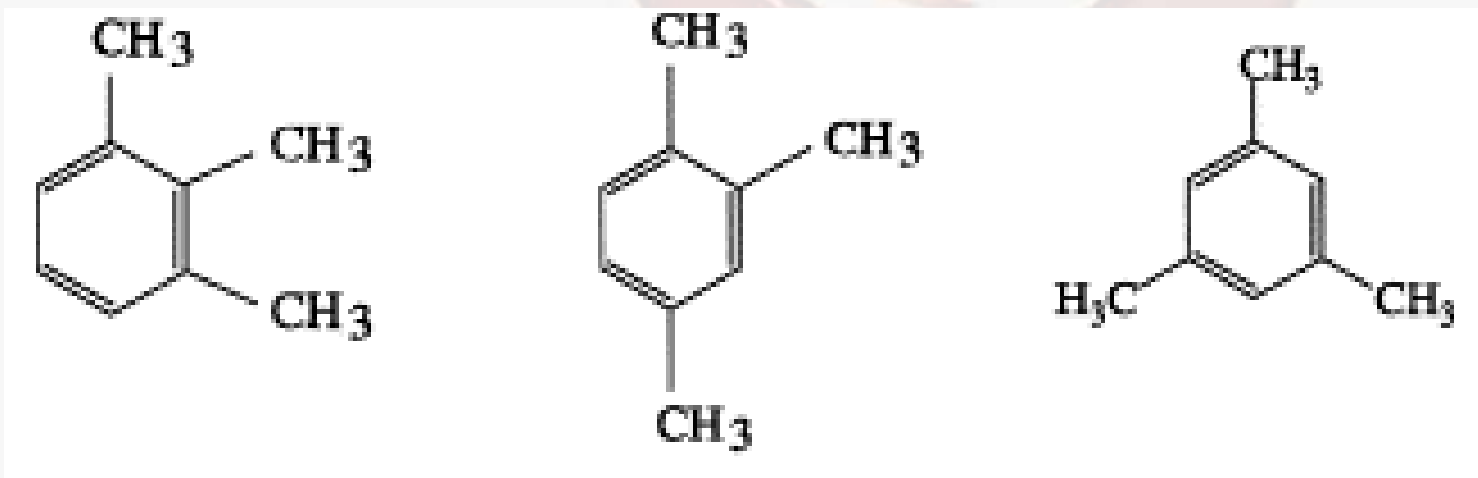
meta-xylene
(1,3-dimethylbenzene)



para-xylene
(1,4-dimethylbenzene)

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- Trimethyl benzene
 - They are assigned systematic names
 - Positions of methyl groups are shown in numbers



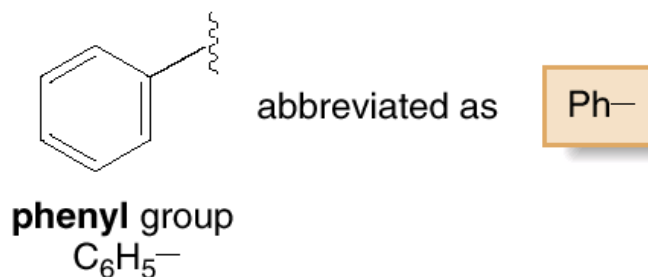
1,2,3-Trimethyl benzene

1,2,4-Trimethyl benzene

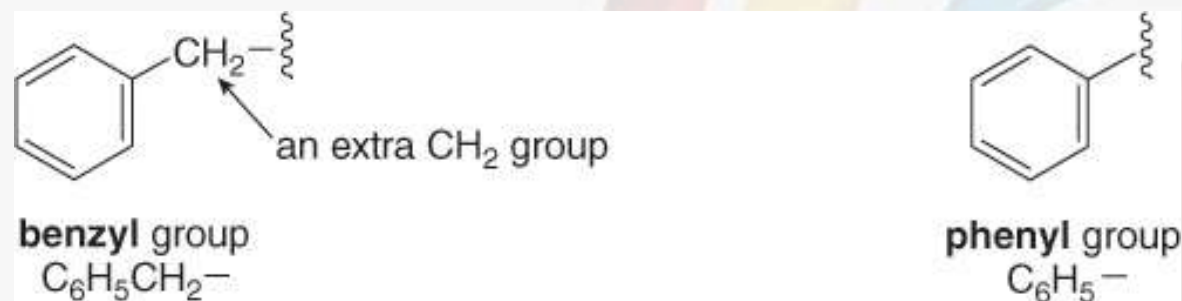
1,3,5-Trimethyl benzene

ARYL GROUPS

- The groups resulting from arenes by dropping a hydrogen atom from the benzene ring are called aryl groups or phenyl groups
- It is represented as C_6H_5-
- The symbol Ar is used to represent any aromatic group
- A benzene substituent is called a **phenyl group**, and it can be abbreviated in a structure as "**Ph-**".

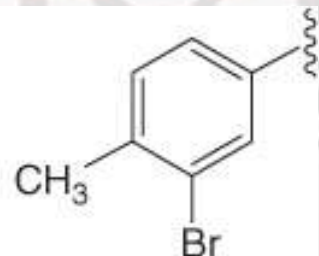
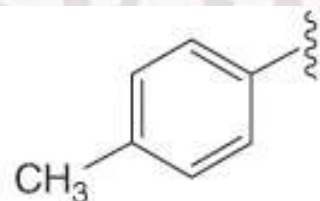


- The **benzyl group**, another common substituent that contains a benzene ring, differs from a phenyl group.



- Substituents derived from other substituted aromatic rings are collectively known as **aryl groups**.

Examples of
aryl groups



STRUCTURE OF BENZENE

Structure of benzene has been derived as follows:

1. Molecular formula:

- Elemental analysis and molecular weight determination showed that benzene had molecular formula as C_6H_6
- This indicated that benzene was a highly unsaturated compound compared with n-hexane (C_6H_{14})

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STRUCTURE OF BENZENE

2. Straight chain structure not possible:

- Benzene could be constructed as a straight chain or ring compound having double and /or triple bonds. C_6H_6
- But benzene does not behave like alkenes or alkynes
- It didn't decolorize bromine in carbon tetrachloride or cold aqueous $KMnO_4$ and it did not add water in the presence of acid

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STRUCTURE OF BENZENE

3. Evidence of cyclic structure:

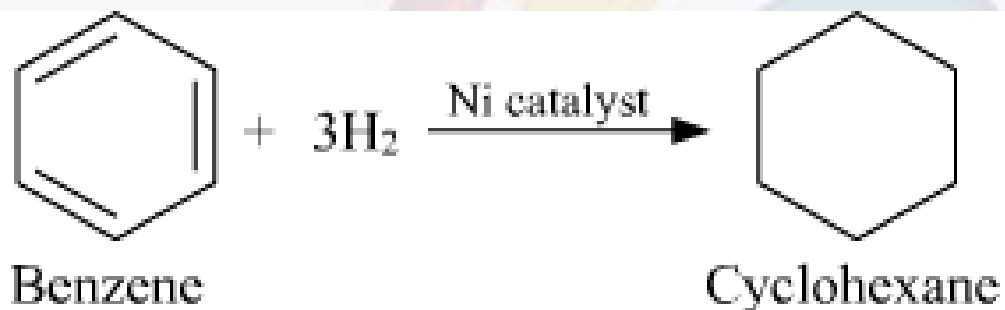
- a) **Substitution of benzene:** Benzene reacts with bromine in the presence of FeBr_3 to form monobromobenzene

The fact that only one monobromo and not isomeric products were obtained indicated that all 6 hydrogen atoms in benzene were identical.

This could be possible only if benzene had a cyclic structure of 6 carbons and one hydrogen is attached to each carbon

This confirmed the cyclic structure of benzene

b) Addition of hydrogen: Benzene added 3 moles of hydrogen in the presence of nickel catalyst to give cyclohexane



This could be possible only if benzene had a cyclic structure of 6 carbons and contains three double bonds

This confirmed the cyclic structure of benzene and also showed the presence of three carbon-carbon double bonds

STRUCTURE OF BENZENE

4. Kekule structure of benzene:

Kekule suggested that benzene consists of a cyclic planar structure of 6 carbons with alternate double and single bonds and one hydrogen attached to each carbon

According to this proposal benzene was simple 1,3,5-cyclohexatriene

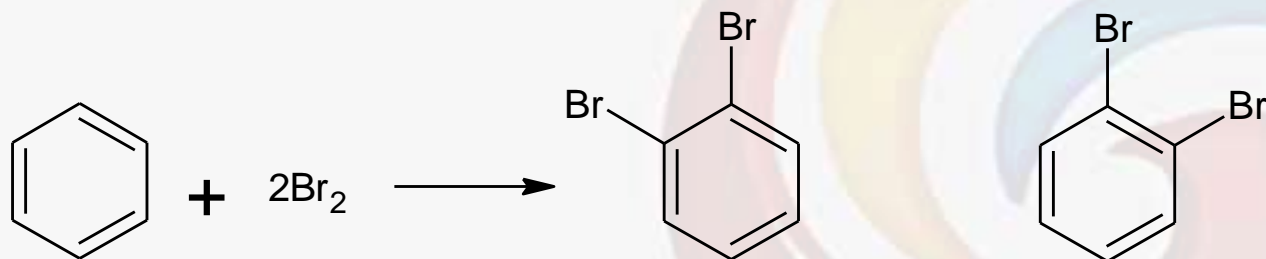
Objections to Kekule structure:

- a) If Kekule structure was correct there should exist two orthoisomers of dibromobenzene

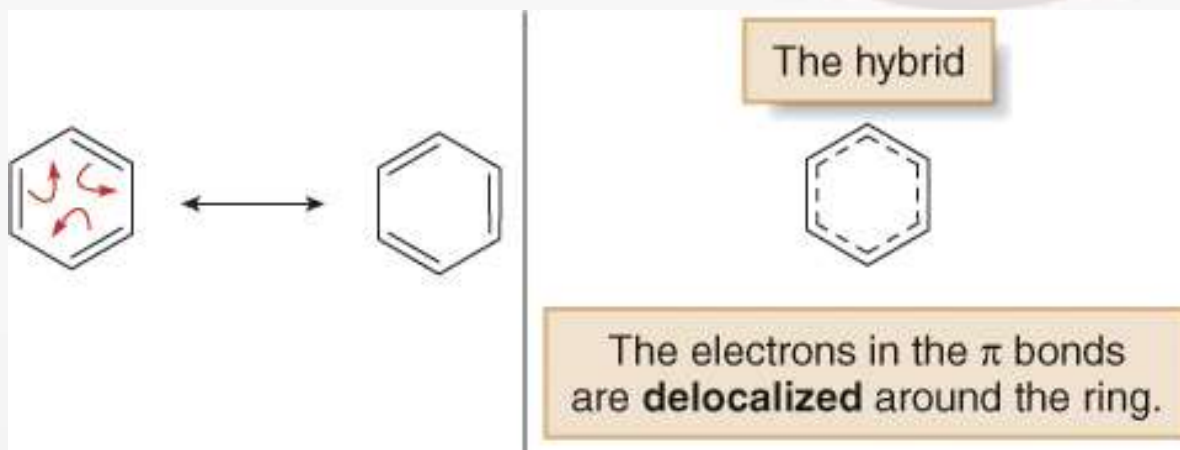
In one isomer the two bromine atoms should be on carbon that are connected by a double bond, while in the other isomer the bromine should be on carbons connected by a single bond.

4. Kekule structure of benzene:

In fact, only one ortho dibromobenzene could be prepared



To overcome this objection Kekule further suggested that benzene was a mixture of two forms in rapid equilibrium



4. Kekule structure of benzene

- b) Kekule's structure failed to explain why benzene with 3 double bonds did not give addition reactions like other alkenes
e.g. benzene did not react with HBr or Br₂ in CCl₄

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STRUCTURE OF BENZENE

5. Resonance description of benzene

The phenomena in which 2 or more structures can be written for a compound with identical positions of atoms is called **RESONANCE**

The actual structure of the molecule is said to be resonance hybrid of various possible alternative structure

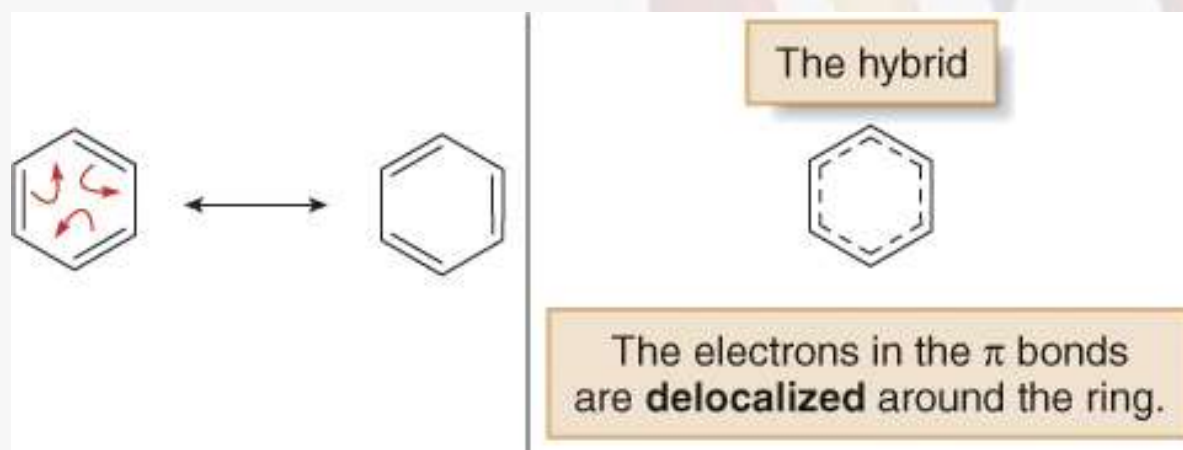
A double headed arrow between the resonance structure is used to represent the resonance hybrid

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5. Resonance description of benzene Chemistry-II

Thus in case of benzene, Kekule's two structures represent the resonance structures

The actual structure of the molecule may be represented as hybrid of these two resonance structures



All single bonds in the first structure are double bonds in the second structure

The C-C bonds in benzene are neither single bonded nor double bonded, they are something halfway between

5. Resonance description of benzene

Spectroscopic measurements show that benzene is planar and all of its C-C bonds are of equal length 1.40\AA . This value lies in between C-C single bond length 1.54\AA and the C-C double bond length 1.34\AA .

Resonance hybrid is more stable than any of its contributing structures for benzene.

The stability due to resonance is so great that pi bonds of the molecule will normally resist breaking and this explains the lack of reactivity of benzene towards addition.

STRUCTURE OF BENZENE

6. Molecular orbital structure of benzene

All six carbon atoms in benzene are sp^2 hybridized. The hybrid orbitals overlap with each other and with s-orbitals of the six hydrogen atoms forming C-C & C-H sigma bonds

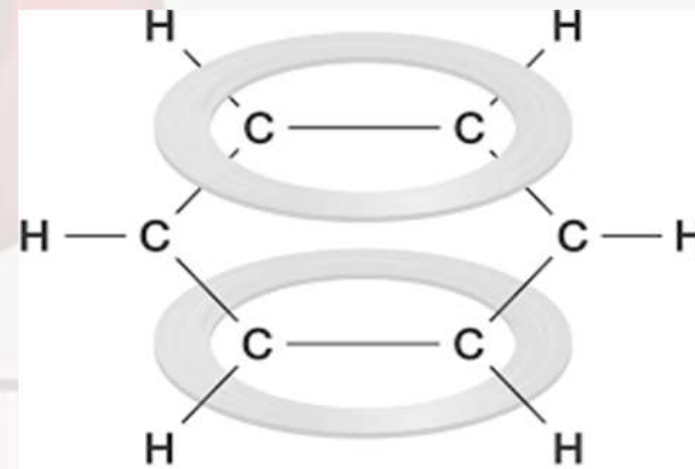
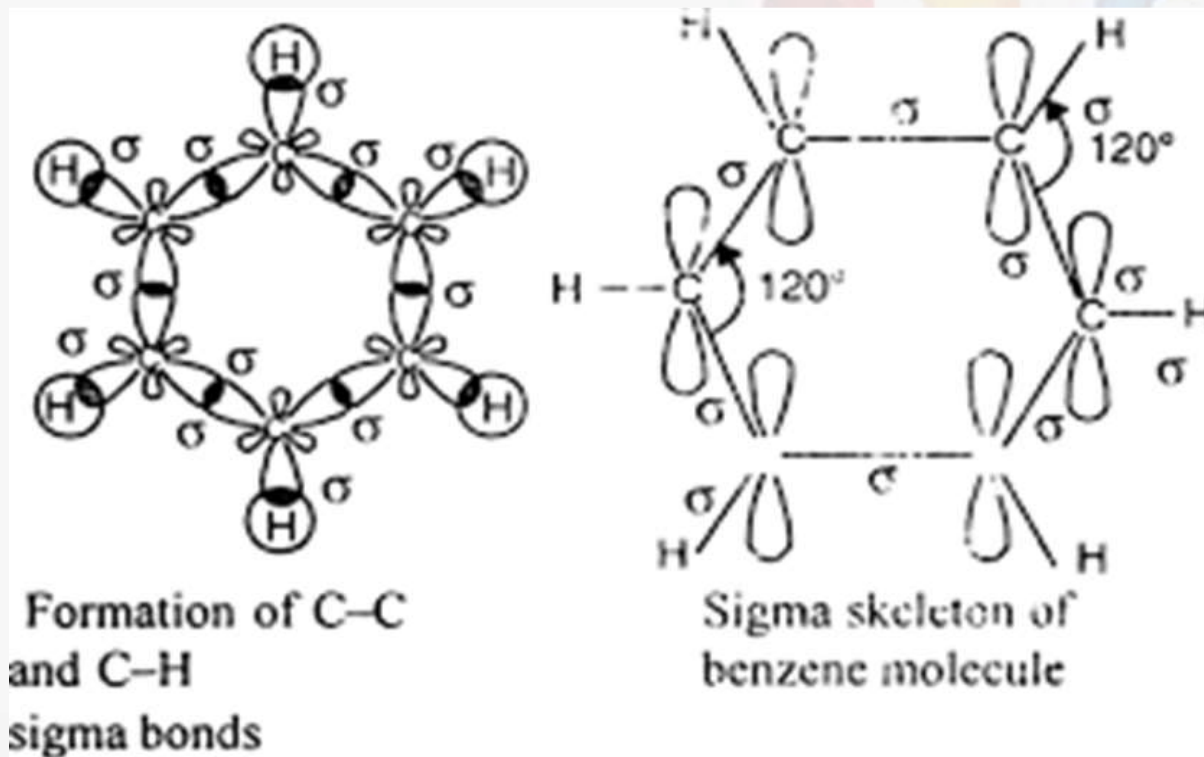
Since the sigma bonds result from the overlap of planar sp^2 orbitals, all C and H atoms in benzene lie in the same plane and all bond angles are 120° .

Also each carbon atom in benzene have an unhybridized p orbital containing one electron.

These p-orbitals are perpendicular to the plane of sigma bonds.

The lateral overlap of these p-orbitals produces a **pi-molecular orbital** containing 6 electrons

- One half of this pi-molecular orbital lies above and the other half lies below the plane of sigma bonds



AROMATICITY

Huckel's rule

- Aromatic compounds contain alternate double bonds and single bonds in a cyclic structure and resemble benzene in chemical behaviour
- They undergo substitution reaction rather than addition reaction. This behaviour is called as AROMATICITY
- It is a property of sp^2 hybridized planar rings in which the p-orbitals allow cyclic delocalization of pi-electrons

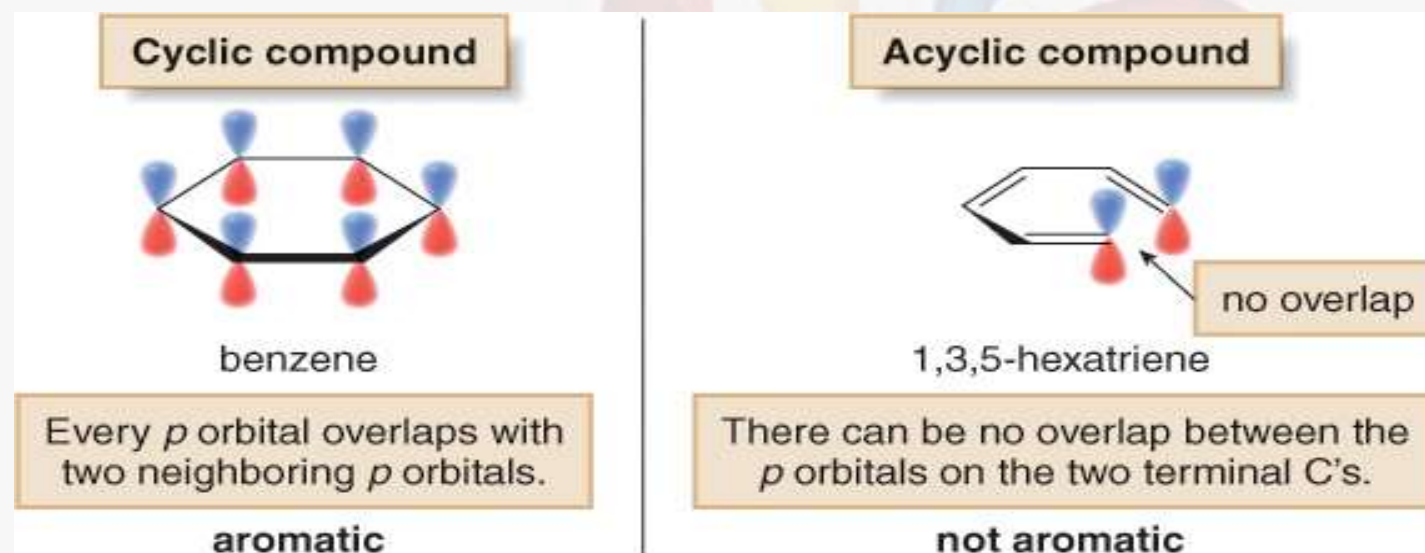
Criteria for aromaticity

- An aromatic compound is cyclic and planar
- The cyclic pi-molecular orbital formed by the overlap of p-orbital must contain $(4n+2)$ pi electrons. This is known as Huckel's rule

The Criteria for Aromaticity—Hückel's Rule

Four structural criteria must be satisfied for a compound to be aromatic.

[1] A molecule must be cyclic.



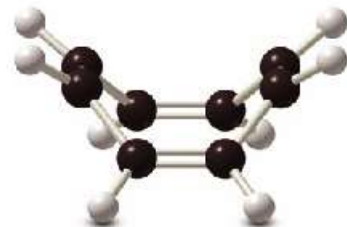
To be aromatic, each p orbital must overlap with p orbitals on adjacent atoms.

[2] A molecule must be planar.

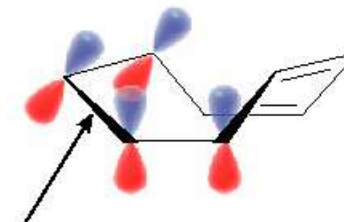
All adjacent p orbitals must be aligned so that the π electron density can be delocalized.



cyclooctatetraene
not aromatic

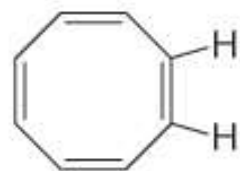


a tub-shaped,
eight-membered ring

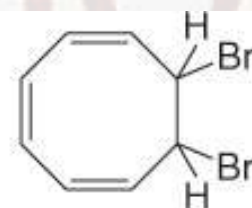
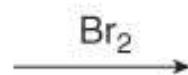


Adjacent p orbitals cannot overlap.
Electrons cannot delocalize.

Since cyclooctatetraene is non-planar, it is not aromatic, and it undergoes addition reactions just like those of other alkenes.



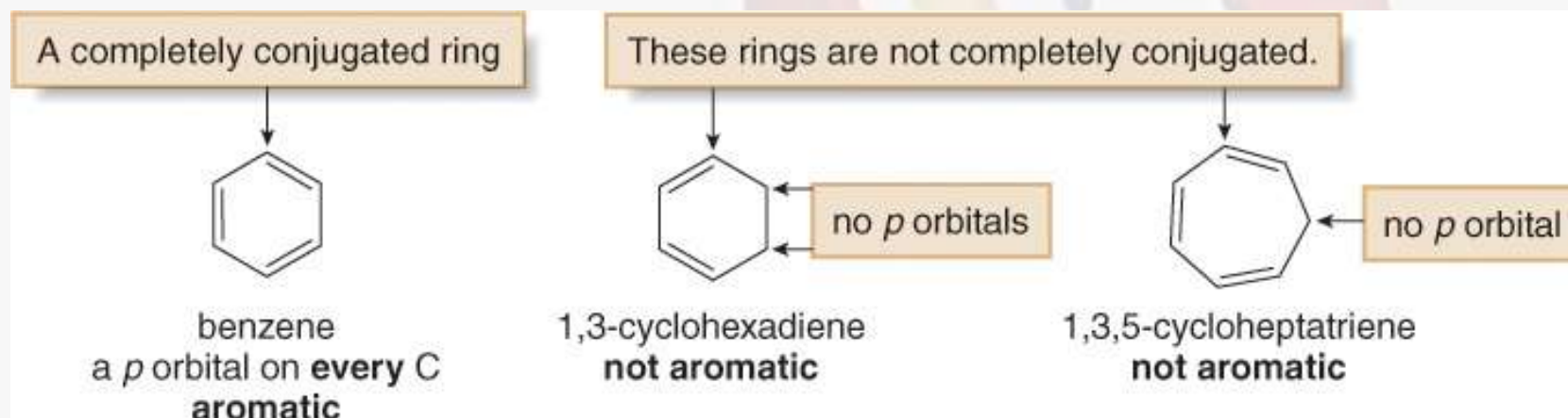
cyclooctatetraene



addition product

[3] A molecule must be completely conjugated.

Aromatic compounds must have a p orbital on every atom.

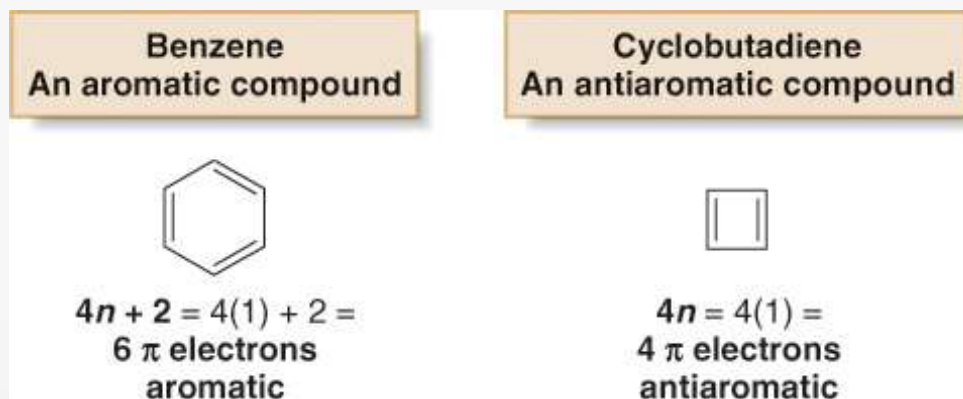


[4] A molecule must satisfy **Hückel's rule**, and contain a particular number of π electrons.

Hückel's rule:

- An aromatic compound must contain $4n + 2 \pi$ electrons ($n = 0, 1, 2,$ and so forth).
- Cyclic, planar, and completely conjugated compounds that contain $4n \pi$ electrons are especially unstable, and are said to be *antiaromatic*.

Benzene is aromatic and especially stable because it contains 6 π electrons. Cyclobutadiene is **antiaromatic** and especially unstable because it contains 4 π electrons.



Considering aromaticity, a compound can be classified in one of three ways:

1. Aromatic—A cyclic, planar, completely conjugated compound with $4n + 2 \pi$ electrons.
2. Antiaromatic—A cyclic, planar, completely conjugated compound with $4n \pi$ electrons.
3. Not aromatic (nonaromatic)—A compound that lacks one (or more) of the following requirements for aromaticity: being cyclic, planar, and completely conjugated.

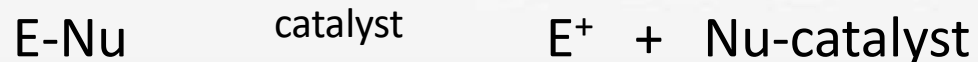
REACTIONS OF BENZENE

Electrophilic aromatic substitution of benzene

- Benzene undergoes electrophilic substitution reaction
- Benzene is an electron rich system and it attacked by electrophile giving substitution products

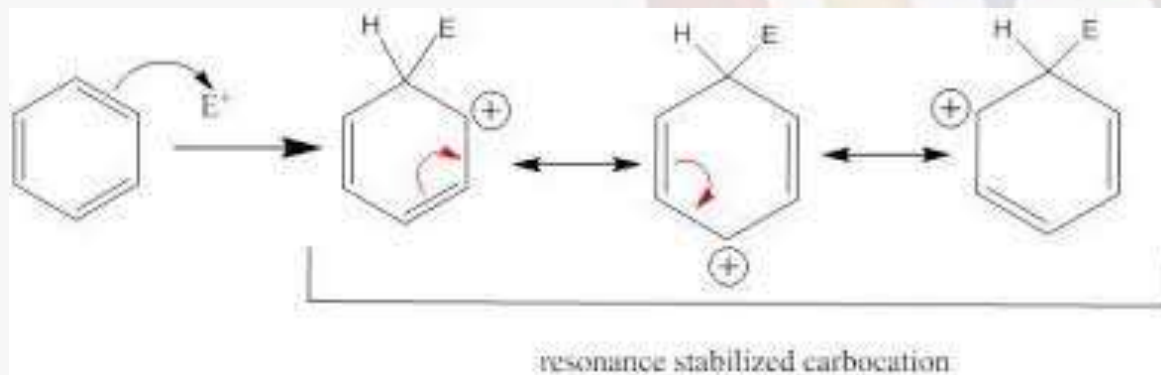


- Mechanism
- **STEP 1: formation of an electrophile**

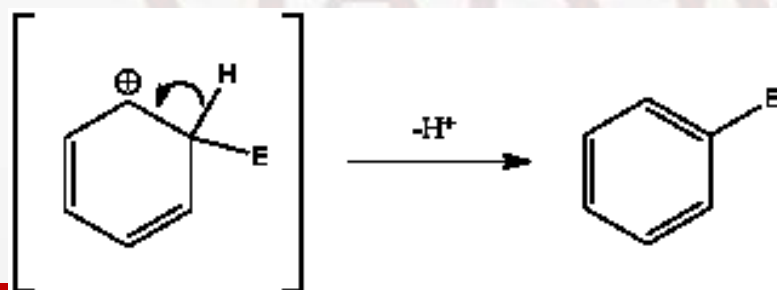


Electrophilic aromatic substitution of benzene

- Mechanism
- **STEP 2: Attack of electrophile on aromatic ring to form the carbonium ion**



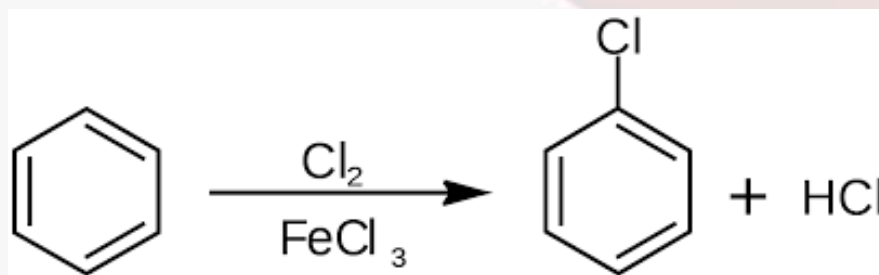
- **STEP 3: Loss of proton**



Electrophilic aromatic substitution of benzene

1. Halogenation reaction

Benzene reacts with chlorine in presence of FeCl_3 or AlCl_3 at room temperature to form chlorobenzene

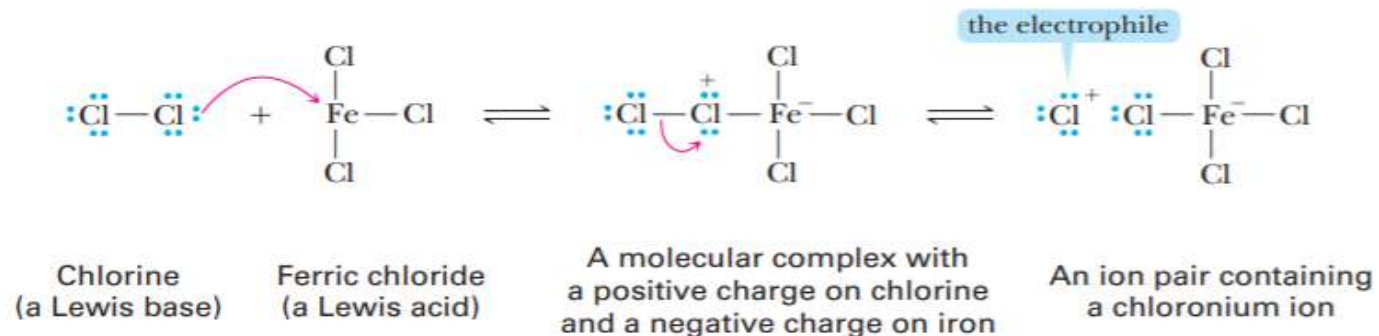


Benzene

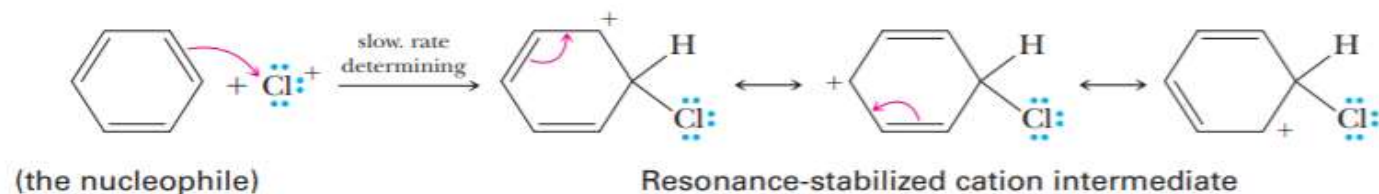
Chlorobenzene

Halogenation reaction- Mechanism

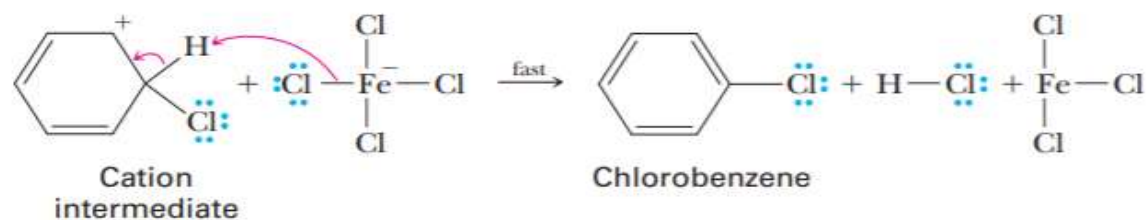
STEP 1: Formation of the Electrophile. Reaction between chlorine (a Lewis base) and FeCl_3 (a Lewis acid) gives an ion pair containing a chloronium ion (an electrophile):



STEP 2: Reaction of a nucleophile and an electrophile to form a new covalent bond. Reaction of the $\text{Cl}_2\text{-FeCl}_3$ ion pair with the pi electron cloud of the aromatic ring forms a resonance-stabilized cation intermediate, represented here as a hybrid of three contributing structures:



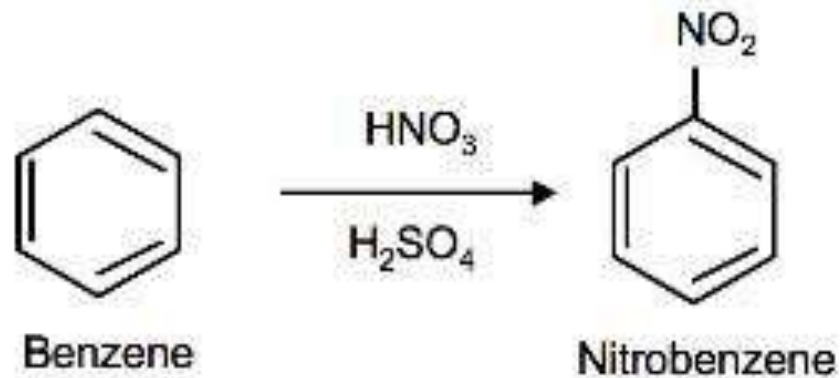
STEP 3: Take a proton away. Proton transfer from the cation intermediate to FeCl_4^- forms HCl , regenerates the Lewis acid catalyst, and gives chlorobenzene:



Electrophilic aromatic substitution of benzene

2. Nitration reaction

Benzene reacts with concentrated nitric acid in presence of conc. Sulphuric acid at 60°C to form nitrobenzene

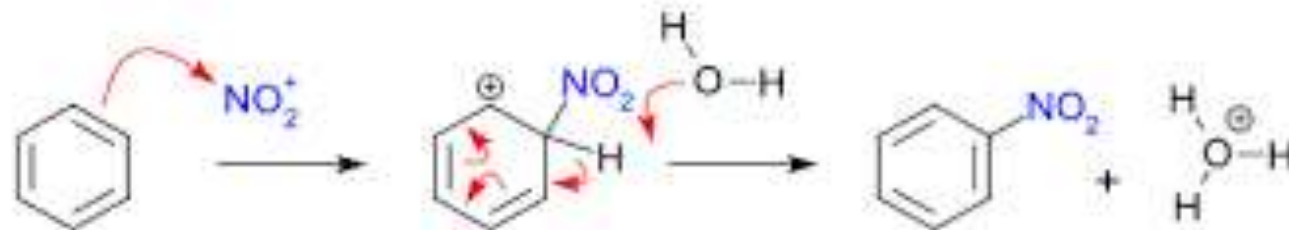


MECHANISM

Step I



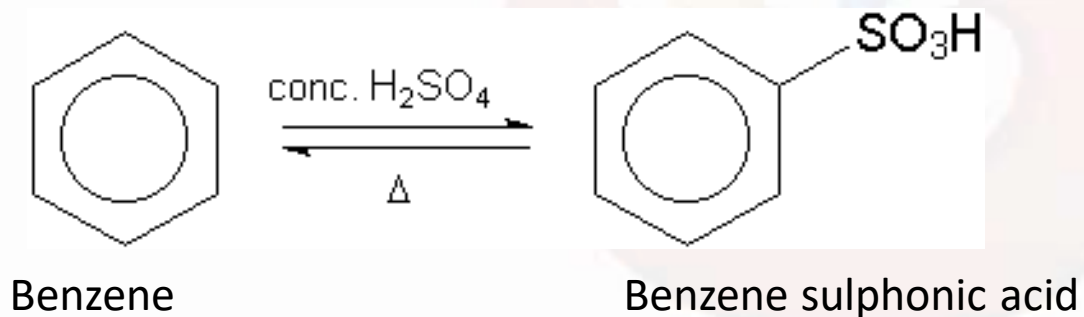
Step II



Electrophilic aromatic substitution of benzene

3. Sulphonation reaction

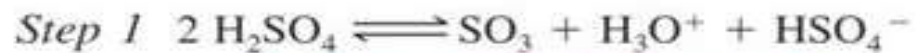
Benzene reacts with concentrated Sulphuric acid at 120°C or with fuming sulphuric acid at room temperature to form benzene sulphonic acid



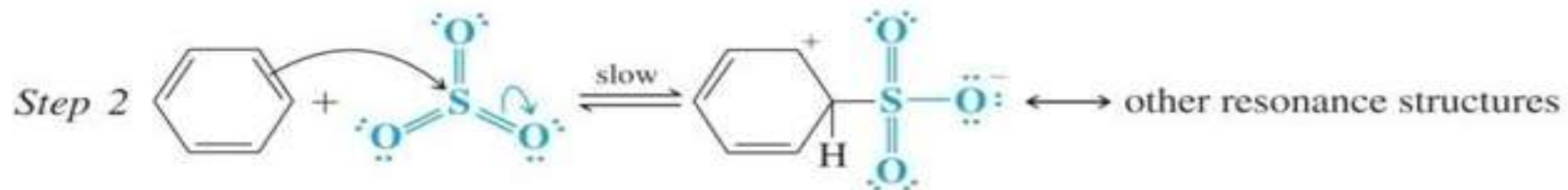
Sulphonation reaction

MECHANISM

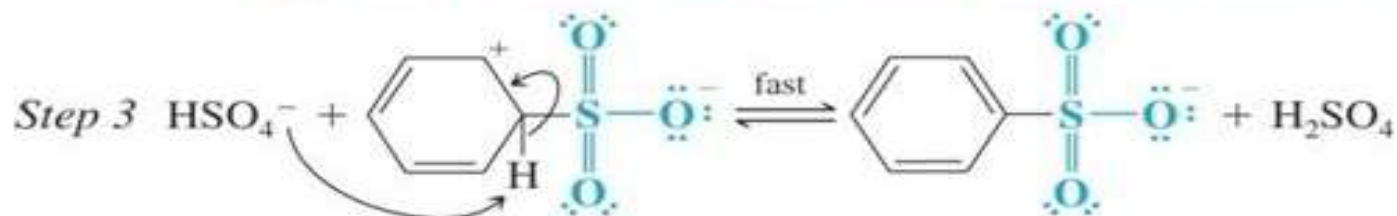
- ⚡ The reaction also occurs in conc. sulfuric acid, which generates small quantities of SO_3 , as shown in step 1 below



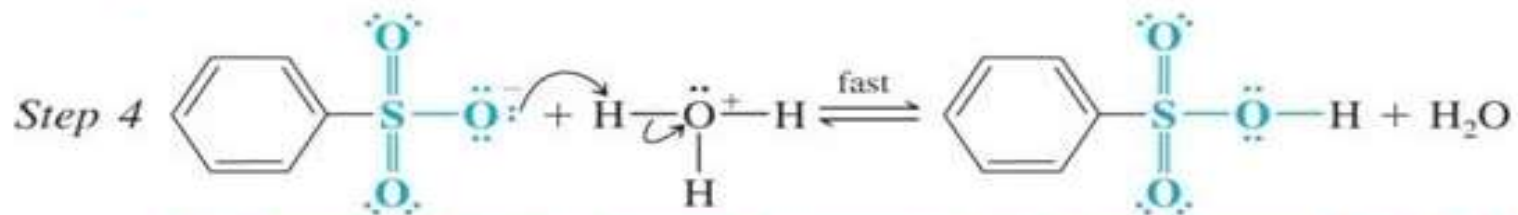
This equilibrium produces SO_3 in concentrated H_2SO_4 .



SO_3 is the actual electrophile that reacts with benzene to form an arenium ion.



A proton is removed from the arenium ion to form the benzenesulfonate ion.

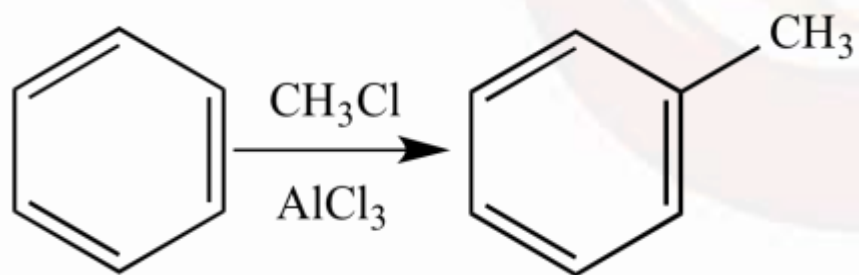


The benzenesulfonate ion accepts a proton to become benzenesulfonic acid.

Electrophilic aromatic substitution of benzene

4. Friedel Craft alkylation

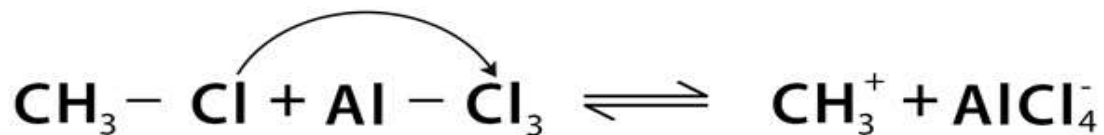
Benzene reacts with alkyl halides in presence of AlCl_3 to form alkyl benzene



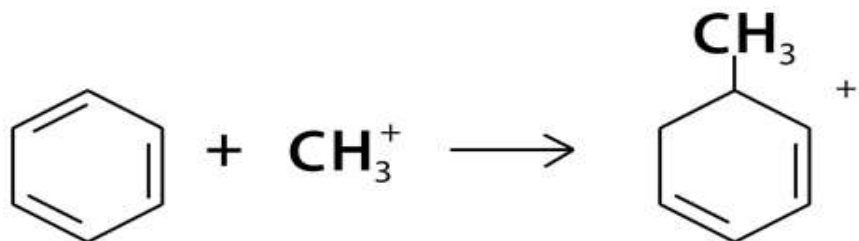
Benzene

Toluene

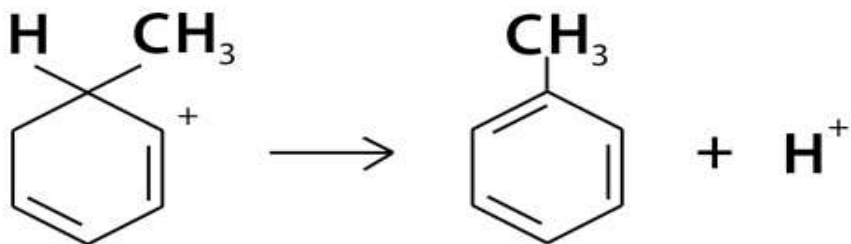
Friedel-Crafts alkylation mechanism



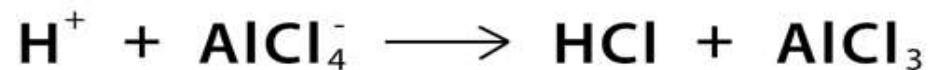
Step1: Removal of Cl from CH_3Cl to form the electrophilic species CH_3^+



Step2: CH_3^+ attacks $\text{C}=\text{C}$ bond in benzene which loses its aromaticity to form a carbocation



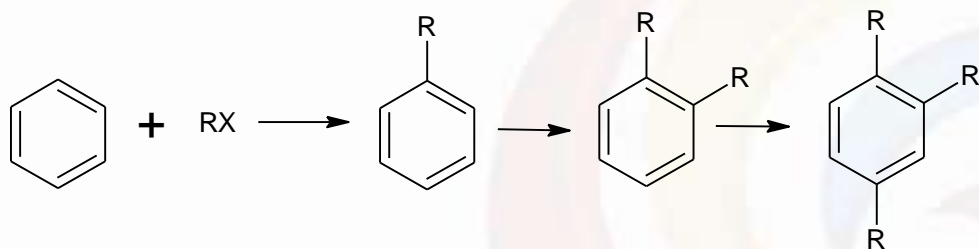
Step3: Loss of proton (H^+) from the carbocation to restore the aromaticity



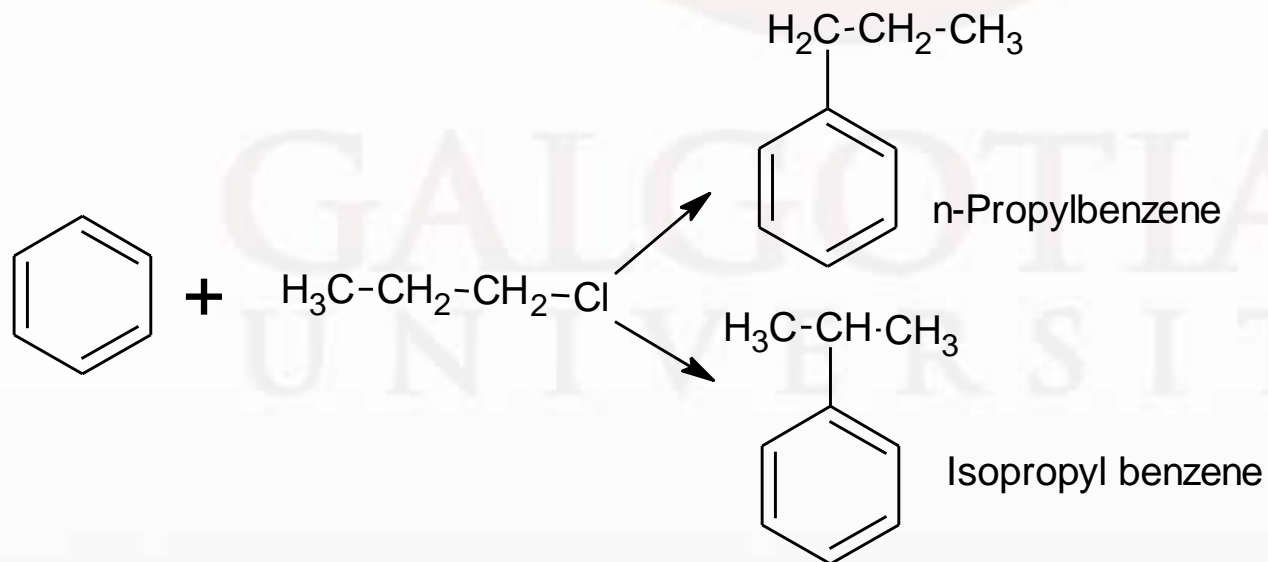
Step4: H^+ reacts with AlCl_4^- to give back AlCl_3

Drawbacks of Friedel Craft alkylation

- i) It is difficult to stop the reaction. When one alkyl group has entered the ring, di and trialkyl benzene are also formed.



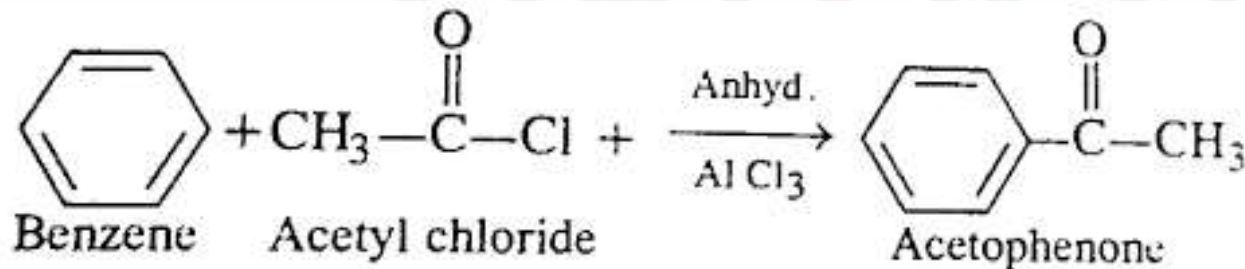
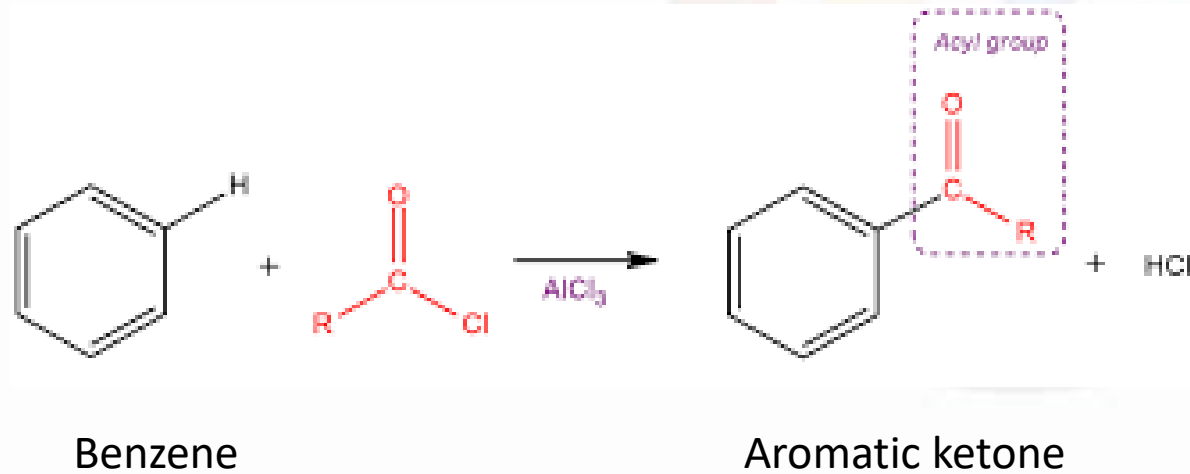
- ii) The alkyl groups often tend to rearrange. e.g. when benzene is treated with n-propyl chloride, the product is isopropyl benzene rather than n-propyl benzene



Electrophilic aromatic substitution of benzene

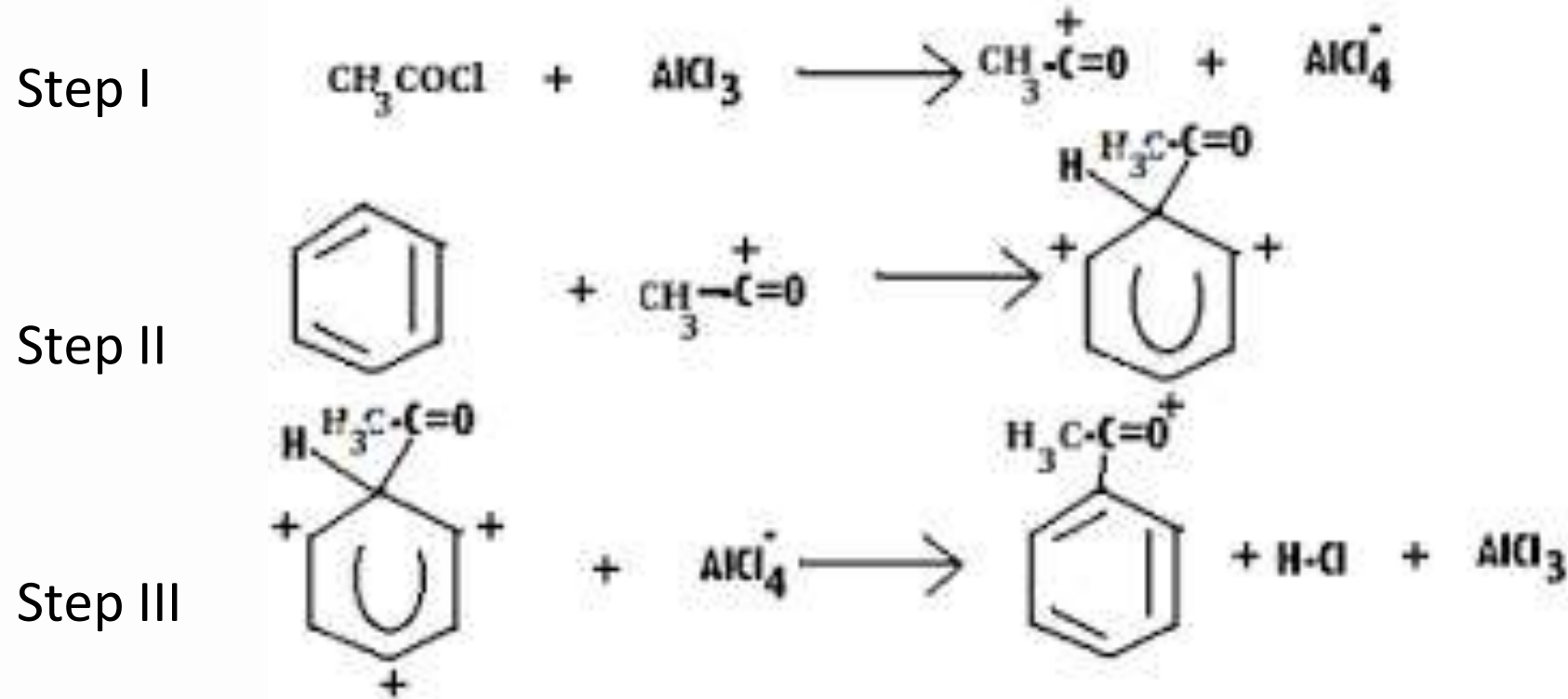
5. Friedel Craft acylation

Benzene reacts with acid chlorides or anhydrides in the presence of AlCl_3 to give aromatic ketone



Friedel Craft acylation

- MECHANISM



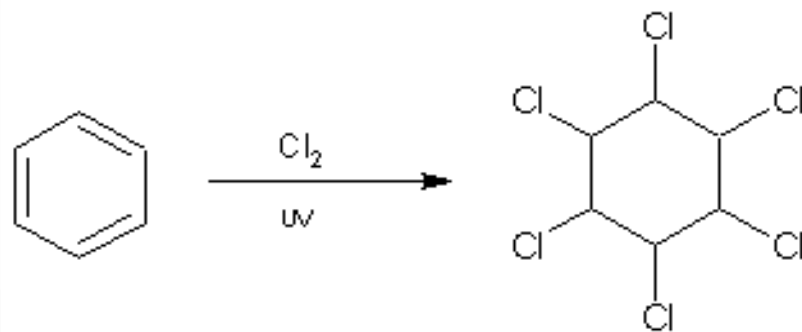
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Addition reaction of benzene

- Addition of hydrogen



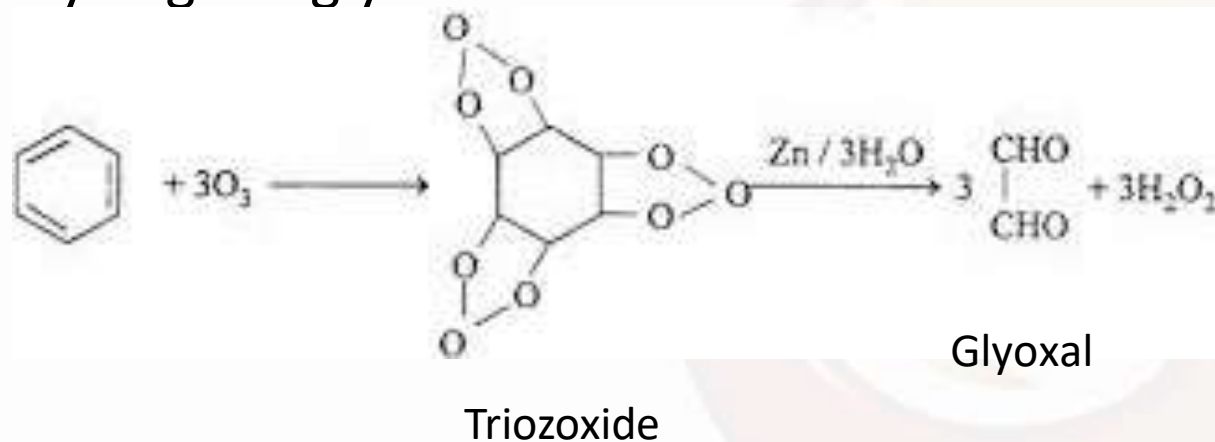
- Addition of halogen



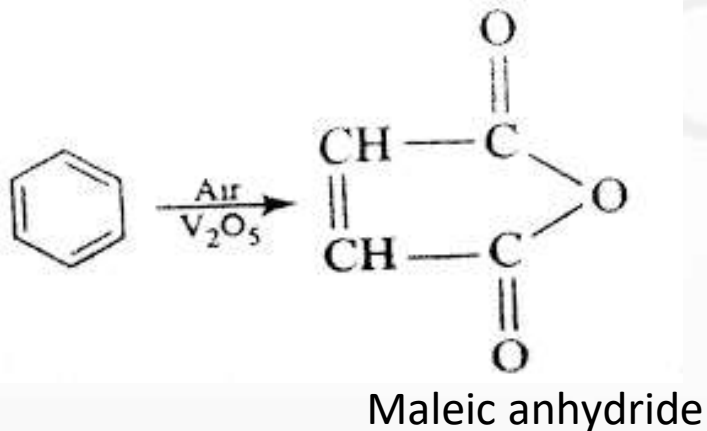
Benzene hexachloride

Oxidation reactions of benzene

- Ozonolysis:** Benzene reacts with ozone to give triozoxide, which on hydrolysis gives glyoxal

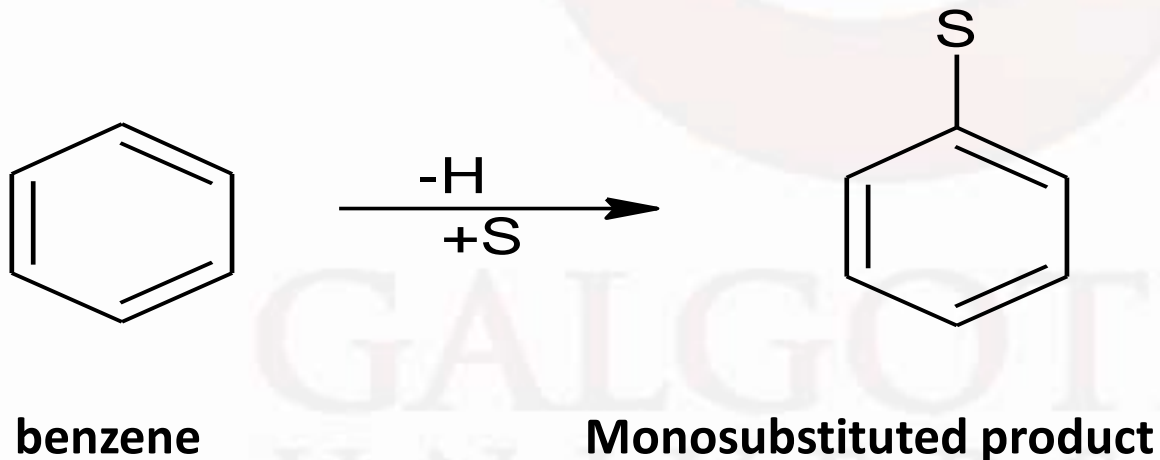


- Vapour phase oxidation:** Upon oxidation with vanadium pentoxide at 450°C , benzene forms maleic anhydride



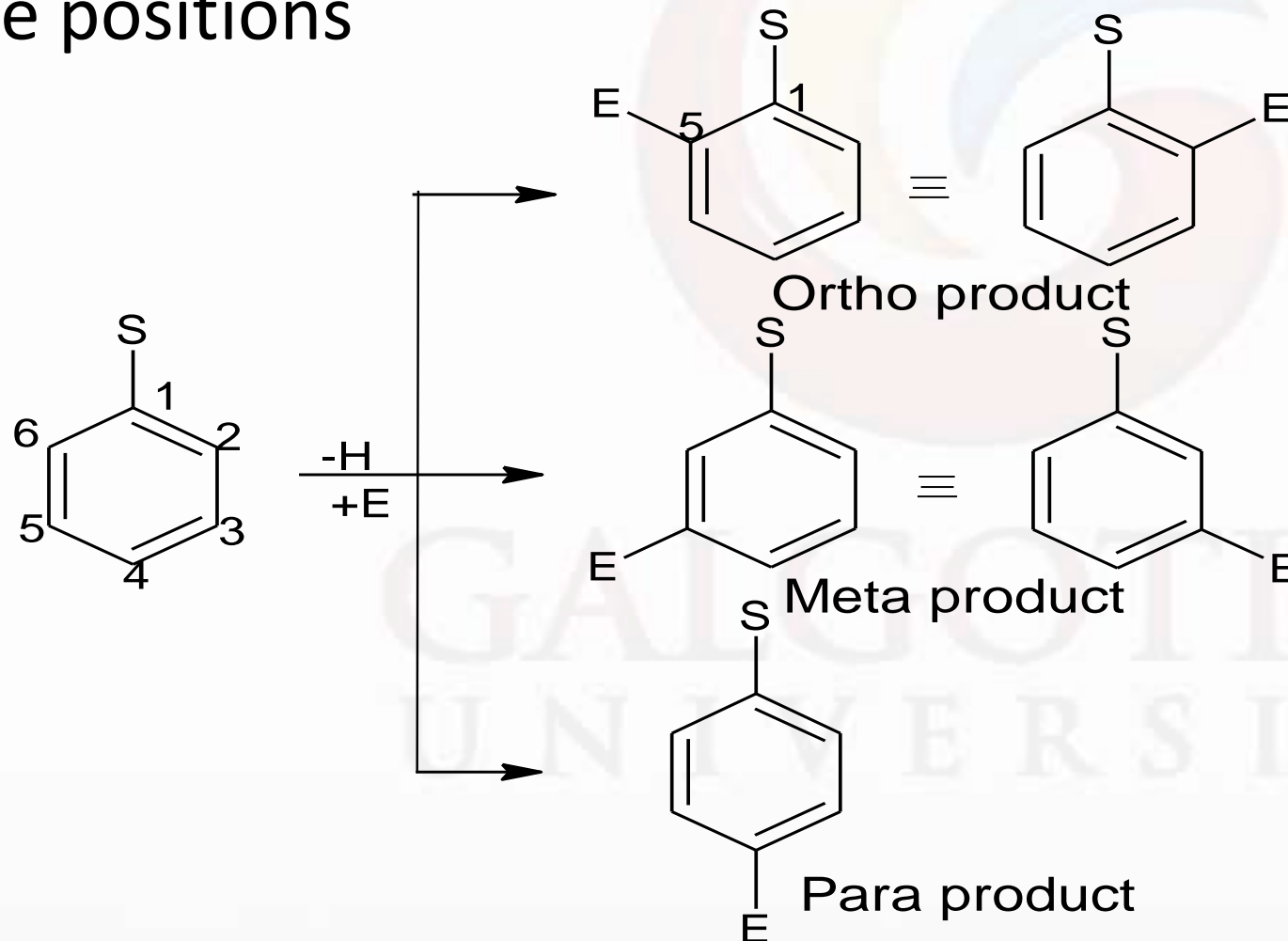
Effect of substituents on electrophilic substitution / Orientation of mono-substituted benzene on electrophilic substitution

- All hydrogens of benzene ring are equivalent, therefore, only one monosubstitution product is possible



Orientation of mono-substituted benzene on electrophilic substitution

- A second substituent E can occupy any of the remaining five positions



Orientation of mono-substituted benzene on electrophilic substitution

- There are two types of influence of substituents
 - A. Directive or orientation effect:** The first substituent may direct the next incoming substituent to ortho, meta or para position, depending on the nature of the first substituent. This is called Directive or orientation effect
 - B. Activity effect:** The substituent already present may activate or deactivate the benzene toward further substitution. These effects are called Activity effects.

Orientation of mono-substituted benzene on electrophilic substitution

A. Directive or orientation effect

In the monosubstituted benzene (C_6H_5S), five hydrogens are available

Out of these 2 are ortho, 2 are meta and 1 para to S.

If the substitution was random, the proportion of the disubstituted products would be

Ortho – 40% meta – 40% para – 20%

This distribution is never observed.

The proportion of the products formed is determined by the nature of first substituent on the ring

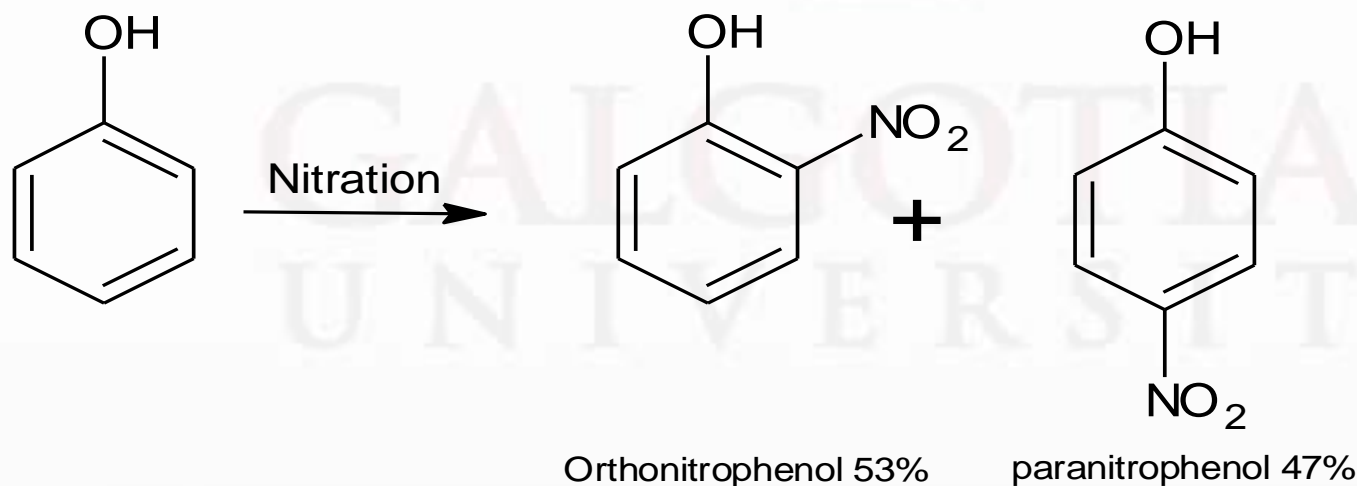
Orientation of mono-substituted benzene on electrophilic substitution

A. Directive or orientation effect

1. **Ortho-Para directive effect:** Certain substituents direct the second substituent to the para and ortho position simultaneously. These are called Ortho-Para directors.

Ex. Nitration of phenol forms o-nitrophenol (53%) and p-nitrophenol (47%). The substituent OH- is said to be ortho-para director.

Common ortho-para directing groups: -Cl, -Br, -I, -OH, -NH₂, -CH₃, -C₂H₅, etc.



Orientation of mono-substituted benzene on electrophilic substitution

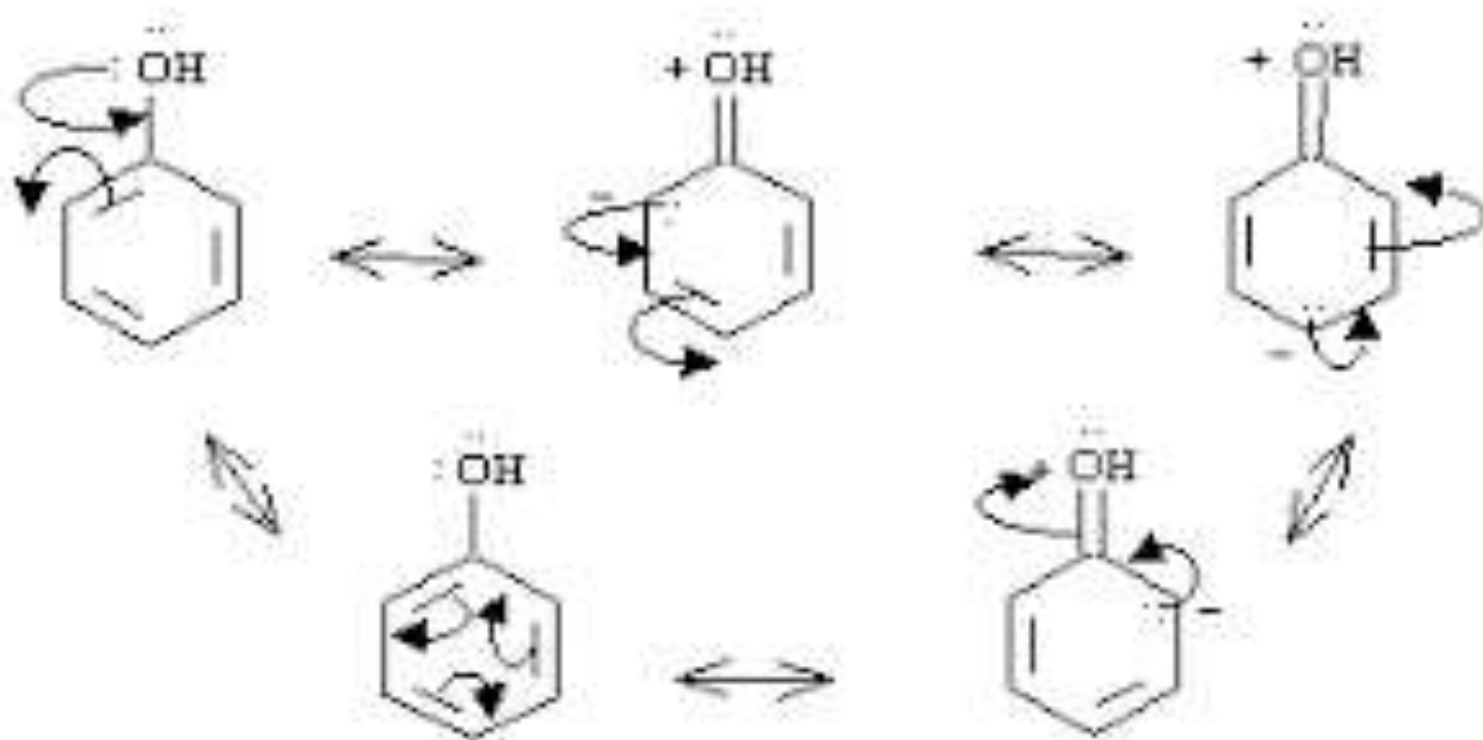
Ortho-Para directive effect: There exist various resonance forms of phenol in which the substituent OH group is ortho-para directing.

There are 2 non-bonding electron pairs on Oxygen atom attached to the ring, one of these is distributed into the ring by interaction with the pi electron system.

The ortho-para position have a greater density of electrons than the meta position

Therefore, the resonance hybrid has negative charge in the o-p position and the electrophile would naturally attack at this electron-rich centre regardless of its nature

Ortho-Para directive effect:



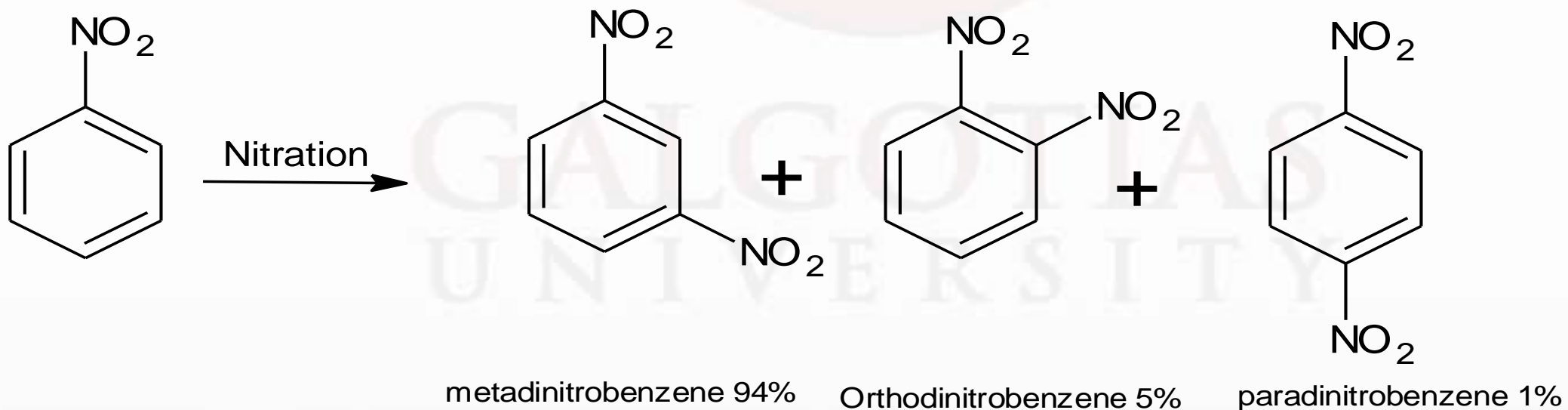
Orientation of mono-substituted benzene on electrophilic substitution

A. Directive or orientation effect

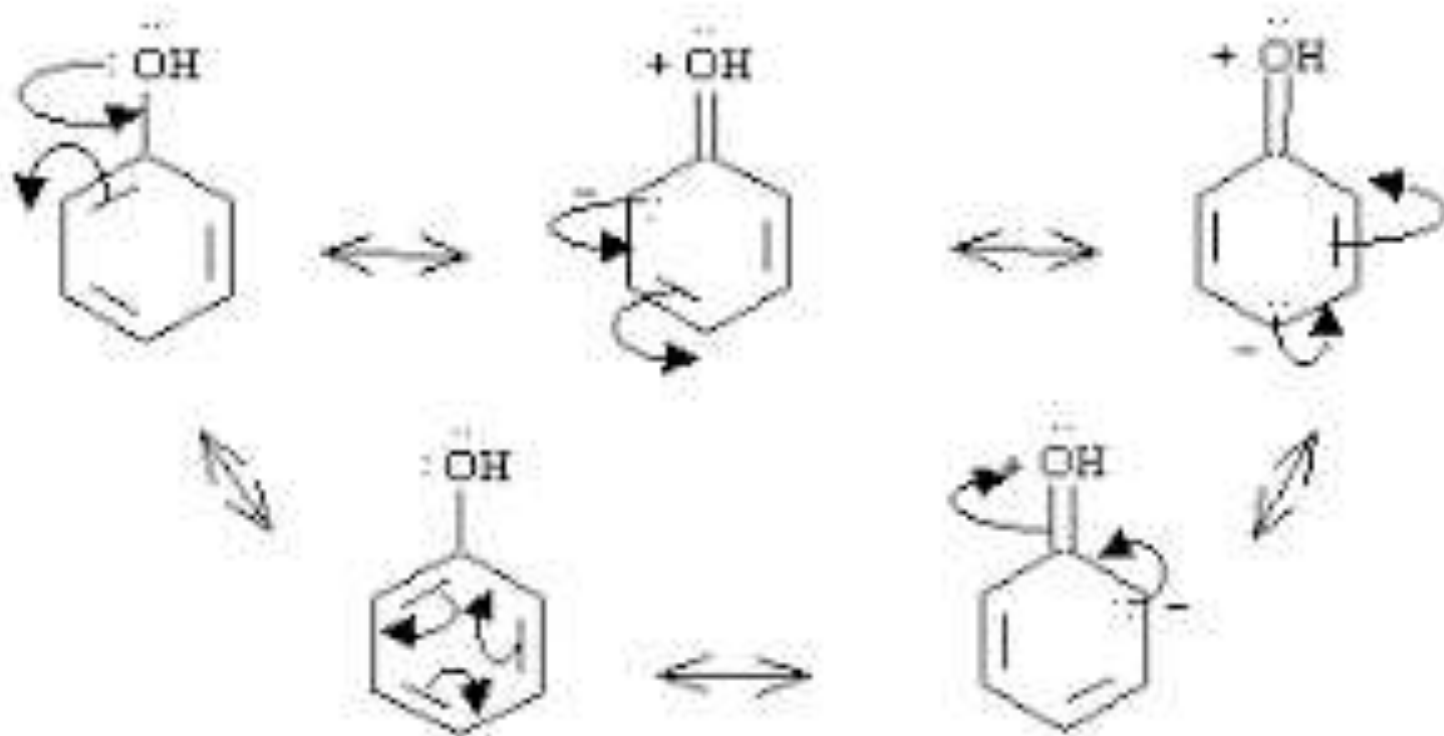
2. **Meta directive effect:** The substituents which direct the second substituent to the meta position are called as meta-directors.

Ex. Nitration of nitrobenzene forms 94% of meta-dinitrobenzene, 5% of ortho-dinitrobenzene and 1% of para-dinitrobenzene. The substituent NO_2 is said to be meta director.

Common meta-directing groups: $-\text{SO}_3\text{H}$, $-\text{CN}$, $-\text{CHO}$, $-\text{NO}_2$, etc.



Ortho-Para directive effect:



LS
FY

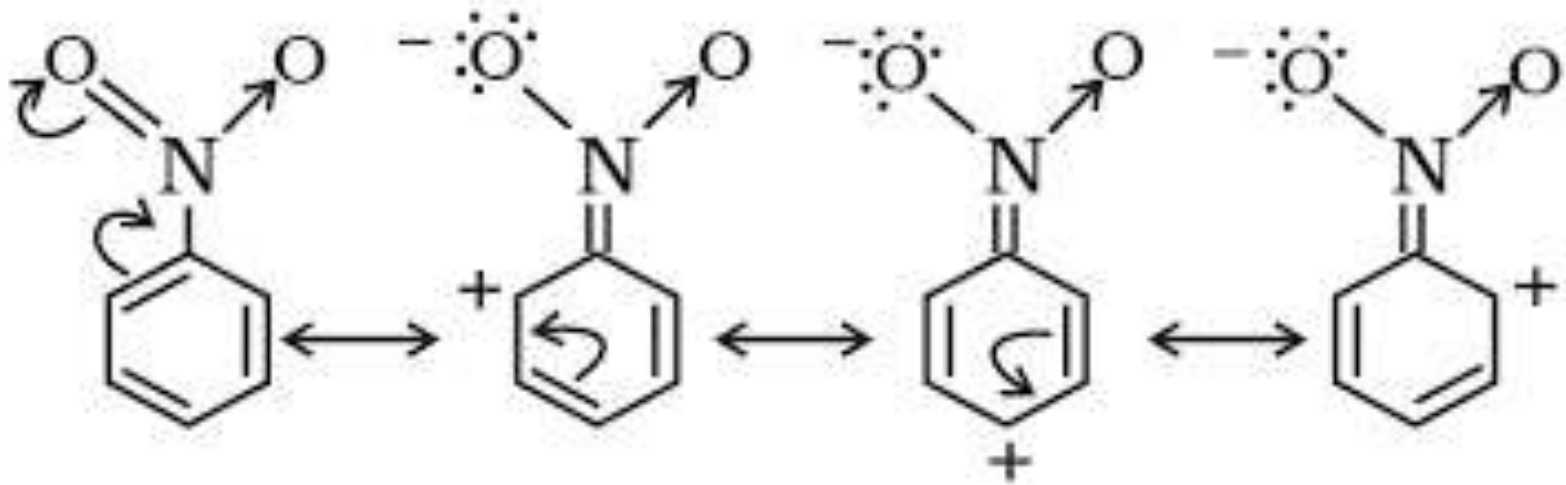
Orientation of mono-substituted benzene on electrophilic substitution

Meta directive effect: The key atom in these substituents is bonded to another highly electronegative atom by a double or triple bond. The electronegative atom pulls the electron pair of the multiple bond and thus places a positive charge on the key atom.

The key atom in turn withdraws electrons from the benzene ring causing resonance. Ex. Nitrobenzene

In those structures ortho-para positions of the resonance forms have a positive charge and there is no scope of electrophile attack at meta position which are relatively electron rich.

Meta directive effect:

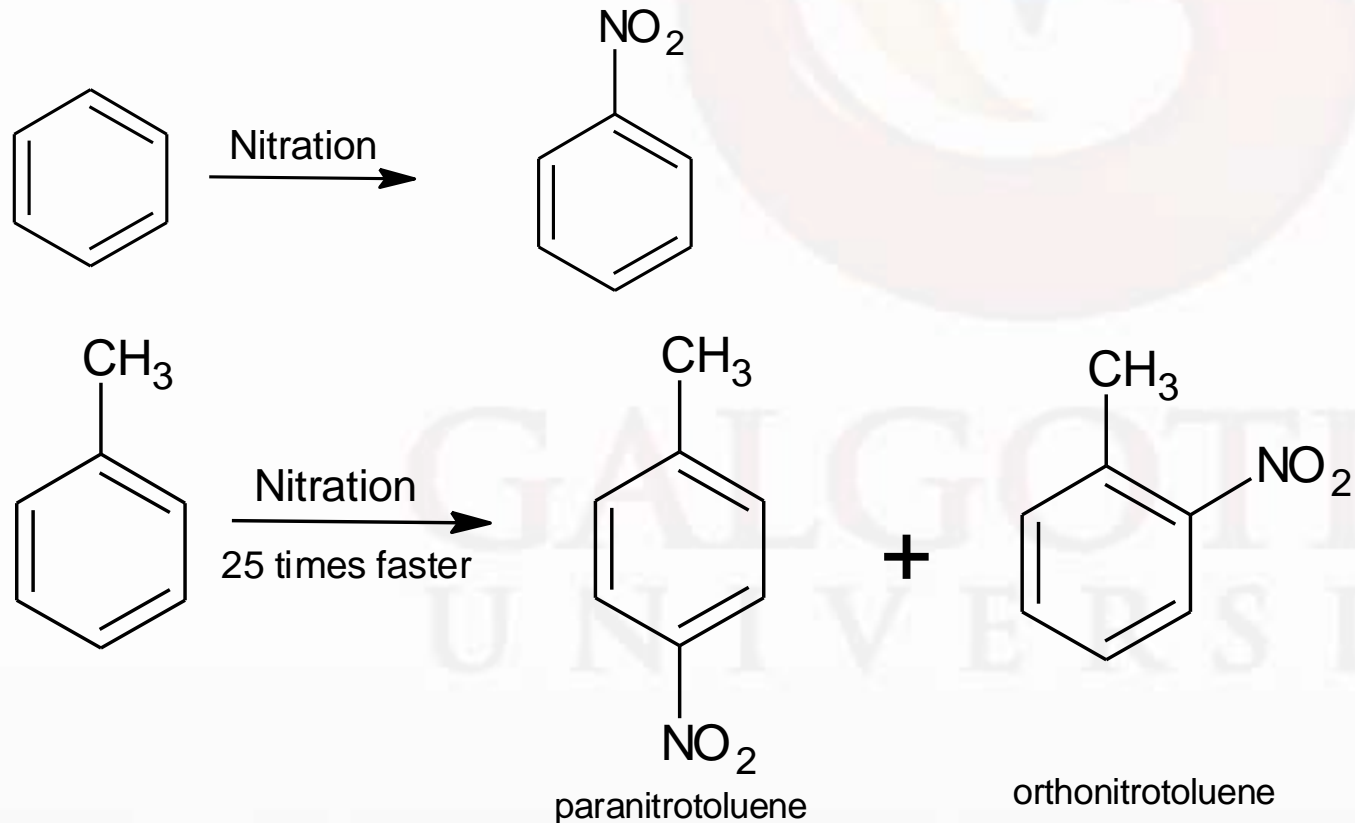


GALGOTIAS
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Effect of substituents on reactivity

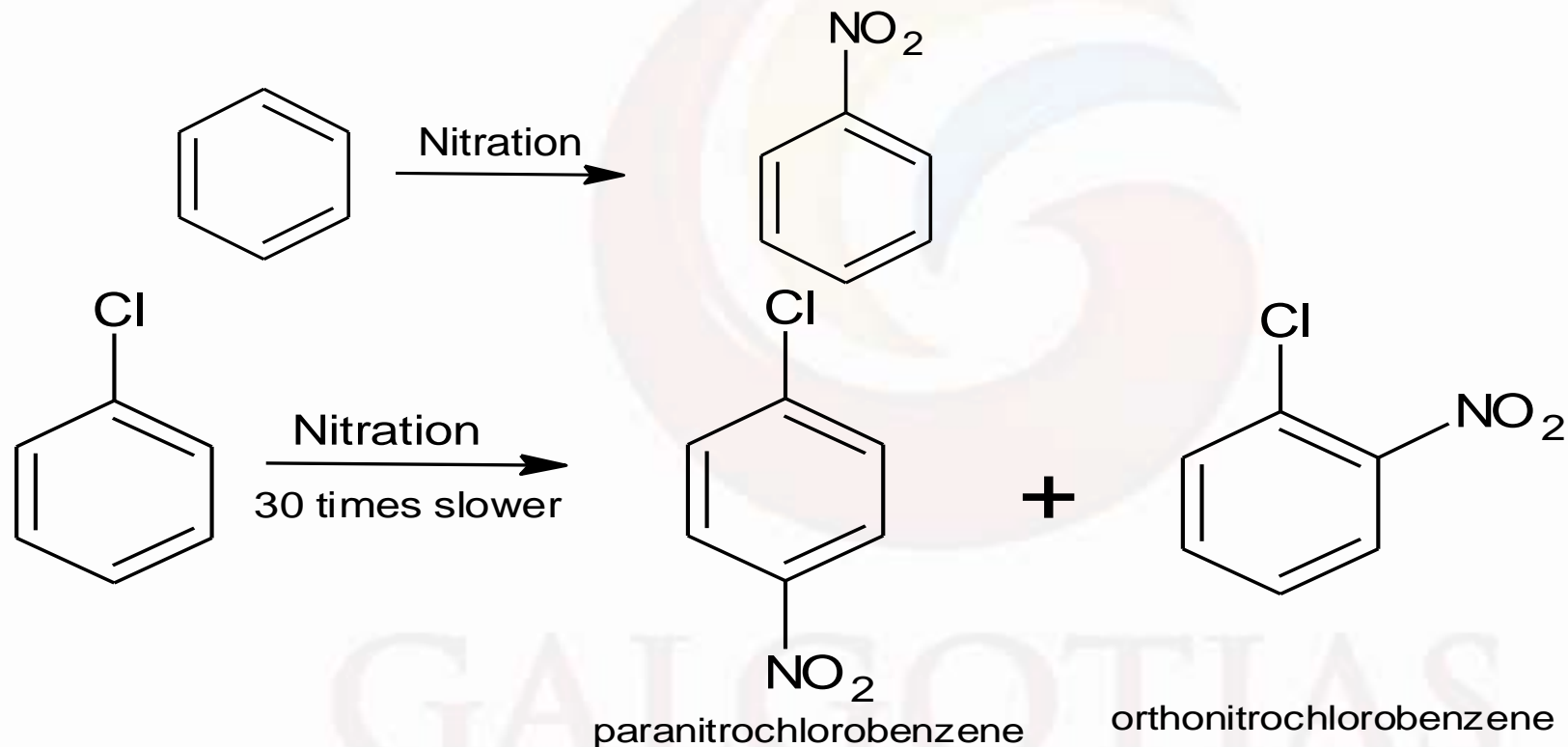
A substituent already present on a benzene ring not only directs the position of an incoming group but also influences the rate of reaction

Ex. 1. Toluene is nitrated 25 times faster than benzene itself



Effect of substituents on reactivity

Ex. 2. Chlorobenzene is nitrated 30 times slower than benzene



This means that presence of methyl group on benzene ring activate the ring to electrophilic aromatic substitution while the presence of chloride group deactivates it.

Effect of substituents on reactivity

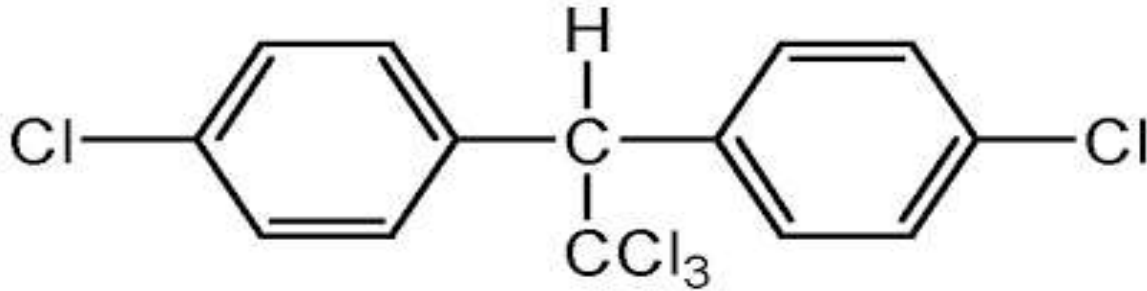
A substituent which activates the aromatic ring to further substitution is called an **activating substituent** or **ring activator** (giving electrons to benzene ring)

A substituent which deactivates the aromatic ring for further substitution is called as **deactivating substituent** or **ring deactivator** (withdrawing electrons from benzene ring)

It is observed that ortho-para directors activate a ring toward electrophilic substitution where as meta-directing groups deactivate the ring toward electrophilic substitution

Exception: Halogen are ortho-para directors but they deactivate the aromatic ring for further substitution

Dichlorodiphenyltrichloroethane (DDT)



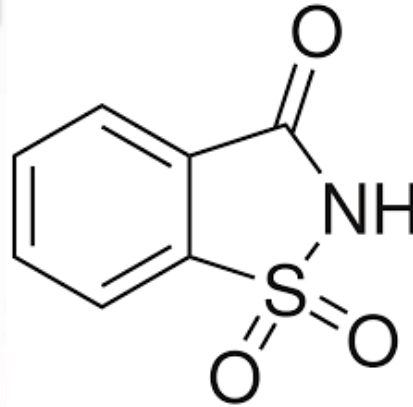
1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane

- Melting point: 108⁰C
- Boiling point: 260⁰C
- It is a white crystalline powder with chlorinated odour
- It shows low solubility in water and high solubility in organic solvents, fats and oils

Dichlorodiphenyltrichloroethane (DDT)

- It doesn't breakdown in environment or in organisms
- It is synthesized by reaction of trichloroethanol with chlorobenzene
- It has potent insecticidal properties.
- It was effective in eradicating malaria from Europe and North America
- It was also extensively used as agricultural insecticide after world war II
- It is an organic pollutant and very highly persistent in the environment
- It is highly toxic to the aquatic life and many species of fish

SACCHARINE



2-benzothiazol-1,1,3-trione

- It is a white crystalline solid
- It is used as an artificial sweetening agent since its intensity of sweetness is much higher than that of sucrose but it is not metabolized and for that reason it is suitable for diabetes and dietary food
- It is mainly used in the food industry both in the form of acid and/or as calcium or sodium salt particularly sodium salt because of its great solubility in water

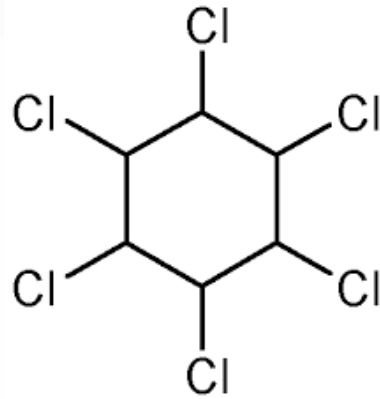
SACCHARINE

- The sweetening intensity of saccharine is inversely proportional to concentration of the solution.

e.g. 1% saccharine solution is about 800 times sweeter while a 3% solution is only 500 times sweeter than sucrose solution

- Since saccharine is not metabolized and excreted unchanged through urine, it is particularly suitable for overweight individuals or diabetic people.
- The recommended maximum daily dose is 5 mg/kg body weight
- It is also used in toothpaste, mouthwash, cosmetics, cigarettes and as a flavouring agent in pig feed.

BENZENEHEXACHLORIDE (BHC)



- It is known as Lindane, gamma-hexachlorocyclohexane, gammaxene, Gammallin
- Benzene hexachloride is an organochlorine compound and an isomer of hexachlorocyclohexane that has been used both as an agricultural insecticide and for treatment of skin disorder
- It is a neurotoxin and interferes with neurotransmitter function.
- It is a carcinogenic agent

CHLORAMINE

- Chloramine are derivatives of ammonia by substitution of 1, 2 or 3 hydrogen atoms
- NH_2Cl - Monochloroamine,
 NHCl_2 - Dichloroamine,
 NCl_3 - Nitrogen trichloride
- Molecular formula: NH_2Cl
- It is an unstable colourless liquid with melting point of -66°C
- It is used in treatment of water for inking, water disinfection and swimming pool disinfection
- Commonly used in low concentration as disinfectant in municipal water as an alternative to chlorination, because it is much more stable than the free chlorine

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