Contents

INTRODUCTION

- Benzene is a chemical that is a colourless or light yellow liquid at room temperature. It has a sweet odour and is highly flammable.
- Natural sources of benzene include volcanoes and forest fires. Benzene is also a natural part of crude oil, gasoline, and cigarette smoke.

History

- The word "benzene" derives historically from "gum benzoin", sometimes called "benjamin" an aromatic resin known to European pharmacists and perfumers since the 15th century as a product of southeast Asia.
- Michael Faraday first isolated and identified benzene in 1825 from the oily residue derived from the production of illuminating gas, giving it the name bicarburet of hydrogen.

IUPAC NOMENCLATURE

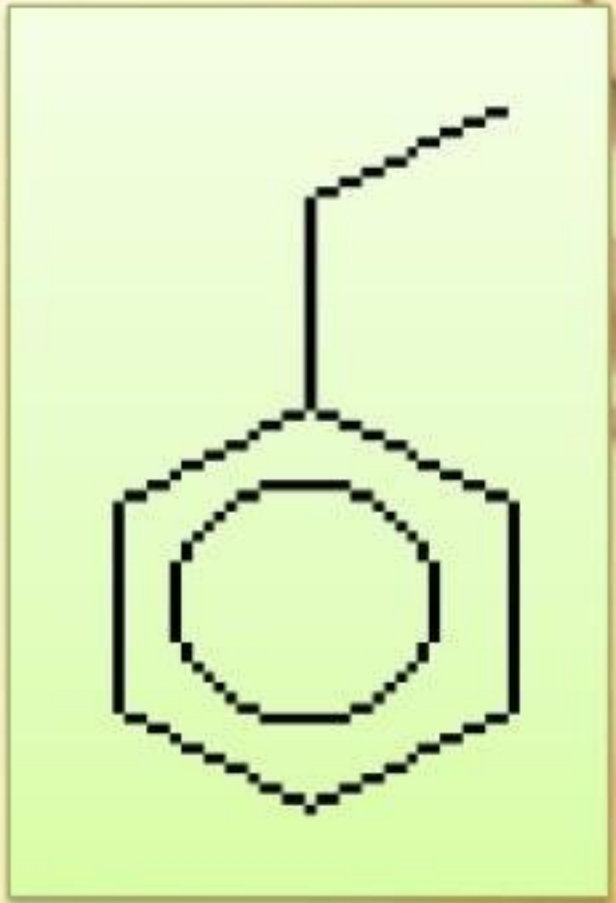
Nomenclature of benzene

1. For naming of benzene, we are giving name as it is benzene some times we called 1,3,5 cyclohexatriene
2. In case of mono substituted benzene , assign the by giving substituent in prefix and benzene in suffix
3. In case of polysubstitution, prefix will be assign as per alphabetically order and locate the position no. 1 for highest priority substituent's

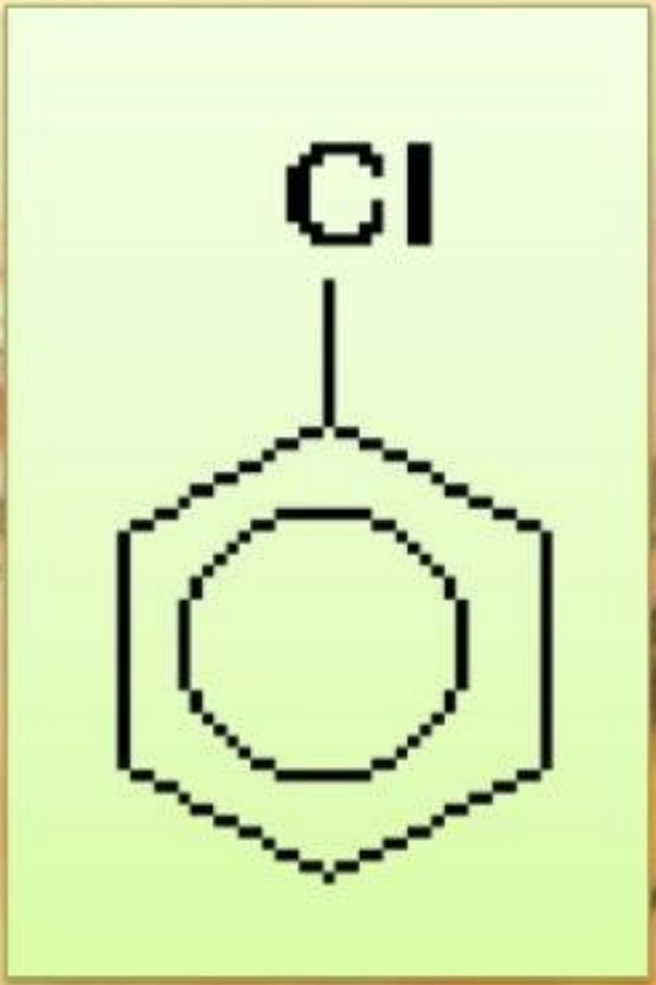
a) MONOSUBSTITUTION

- 1) Benzene as the parent name:

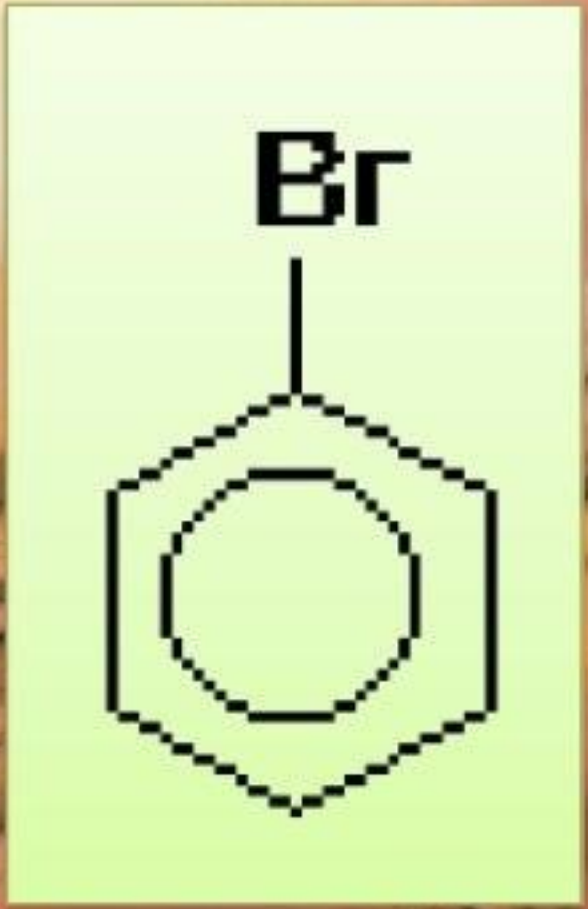
ethylbenzene



chlorobenzene

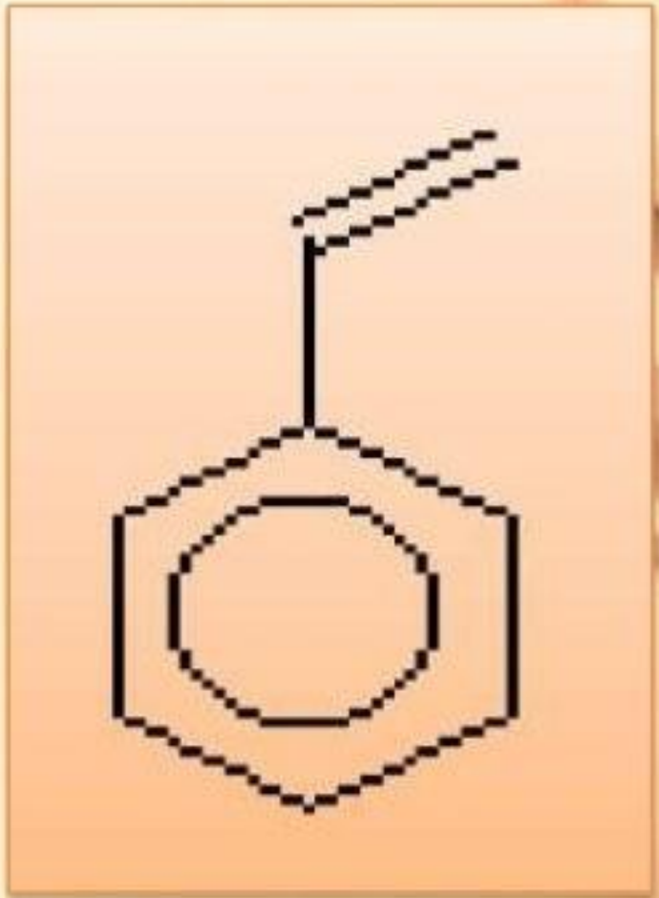


bromobenzene

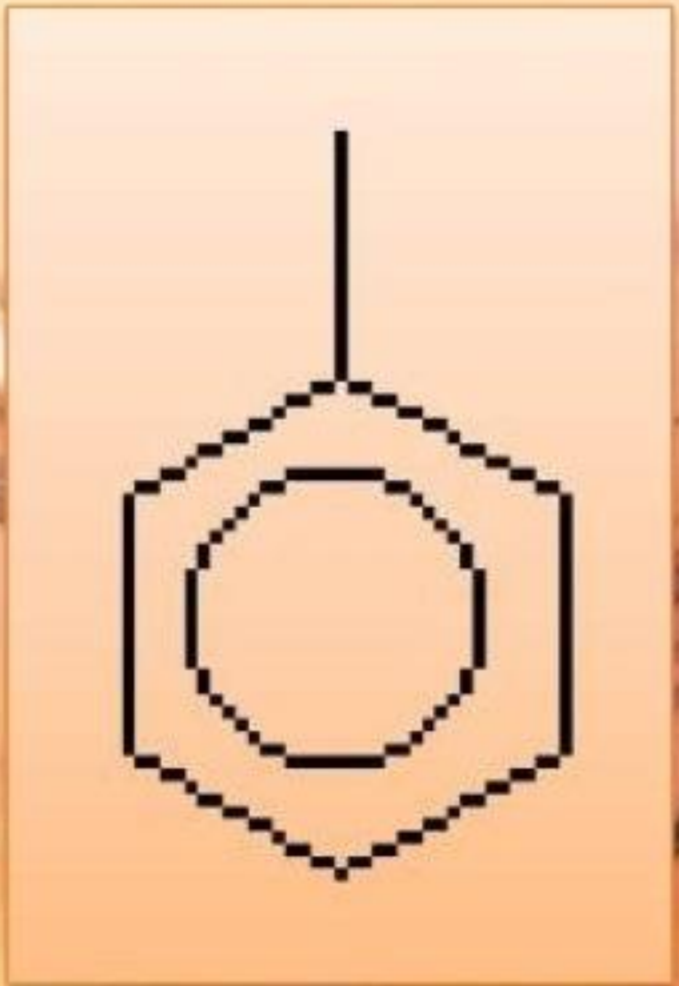


2)Common name:

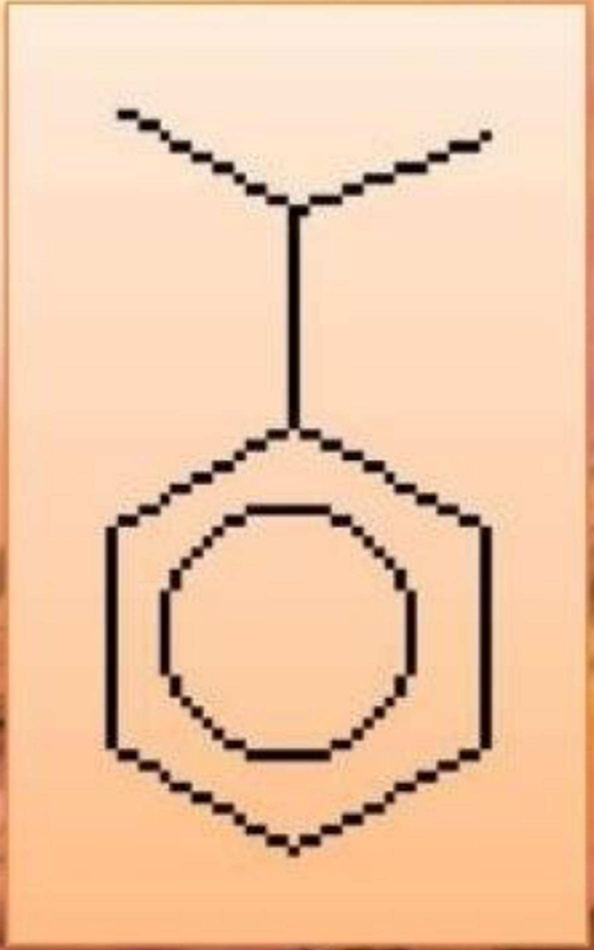
styrene



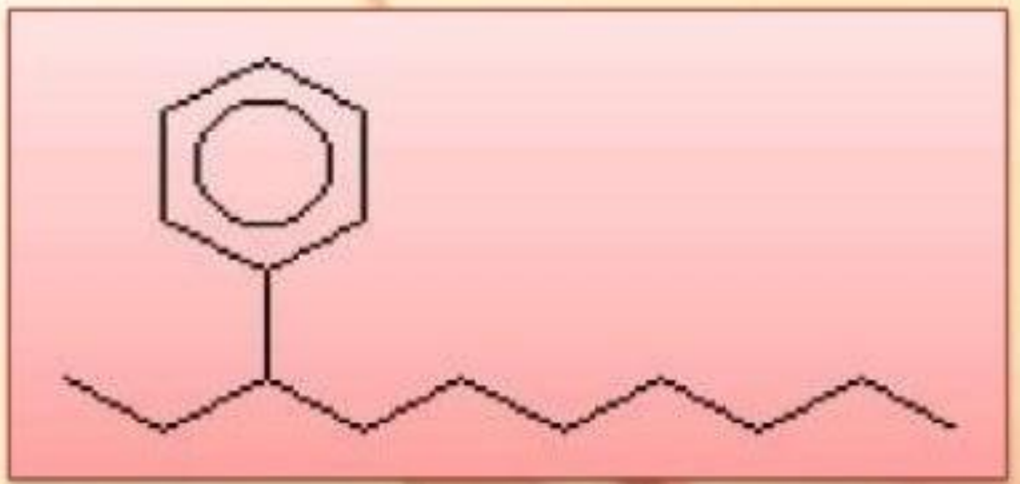
toluene



cumene

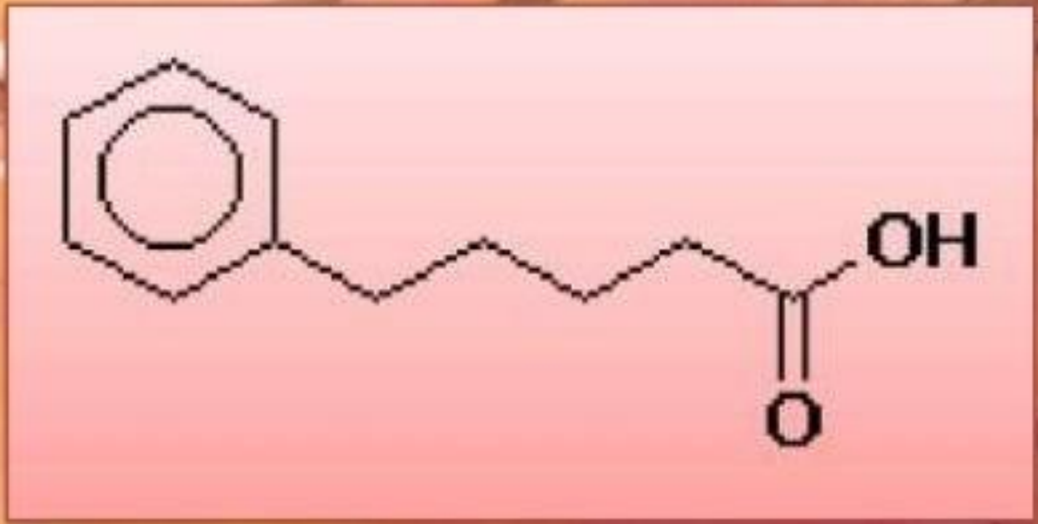


3)Alkyl substituent is larger than ring:



3-phenyldecane

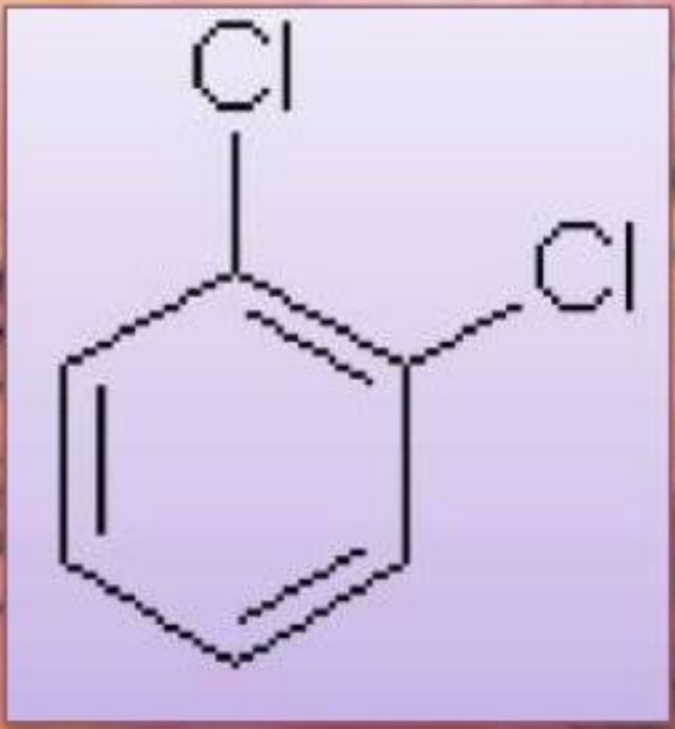
5-phenylpentanoic acid



b) DISUBSTITUTION

- 1)Ortho- disubstituted benzene has two substituent in a 1,2 positions:
- Principle functional group is the benzene therefore root = benzene
- There are two chlorine substituent therefore dichloro.
- The substituent locants are 1 and 2 therefore ortho.

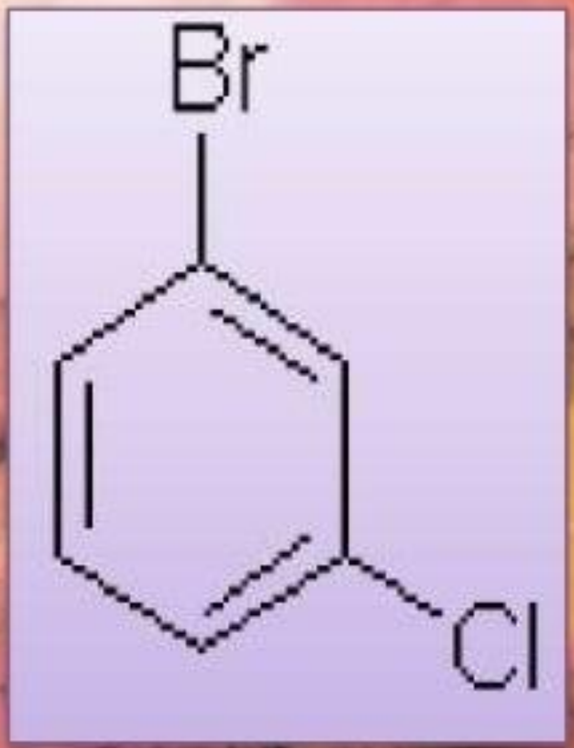
O-dichlorobenzene



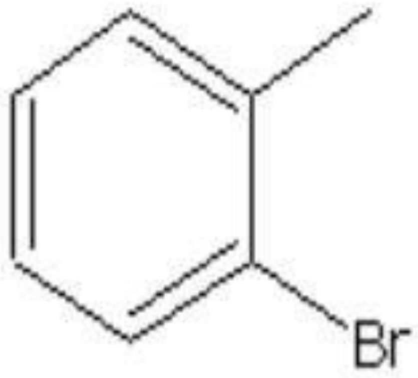
2) Meta -disubstituted benzene has two substituents in a 1,3 positions:

- Principle functional group is the benzne therefore root = benzene
- There is a chlorine substituent therefore chloro.
- There is a bromine substituent therefore bromo.
- The substituent locants are 1 and 3 therefore meta.

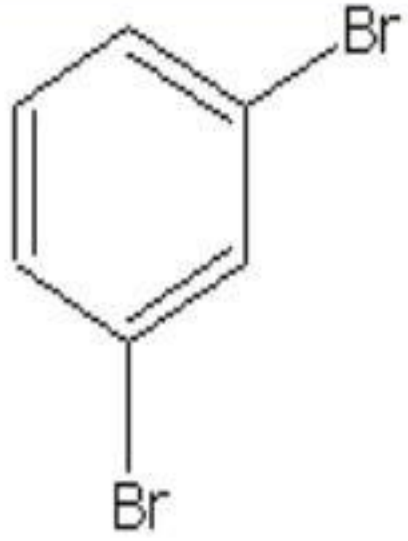
m-bromochlorobenzene



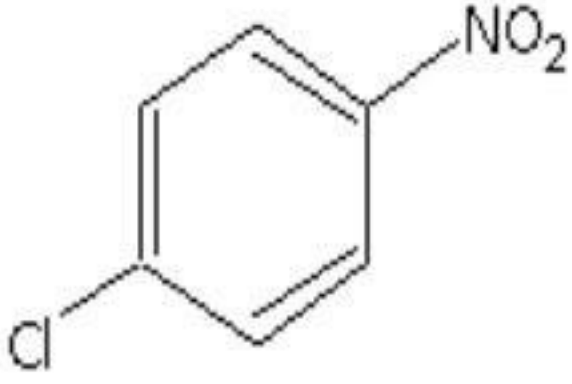
3) Para-disubstituted benzene has two substituents in a 1,4 positions:



ortho-bromotoluene

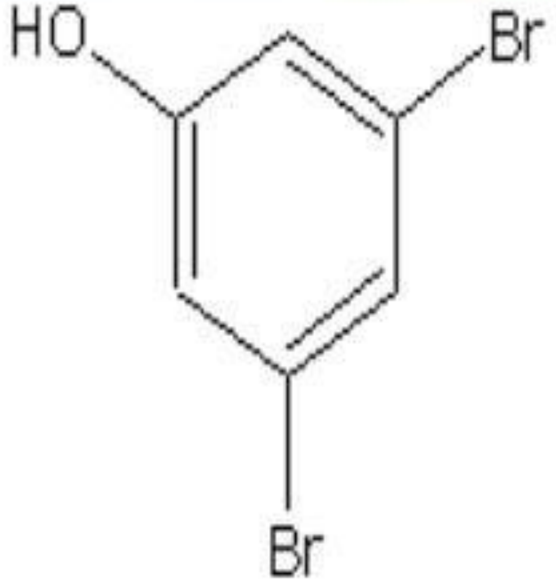


meta-dibromobenzene

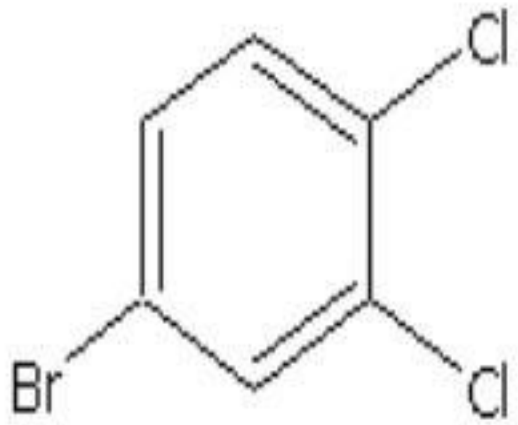


para-chloronitrobenzene

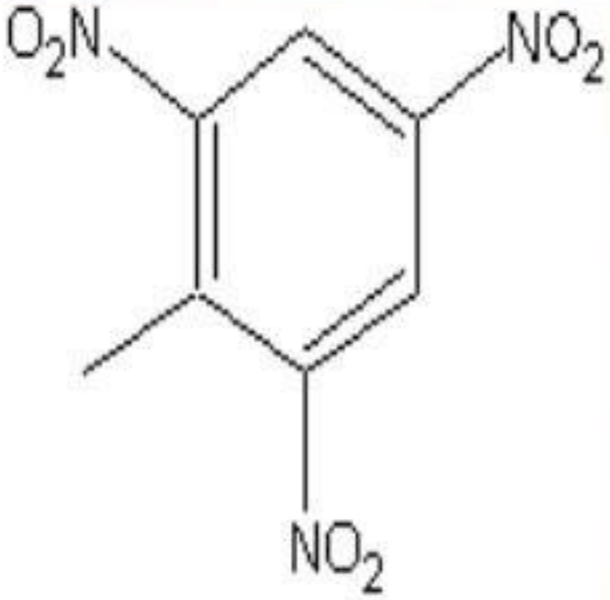
Polydisubstituted benzene derivatives:



3,5-dibromophenol



4-bromo-1,2-dichlorobenzene

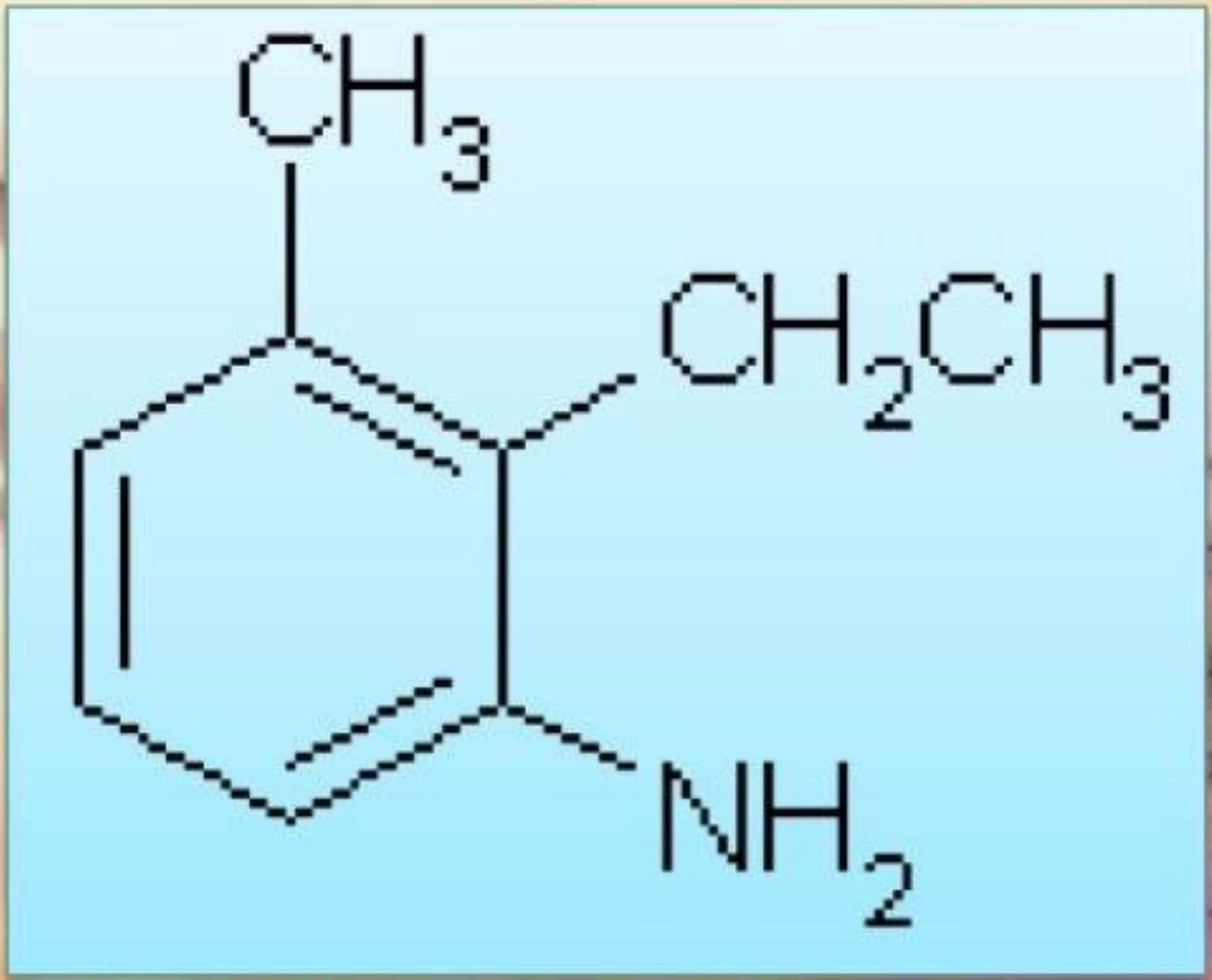


2,4,6-trinitrotoluene

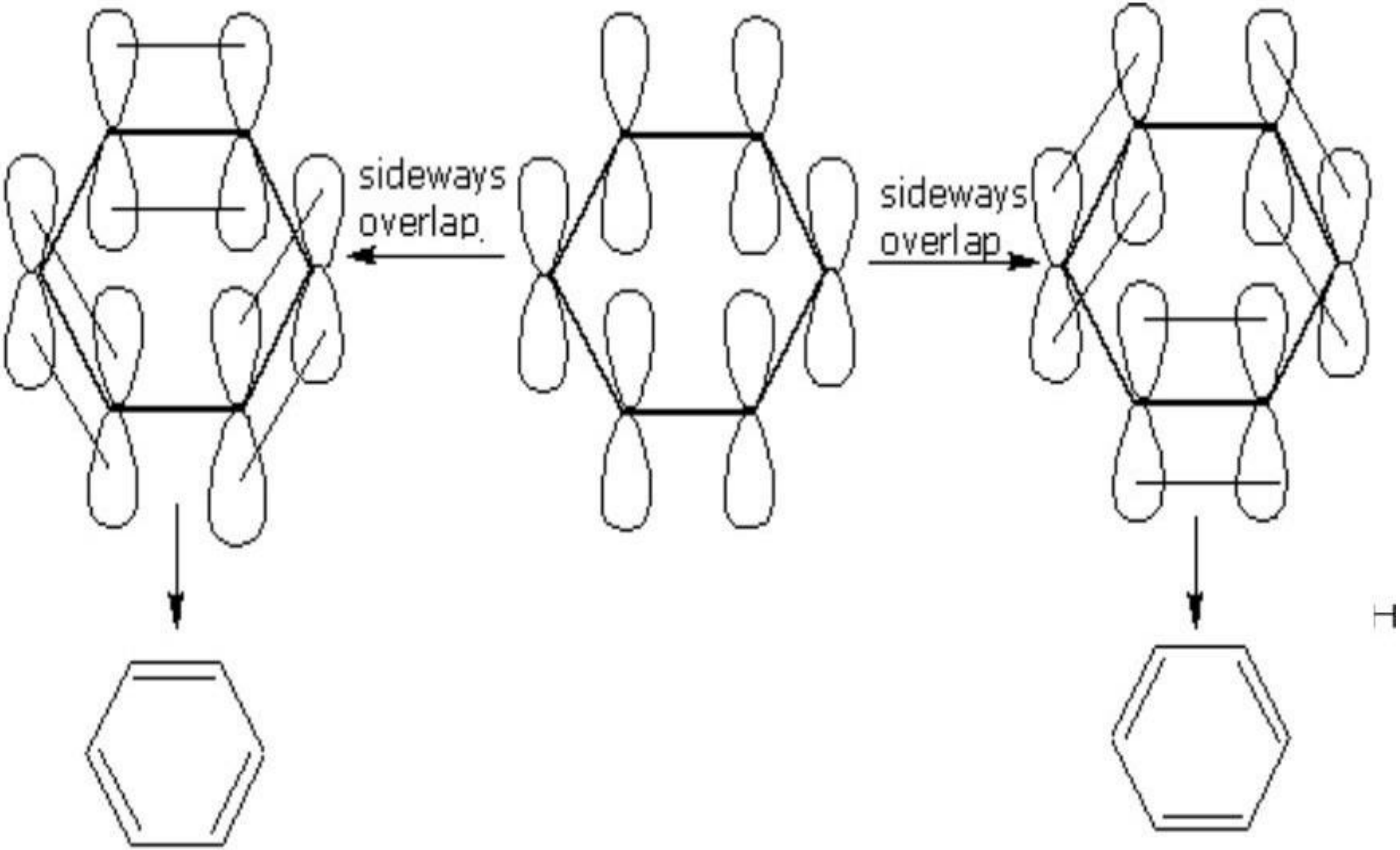
c) POLYSUBSTITUTION

- Benzene with more than 2 substituents are named by numbering the position of each substituent with lowest possible numbers:
- Principle functional group is the aromatic amine therefore = aniline
- There is a C1 substituent therefore methyl
- There is a C2 substituent therefore ethyl
- Numbering from the -NH_2 (priority group at C1) gives the substituents the locants =2 and 3

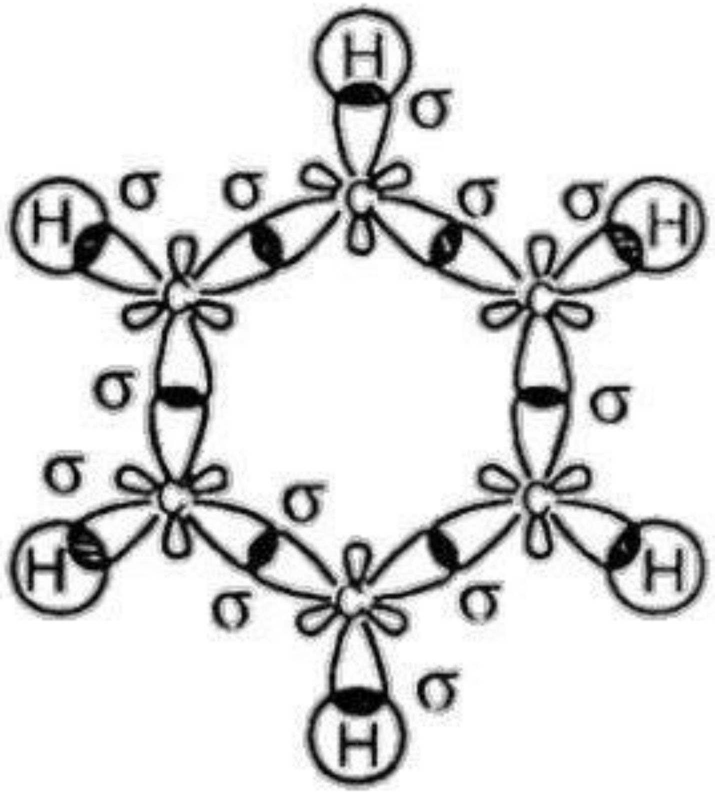
2-ethyl-3-methylaniline



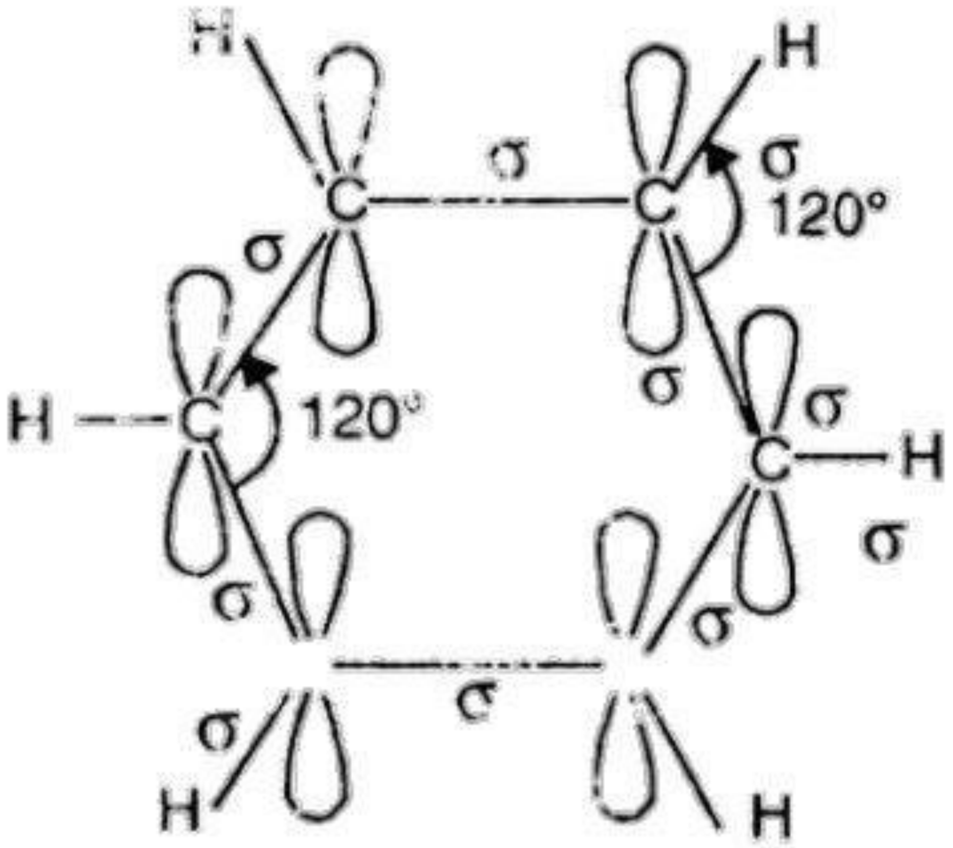
Molecular Structure of **BENZENE**:



Orbital structure of benzene



Formation of C–C and C–H sigma bonds



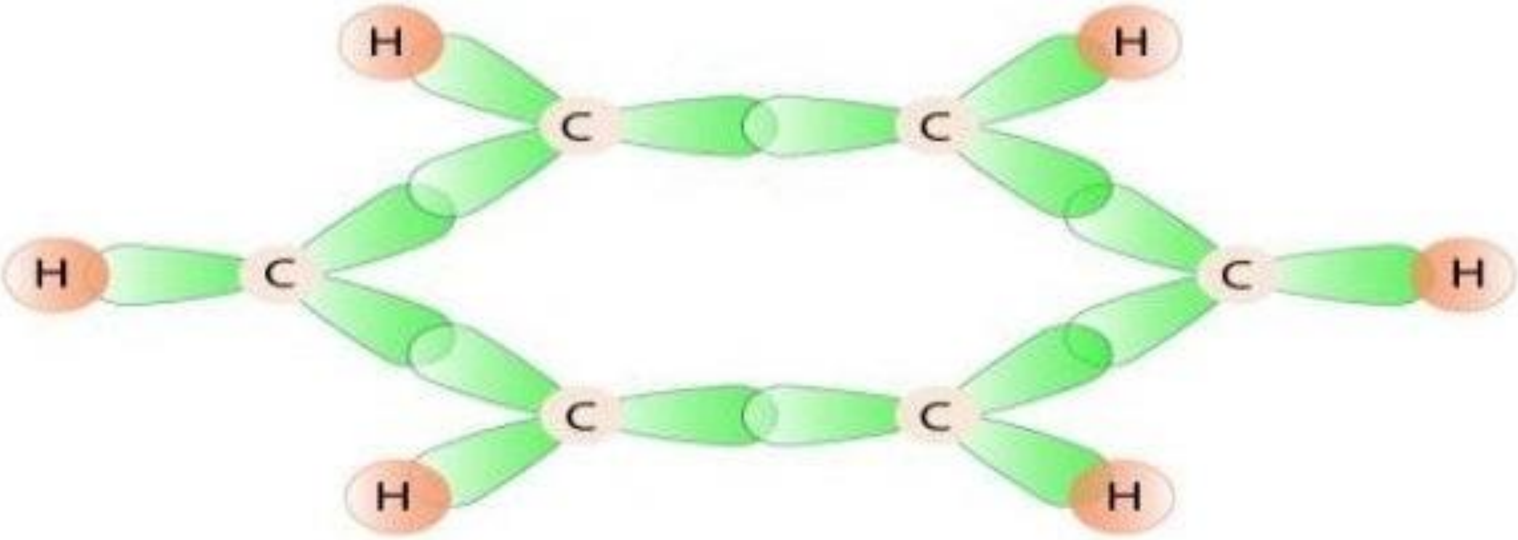
Sigma skeleton of benzene molecule

Orbital picture shows 1.all carbons are sp2 hybridized

2. Carbons linked together with sigma linkage
3. Carbon and hydrogen linked by sigma linkage
4. The bond angle present is 120°
5. The distance between carbon and hydrogen is 1.34A°

Hybridization of benzene:

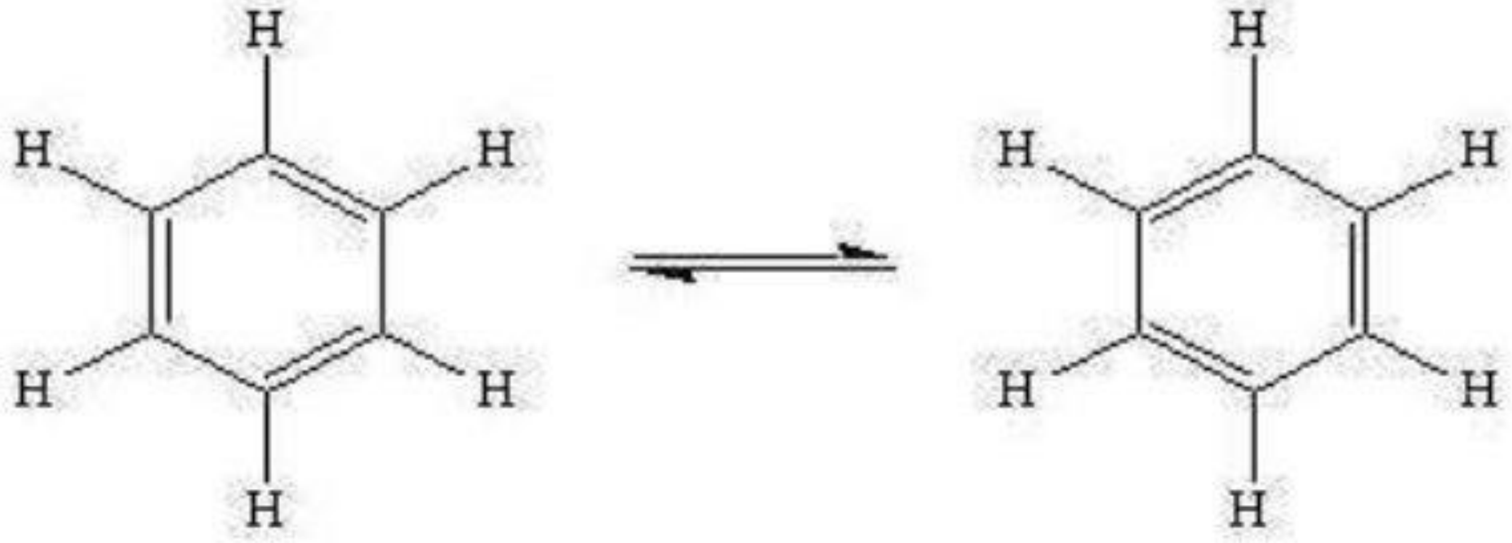
All carbons are SP2 hybridized.
Because the carbons are linked with other carbon atom with double bond .i.e one sigma(σ) and one π bond.
Hence carbon has only two 2p orbital's are free to join . Hence 1P orbital links with other carbon atom by sigma(σ) linkage and 1P orbital links with hydrogen atom by sigma (σ) linkage to form SP2 hybrid structure.



σ bond framework

1.The Kekulé Structure of Benzene

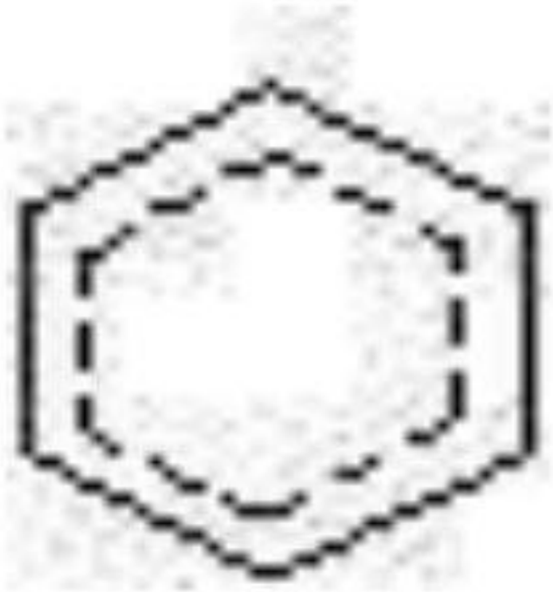
- German chemist Friedrich August Kekulé von Stradonitz
- A structure of benzene, containing 3 cyclic conjugated double bonds which systematically called 1,3,5-cyclohexatriene



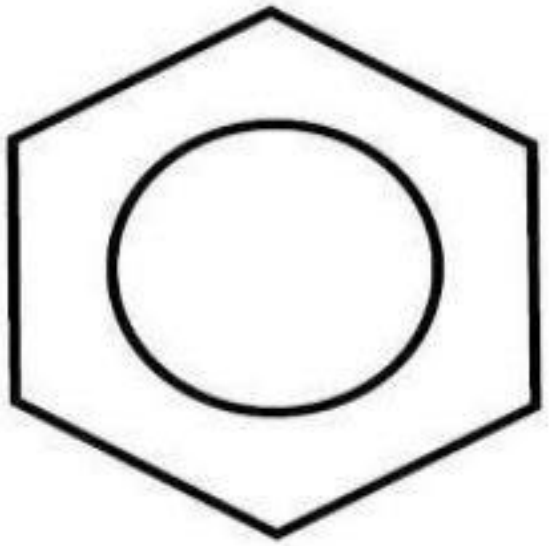
Kekule's structure of benzene

Cont.

- The true structure of benzene is a resonance hybrid of the two Lewis structures, with the dashed lines of the hybrid indicating the position of the π bonds.

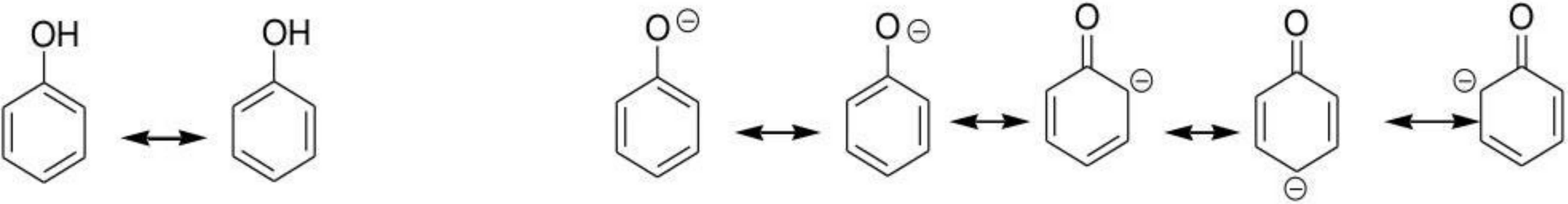


hybrid



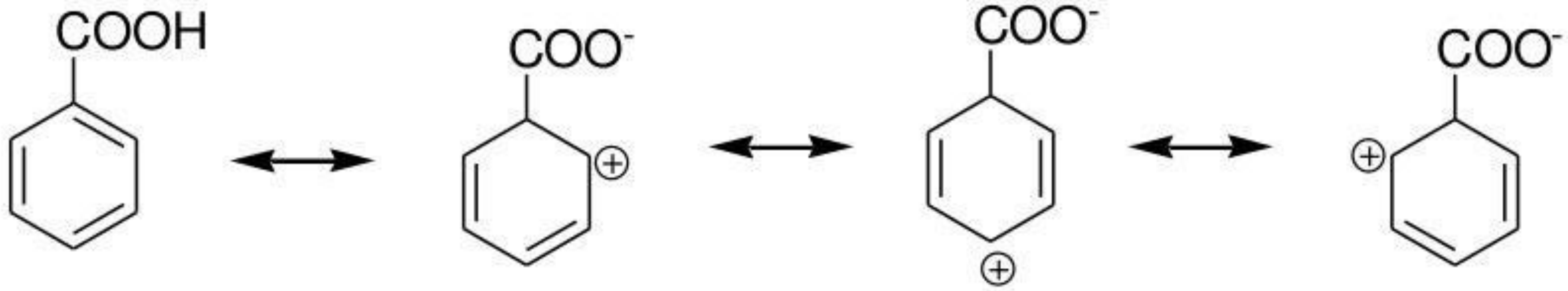
Resonance structure of Phenol

When Electron donating group attaches to benzene and gives electron density to ortho and Para position hence produce resonance structure as follows



Resonance structure of benzoic acid

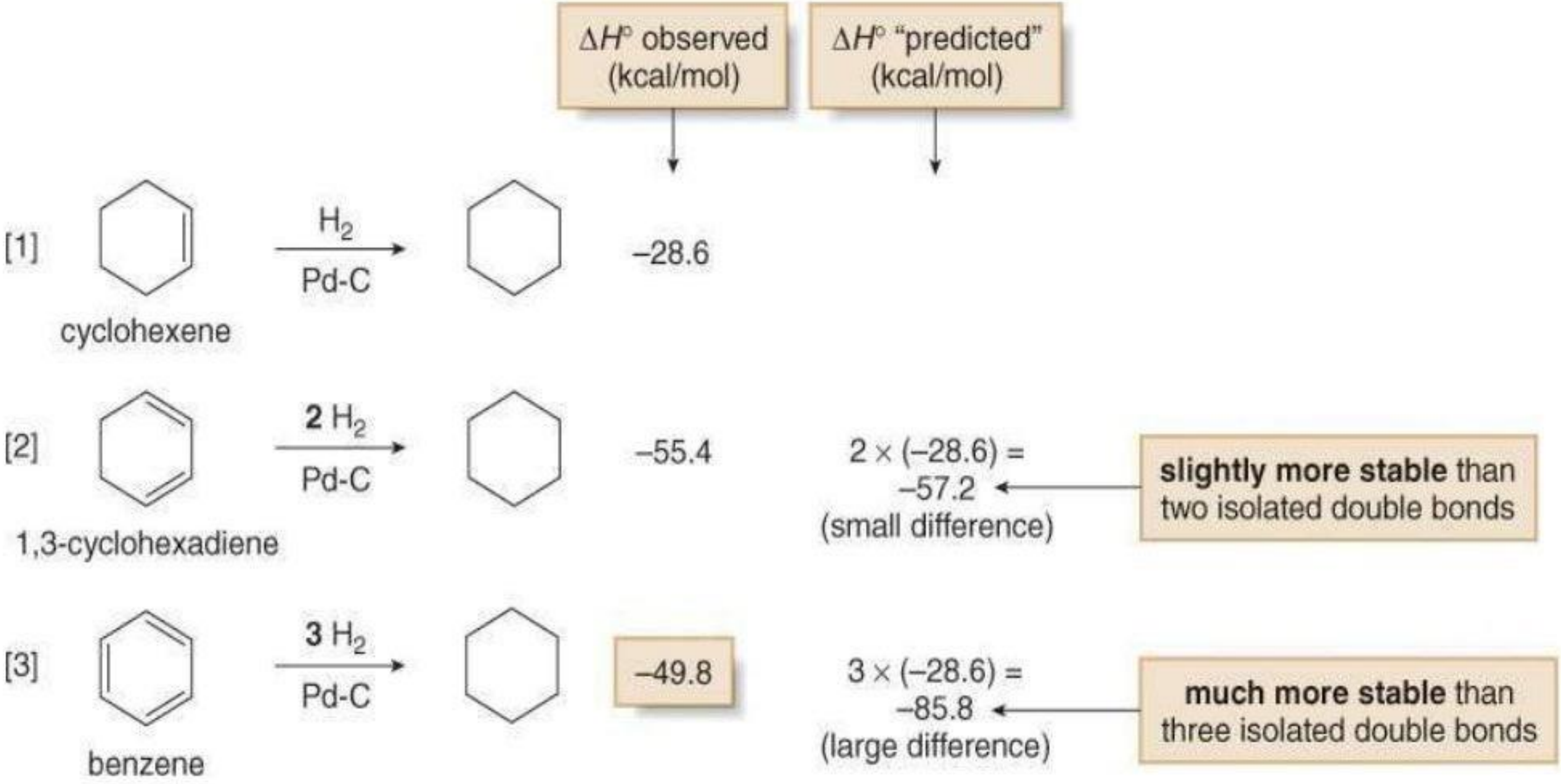
When electron withdrawing group attaches to benzene and withdraws electron density from benzene to produce positive sites at ortho and Para positions. Hence benzoic acid produces following resonance structures.



Resonance description of benzene

Resonance: the phenomenon in which two or more structures can be written for a substance which involve identical positions of atoms is called as resonance. Actual structure is called as resonance hybrid. Alternating structure is called as resonance structure. **Resonance energy:** resonance energy is a measure of how much more stable a resonance hybrid structure than extreme resonance structures

2.Stability



ΔH° observed (kcal/mol)

ΔH° "predicted" (kcal/mol)

[1] cyclohexene $\xrightarrow[\text{Pd-C}]{H_2}$ –28.6

[2] 1,3-cyclohexadiene $\xrightarrow[\text{Pd-C}]{\mathbf{2}\ H_2}$ –55.4

2 × (–28.6) = –57.2 (small difference)

slightly more stable than two isolated double bonds

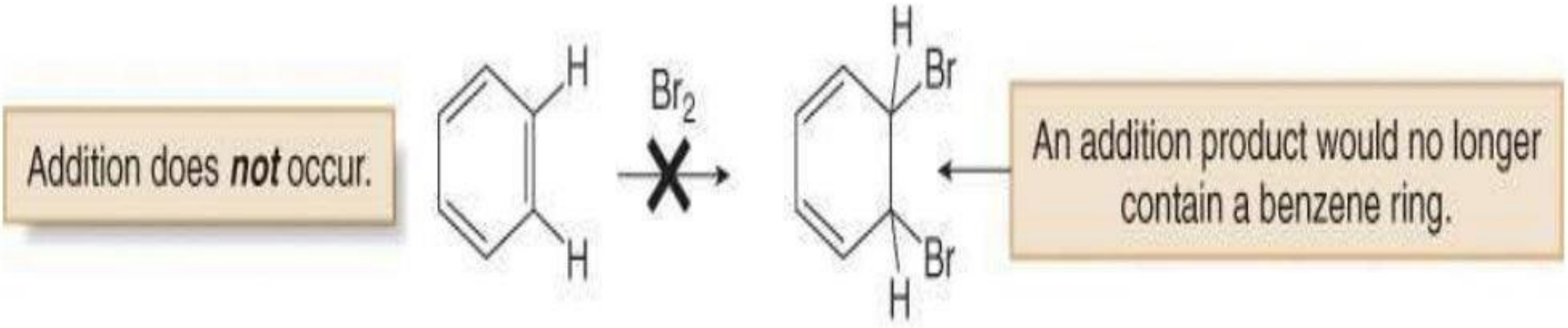
[3] benzene $\xrightarrow[\text{Pd-C}]{\mathbf{3}\ H_2}$ –49.8

3 × (–28.6) = –85.8 (large difference)

much more stable than three isolated double bonds

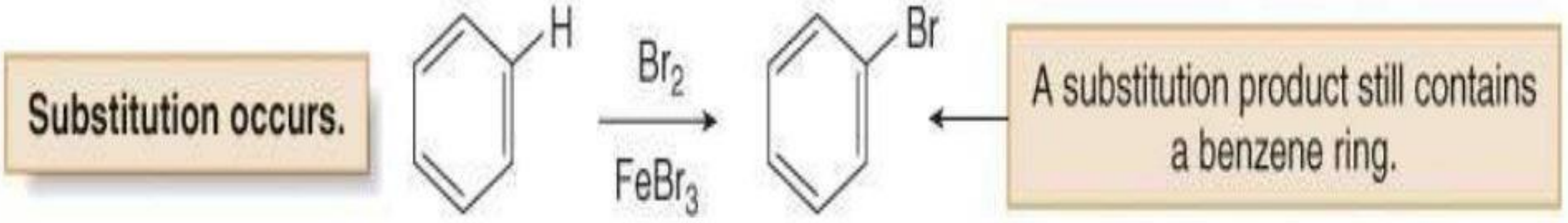
Cont.

- Benzene does not undergo addition reactions typical of other highly unsaturated compounds, including conjugated dienes.
- Benzene does not react with Br_2 to yield an addition product. Instead, in the presence of a Lewis acid, bromine substitutes for a hydrogen atom, yielding a product that retains the benzene ring.



Addition does ***not*** occur.

An addition product would no longer contain a benzene ring.



Substitution occurs.

A substitution product still contains a benzene ring.

Synthetic and structural evidences of benzene

Synthetic evidedences of benzene

A. Benzene is not straight chain form:

Unsaturation test

1.Benzene reacts with bromine but there is no decolorization of bromine indicates benzene.

2. Benzene reacts with KMnO4 hence no decolorization of KMnO4

B. Benzene undergoes electrophilic substitution reaction

C. Benzene undergoes addition of hydrogen in presence of nickel or zinc

Structural evidences of benzene:

1. Molecular formula: C6H6
2. Aromatic compounds
3. Contains alternate double bonds in ring
4. Kekule structure of benzene
5. Resonance energy of benzene
6. Orbital structure of benzene

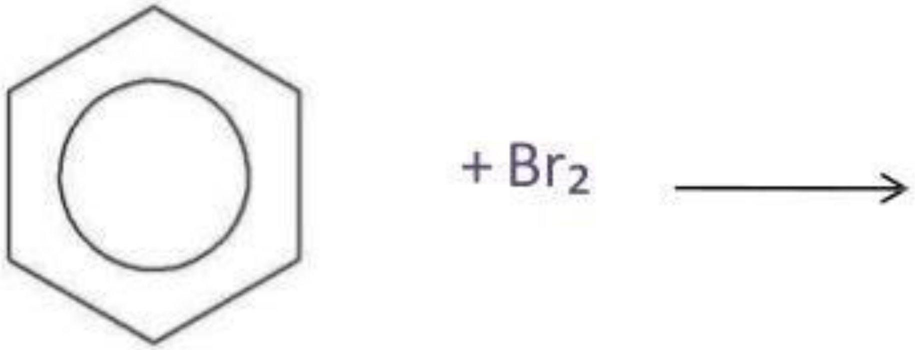
Synthetic evidences of benzene

A. Benzene is not straight chain structure:

Alkene reacts bromine to form dihalogenated alkane.

e.g. when compound contains alkene treated with bromine solution and after reaction bromine color will decolorizes.

But benzene is cyclic compounds and there is no free end for addition of bromine or KMnO4 and require high energy. So benzene is not reacted with bromine and color of bromine or KMnO4 will remain same .

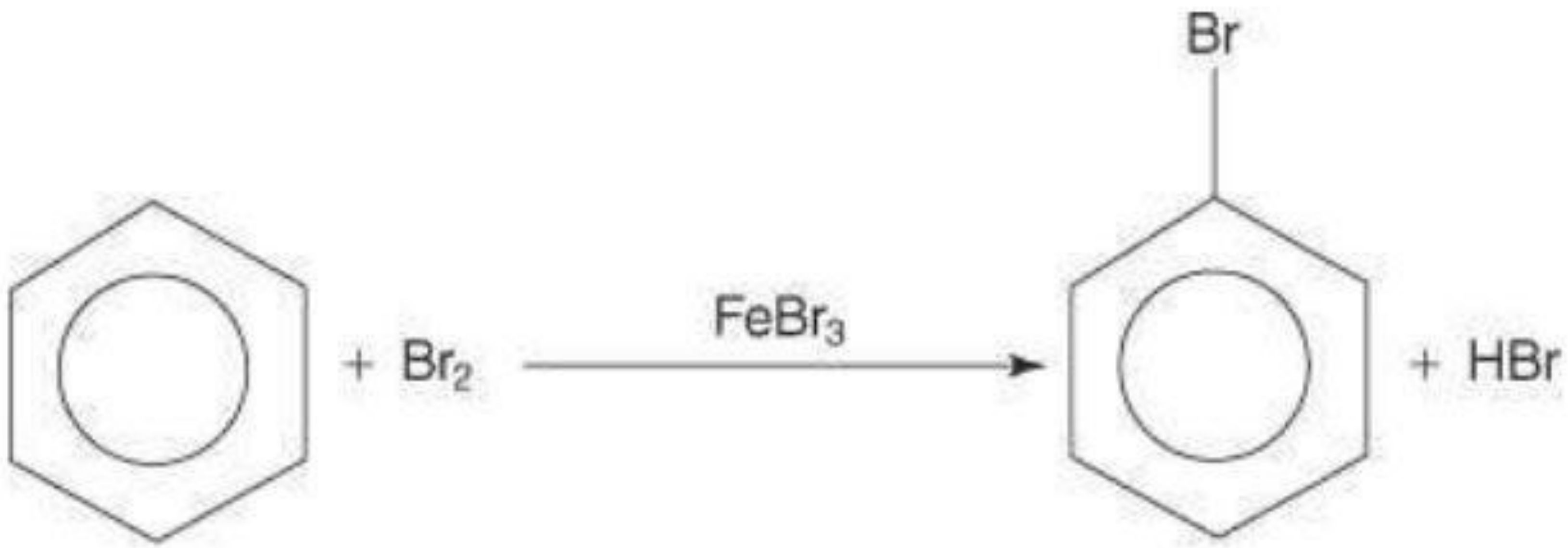


no reaction
(decolorization of bromine or KMnO4 not observed)

Synthetic evidences of benzene

B. Benzene undergoes electrophilic substitution

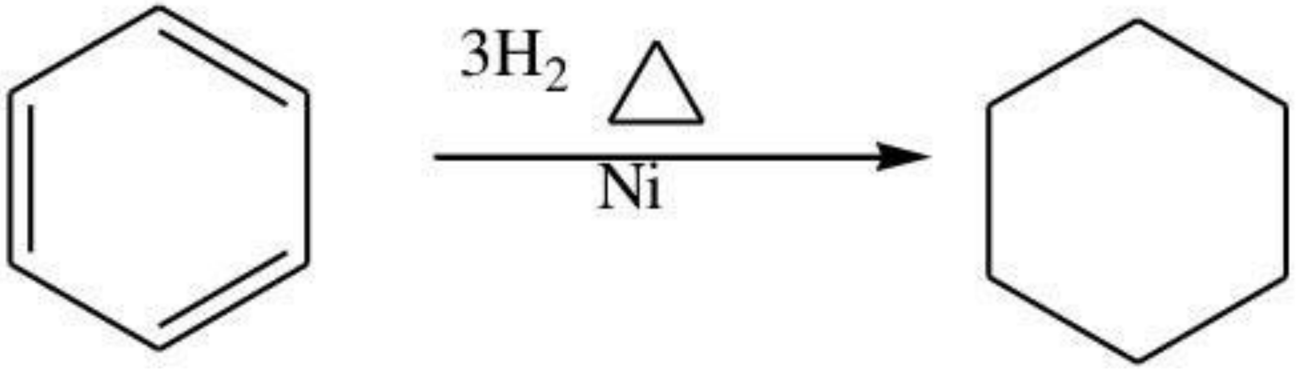
Benzene reacts with bromine in presence of FeBr3 (Lewis acid) to undergo electrophilic substitution reaction to form 1-bromo benzene .
Formation of 1-bromo benzene is the evidence of benzene structure.



Synthetic evidences of benzene

C. Benzene undergoes hydrogenation reaction(Addition of hydrogen or reduction reaction)

Benzene undergoes reduction in presence of Nickel catalyst to produce cyclohexane and liberates ΔH=49.8KCal/mole energy that will tell the compound is benzene



ΔH=-49.8KCal/mole

Analytical evidences of benzene

IR spectroscopy: When sample mix together with KBr and converted into Pellets.
Pillets passed to IR beam gets vibrated or rotated and shows peak . (Functional Group)
Purpose: to determine functional group

NMR spectroscopy: When sample is kept in magnetic field hence proton present in the
Sample acquires resonance and gives peak.(Number of proton and carbon)
Purpose: to determine chemical structure including carbon and hydrogen

Mass Spectroscopy: Electron bombardment on sample hence ionization of samples to
Form molecular ion peak and fragment peak. (Molecular weight)
Purpose: to determine molecular weight

IR spectroscopy:
C-C stretch=1500cm-1
C=C stretch =1600cm-1
C-H stretch= 3000cm-1

H1 NMR spectroscopy:
6 proton gives one single peak
Chemical shift: 5-7.8 δ

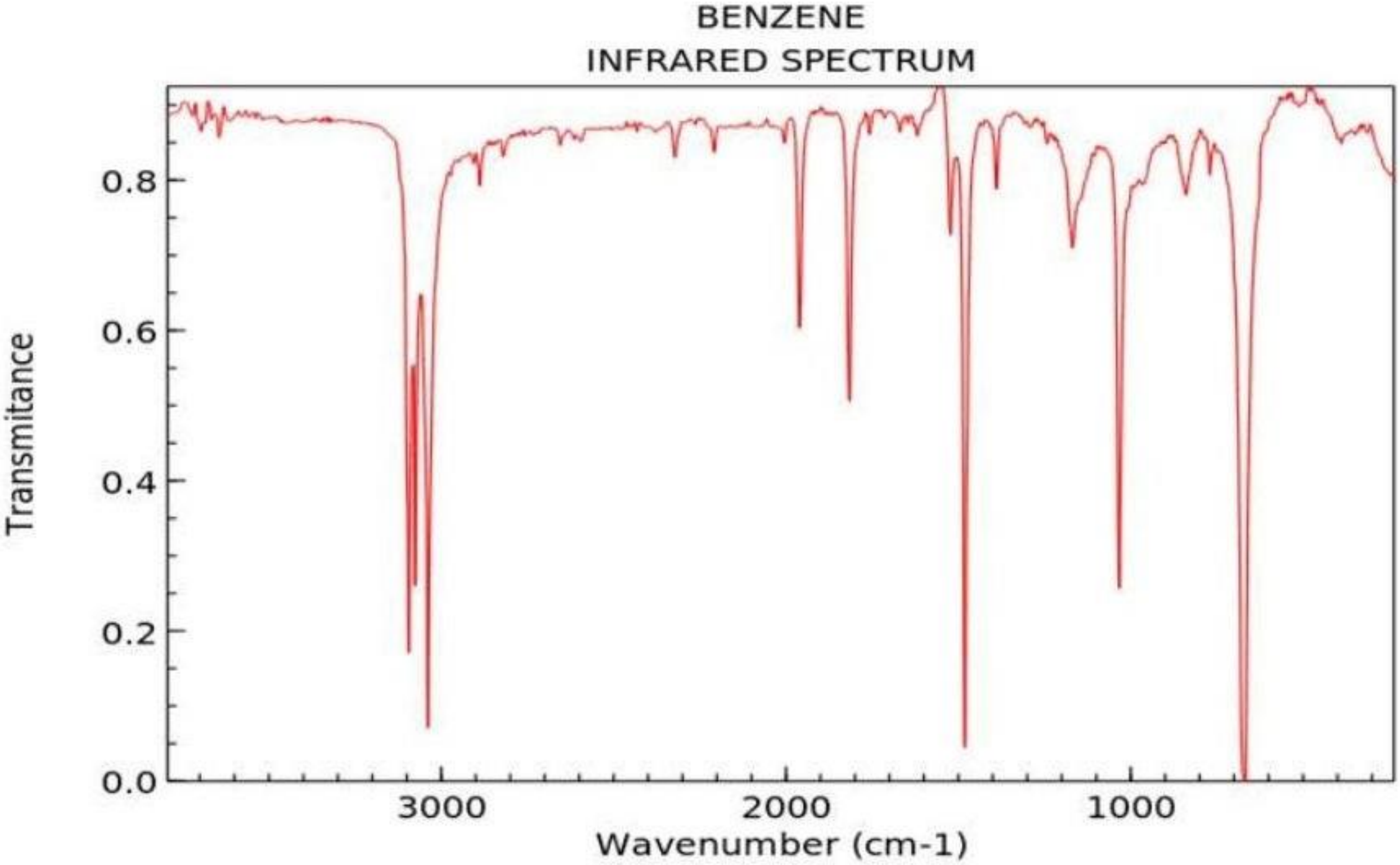
C13 NMR Spectroscopy:
Chemical shift:150-160 δ
6 carbon couples together give single peak

Mass spectroscopy:
Molecular ion peak at 78

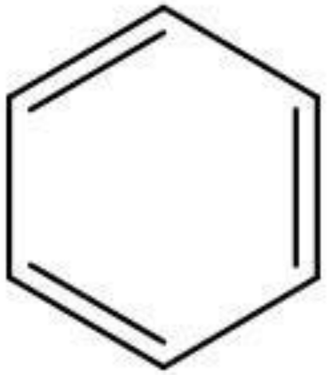
Analytical Evidences of benzene

IR spectroscopy:
Principle: An IR spectrum is essentially a graph plotted with the infrared light absorbed on the Y-axis against frequency or wavelength on the X-axis.
IR Spectroscopy detects frequencies of infrared light that are absorbed by a molecule. Molecules tend to absorb these specific frequencies of light since they correspond to the frequency of the vibration of bonds in the molecule.

Procedure: When sample mix together with KBr and converted into Pillets.
Pillets passed to IR beam gets vibrated or rotated and shows peak



Types of stretch
C=C stretch=1500cm$^-$
C-C stretch =1600cm$^-$
C-H stretch =3000cm$^-$



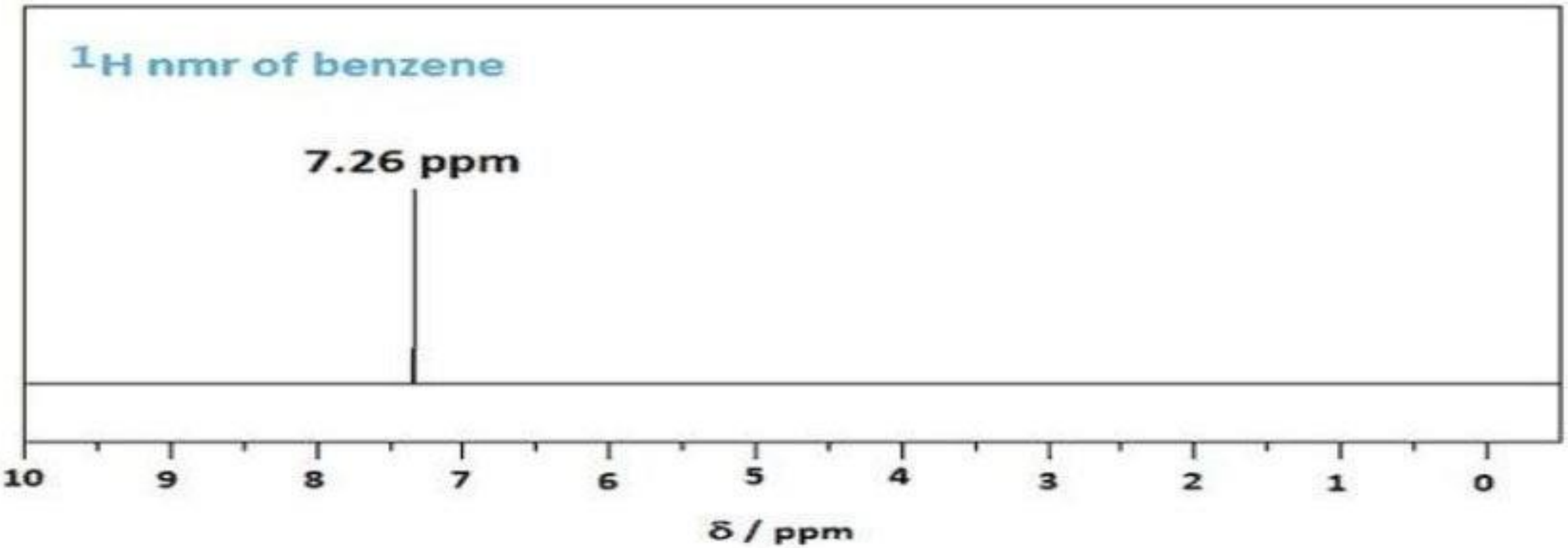
Analytical Evidences of Benzene

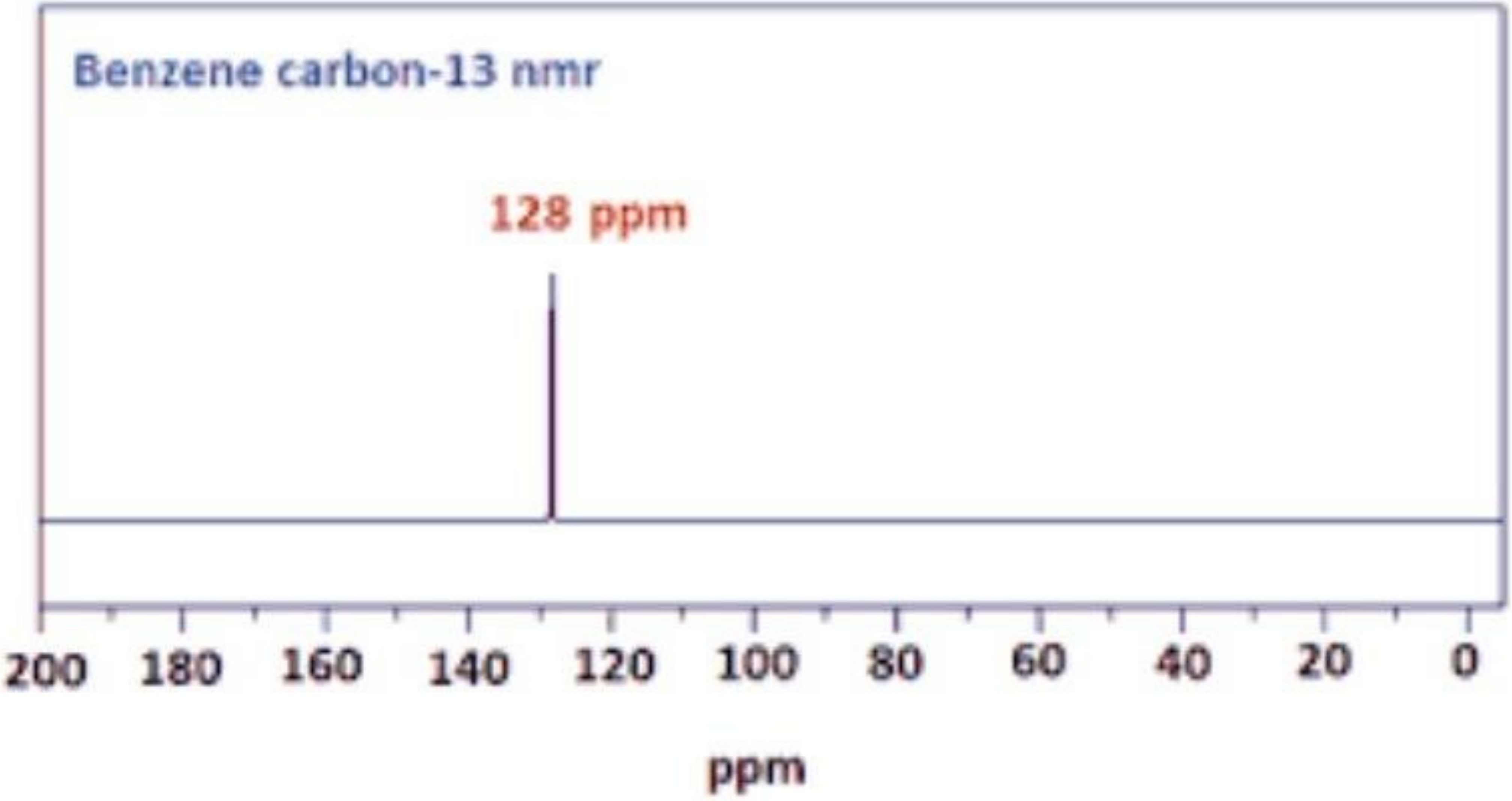
NMR Spectroscopy:

Purpose : Nuclear Magnetic Resonance (NMR) spectroscopy is an analytical chemistry technique used in quality control and research for determining the content and purity of a sample as well as its molecular structure. It will detects Number of Proton and number of carbons.

Number of protons determined by H1 NMR and Number of hydrogen by C13 NMR

Benzene contain 6 hydrogen and 6 carbon atoms. H1 and C13 NMR gives single peak with chemical shift 7.26δ


^{1}H nmr of benzene
7.26 ppm
10
9
8
7
6
5
4
3
2
1
0
δ / ppm

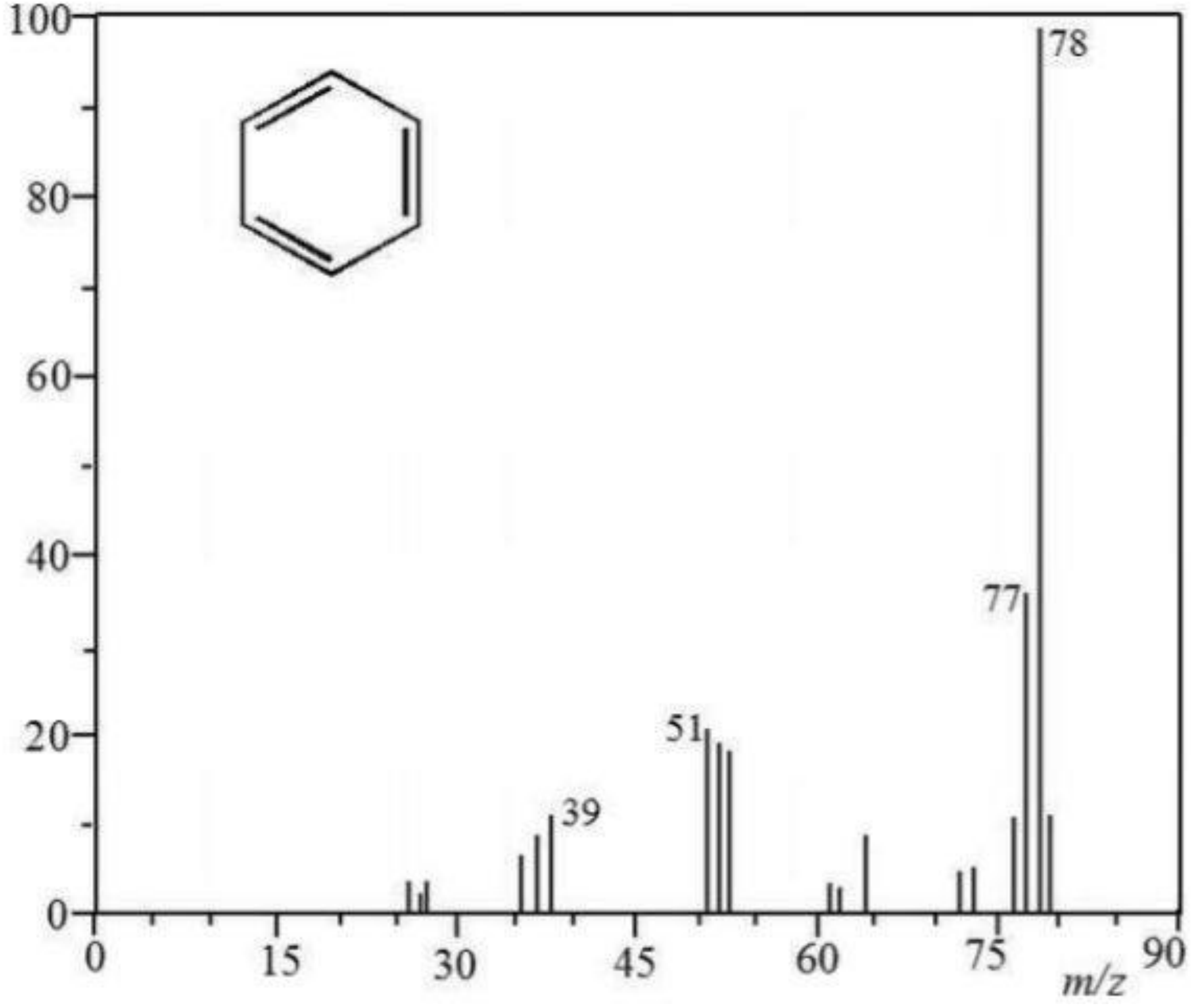

Benzene carbon-13 nmr
128 ppm
200
180
160
140
120
100
80
60
40
20
0
ppm

Analytical Evidences

Mass Spectroscopy:

Principle : Electron bombardment on sample hence ionization of samples to Form molecular ion peak and fragment peak. (Molecular weight)

Purpose: to determine molecular weight



Molecular ion peak(C6H6): 78m/z

Fragment ion Peak (C4H4): 51m/z

Fragment ion Peak (C3H3): 39m/z

4. The Criteria for Aromacity :
Hückel's Rule

- 4 structural criteria must be satisfied for a compound to be aromatic:

a) Cyclic
b) Planar
c) Completely Conjugated
d) Contain a particular number of π electrons

Cont.

[4] A molecule must satisfy Hückel's rule, which requires a particular number of π electrons.

Hückel's rule:

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

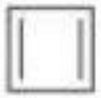
•Benzene is aromatic and especially stable because it contains 6 π electrons.

•Cyclobutadiene is antiaromatic and especially unstable because it contains 4 π electrons.

Benzene
An aromatic compound

4*n* + 2 = 4(1) + 2 =
6 π electrons
aromatic

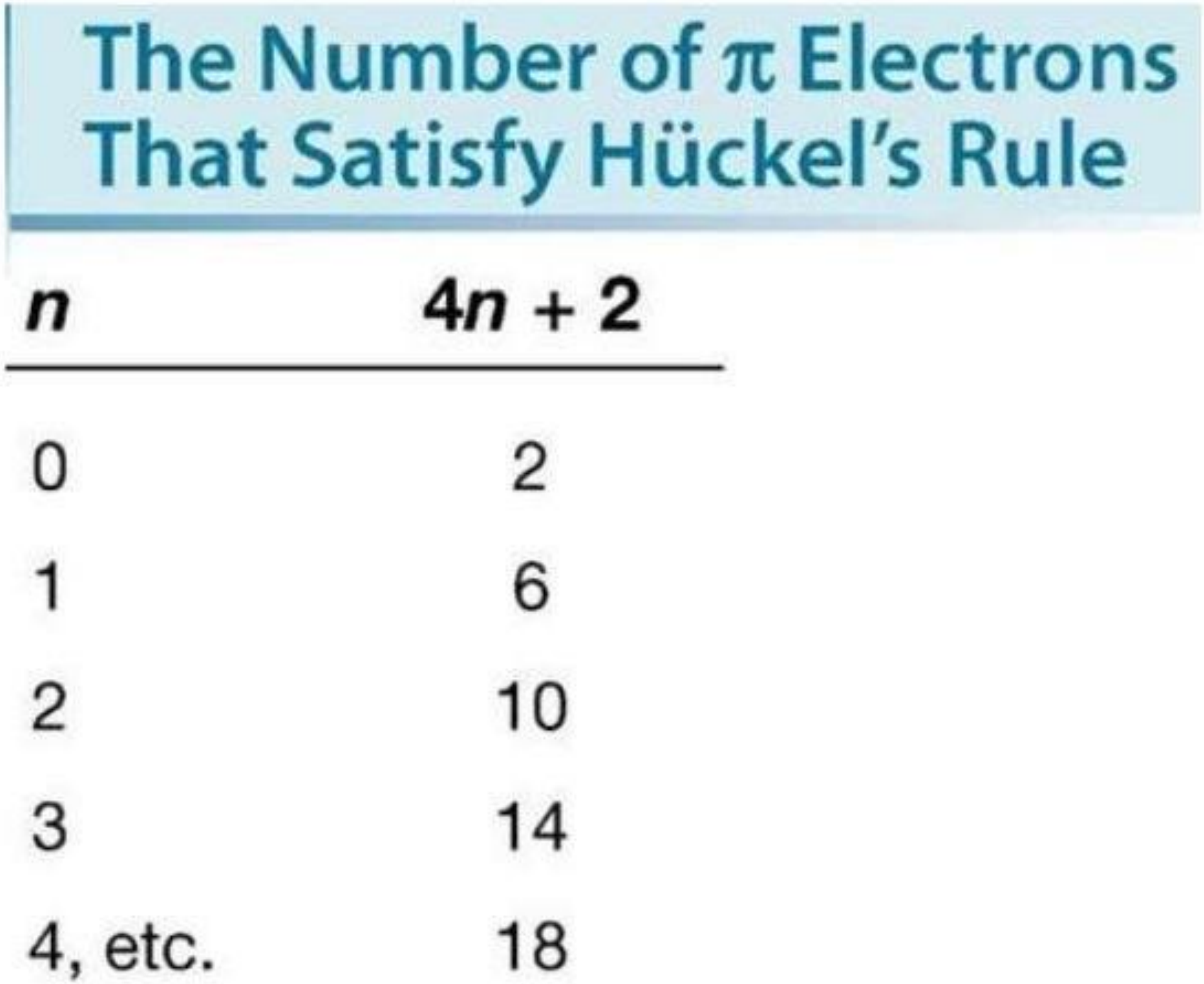
Cyclobutadiene
An antiaromatic compound



4*n* = 4(1) =
4 π electrons
antiaromatic

Cont.

Note that Hückel's rule refers to the number of π electrons, not the number of atoms in a particular ring.



The Number of π Electrons That Satisfy Hückel's Rule

n	$4n + 2$
0	2
1	6
2	10
3	14
4, etc.	18

Benzene and its aromatcity

Calculation of "n"

Huckel Rule: 4n+2π

1 Double bond gives 2 π electron hence benzene contains 3 double bond gives 6 π.

Huckel rule=4n+2

6 π=4n+2

4n=6-2

4n=4

N=4/4= 1

Hence n=1

Huckel Rule: 4n+2
4(1)+2
Huckel rule = 6 **π electron**

According to Huckel Rule Benzene is aromatic because it

1. Cyclic
2. Planner
3. Pressence alternate conjugate double bond
4. Follows huckel rule: means it satisfy 2π, 6 **π**, 10 **π**,14 **π**,18 **π**,22 **π**,26 **π**, **30 π**

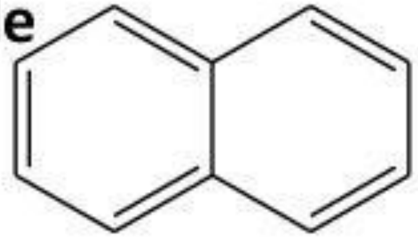
Examples of aromatic compounds

Aromaticity in Naphthalene

Calculation of "n"

Huckel Rule: 4n+2π

1 Double bond gives 2 π electron hence Naphthalene contains 5 double bond gives 10 π electron .



naphthalene

Huckel rule=4n+2

10 π=4n+2

4n=10-2

4n=8

N=8/4= 2

Hence n=2

Huckel Rule: 4n+2
4(2)+2
Huckel rule = 10 **π electron**

According to Huckel Rule Naphthalene is aromatic because it

1. Cyclic
2. Planner
3. Pressence alternate conjugate double bond
4. Follows huckel rule: means it satisfy 2π, 6 **π**, 10 **π**,14 **π**,18 **π**,22 **π**,26 **π**, **30 π**

Examples of aromatic compounds

Aromaticity in Phenanthrene

Calculation of "n"

Huckel Rule: 4n+2π

1 Double bond gives 2 π electron hence phenanthrene contains 7 double bond gives 14 π.

Huckel rule=4n+2

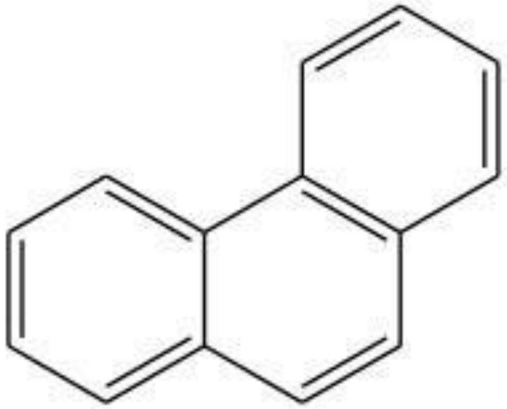
14 π=4n+2

4n=14-2

4n=12

N=12/4= 3

Hence n=3



phenanthrene

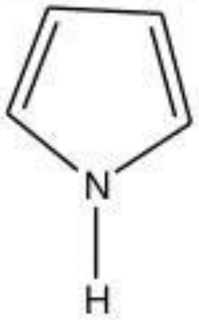
Huckel Rule: 4n+2
4(3)+2
Huckel rule = 14 **π electron**

According to Huckel Rule Phenanthrene is aromatic because it

1. Cyclic
2. Planner
3.Pressence alternate conjugate double bond
4. Follows huckel rule: means it satisfy 2 π, 6 **π**, 10 **π**,14 **π**,18 **π**,22 **π**,26 **π**, **30 π**

Examples of aromatic compounds

Aromaticity in Heterocyclic compounds



pyrrole

furan

thiophene

Calculation of "n"

Huckel Rule: 4n+2π

1 Double bond gives 2 π electron and hetero atom contains 2 lone pair of electron.

Examples of hetero atom N, O,S etc

Hence Pyrrole, Furan, Thiophene contains 6 π

Huckel rule=4n+2

6 π=4n+2

4n=6-2

4n=4

N=4/4= 1

Hence n=1

Huckel Rule: 4n+2

4(1)+2

Huckel rule = 6 **π electron**

According to Huckel Rule Pyrrole, Furan and thiophene are aromatic because it

1. Cyclic
2. Planner
3. Pressence alternate conjugate double bond
4. Follows huckel rule: means it satisfy 2π, 6 **π**, 10 **π**,14 **π**,18 **π**,22 **π**,26 **π**, **30 π**

Examples of anti-aromatic compounds

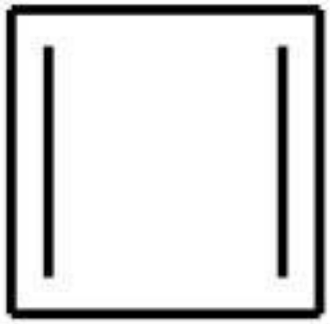
Calculation of "n"

Huckel Rule: $4n+2\pi$

1 Double bond gives 2 π electron Hence cyclobutadiene contains 4 π

$$4\pi=4n+2$$
$$4n=4-2$$
$$4n=2$$
$$N=2/4=0.5$$

Hence n=0.5



cyclobuta-1,3-diene

Huckel Rule: $4n+2$

$4(0.5)+2$

Huckel rule = 4

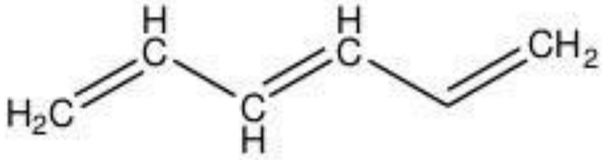
According to Huckel Rule 1,3 Cyclobutadiene is anti-aromatic because it

1. Cyclic
2. Planner
3. Pressence alternate conjugate double bond
4. Doesnot Follows huckel rule: means it IS NOT gives 2 **π**,6 **π**, 10 **π**,14 **π**,18 **π**,22 **π**,26 **π**, **30 π**

Examples of non aromatic compounds.

According to Aromatcity criteria , 1,3,5 hexatriene is **non aromatic** because it is

1. Non Cyclic
2. Planner
3. Pressence alternate conjugated double bond
4. Follows huckel rule: means it satisfy 6 **π**, 10 **π**,14 **π**,18 **π**,22 **π**,26 **π**, **30 π**

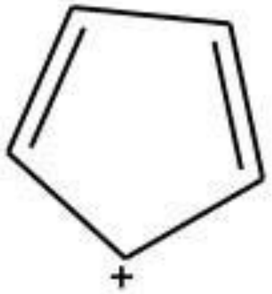


(*E*)-hexa-1,3,5-triene

Exercise Questions

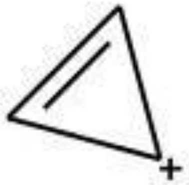
1.Cyclic
2. Planner
3. Pressence of Conjugated bonds
4. Number of pi electron=6
Result: Compoud is Aromatic

1.Cyclic
2. Planner
3.No Pressence of Conjugated bonds
4. Number of pi electron=4
Result: Compoud is Anti-Aromatic

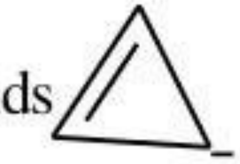


1.Cyclic
2. Planner
3.Pressence of Conjugated bonds
4. Number of pi electron=4
Result: Compoud is Anti-Aromatic

1.Cyclic
2. Planner
3.No Pressence of Conjugated bonds
4. Number of pi electron=6
Result: Compoud is Anti-Aromatic



1.Cyclic
2. Planner
3.Pressence of alternate Conjugated bonds
4. Number of pi electron=2
Result: Compoud is Aromatic



1.Cyclic
2. Planner
3.Pressence of alternate Conjugated bonds
4. Number of pi electron=4
Result: Compoud is Anti-Aromatic

REACTION OF BENZENE

Electrophilic Aromatic substitution

- An electrophile (E^+) reacts with an aromatic ring and substitutes for one of the hydrogen
- Benzene **does not** undergo addition reactions because addition would yield a product that is not aromatic.

5 MAIN ELECTROPHILIC SUBSTITUTION

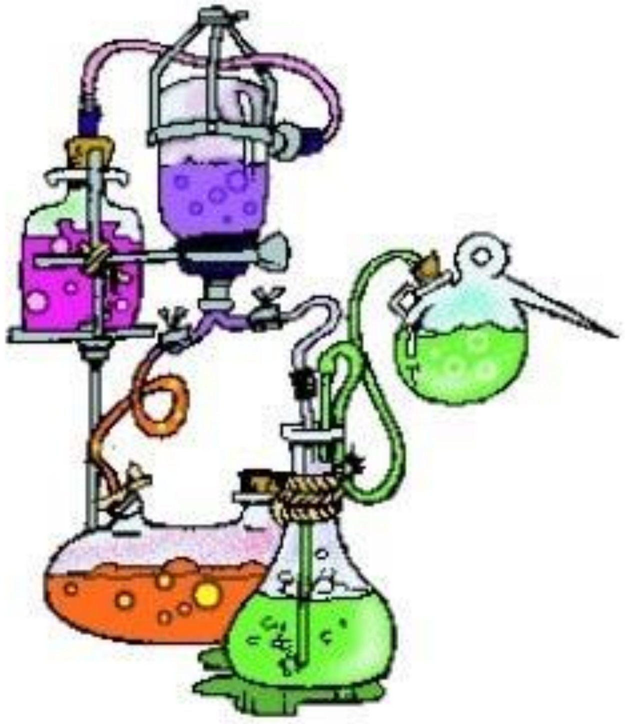
Aromatic Halogenation

Aromatic Nitration

Friel-Crafts Alkylation

Friel-Crafts Acylation

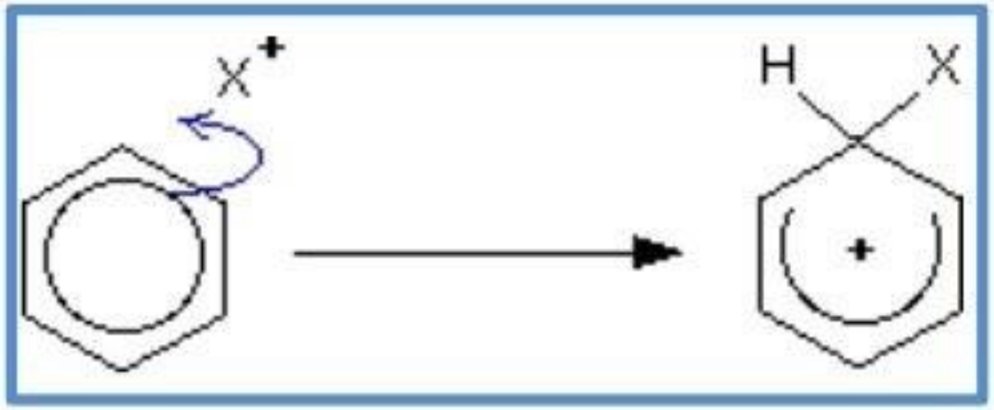
Aromatic sulfonation



GENERAL MECHANISM

Step 1 : Formation of X^+ = electrophile

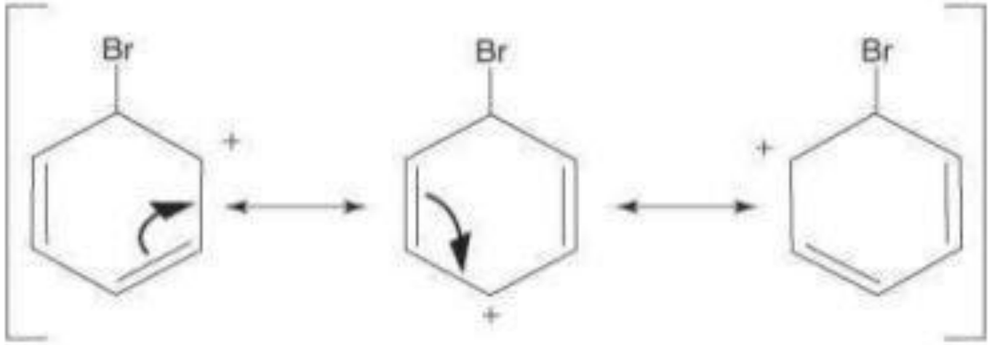
$XY \rightarrow X^+ + Y^-$



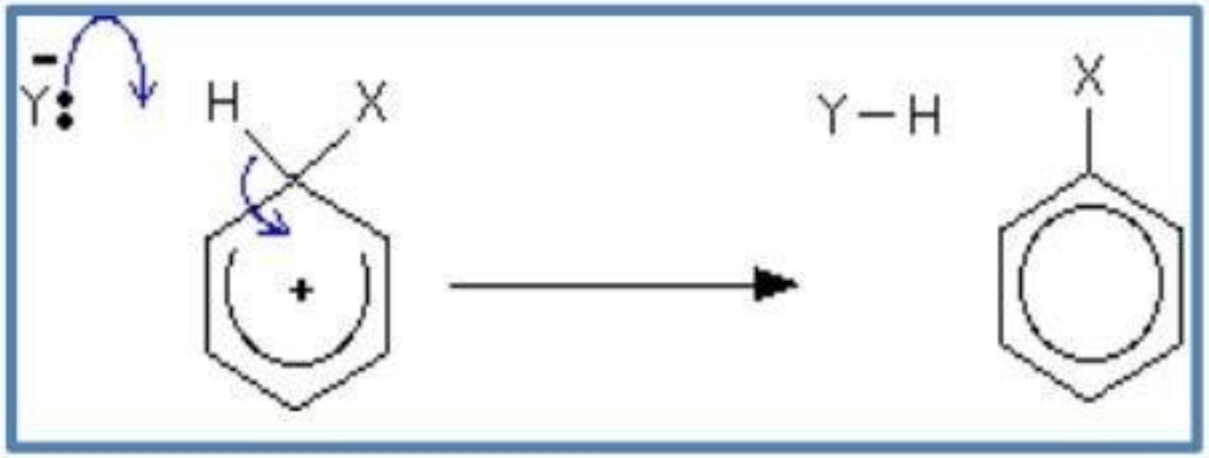
Step 2 : Formation of arenium ion

Positive ion.

Example :



Step 3 : Loss of H^+



AROMATIC HALOGENATION

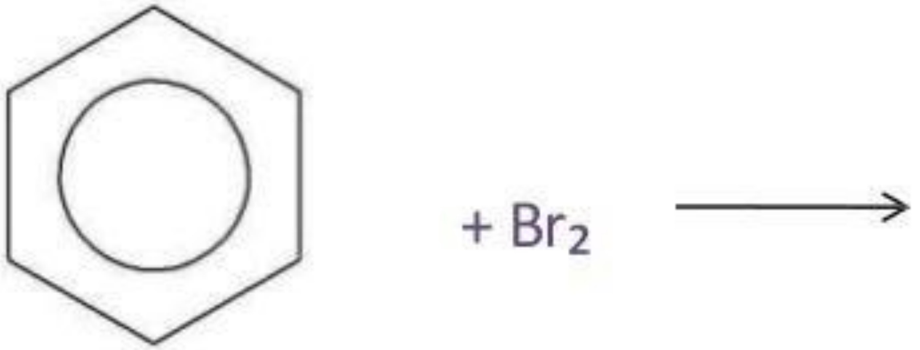
Reactants : Benzene and halogens (Chlorine or Bromine)

Conditions : Lewis acid like $FeCl_3$ or $FeBr_3$

- Analogous reaction with I_2 and F_2 are not synthetically useful because I_2 is too unreactive and F_2 is too violently

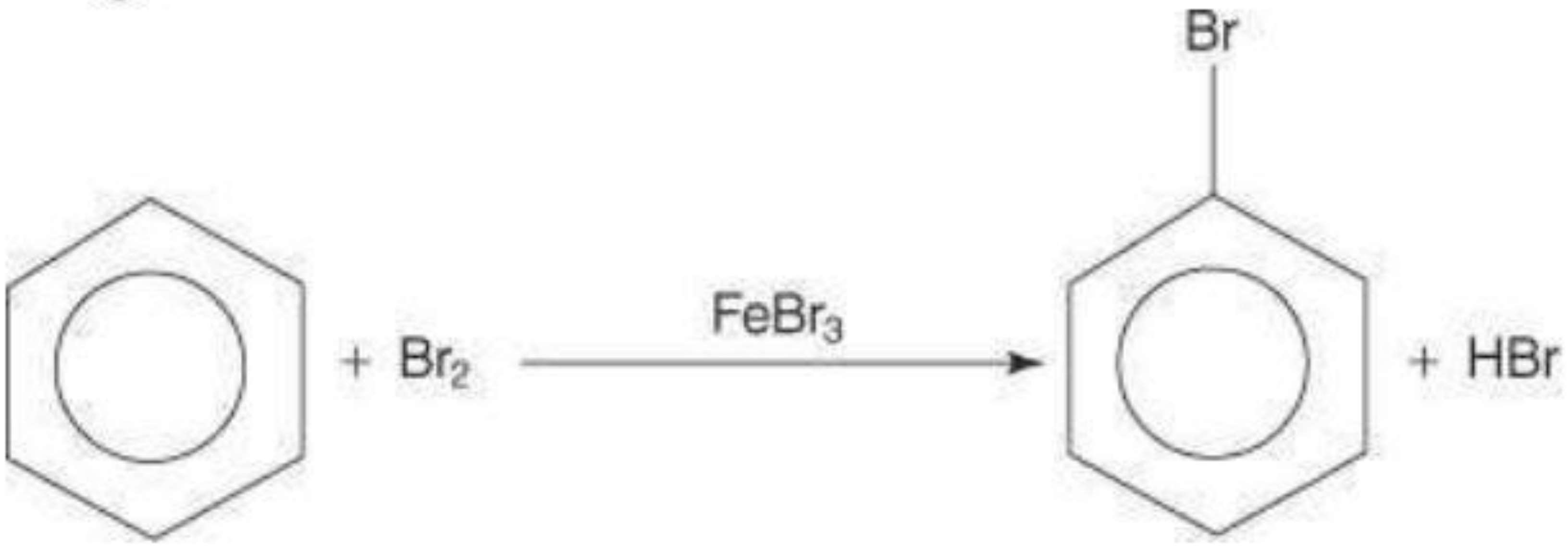
Electrophile : Cl^+ or Br^+

Example :



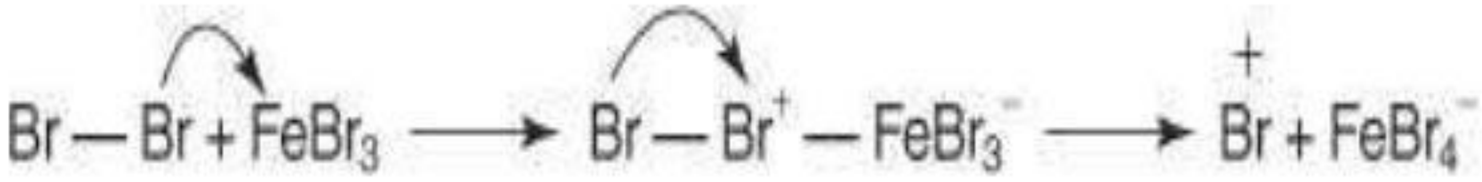
no reaction

(decolorization not observed)



MECHANISM :

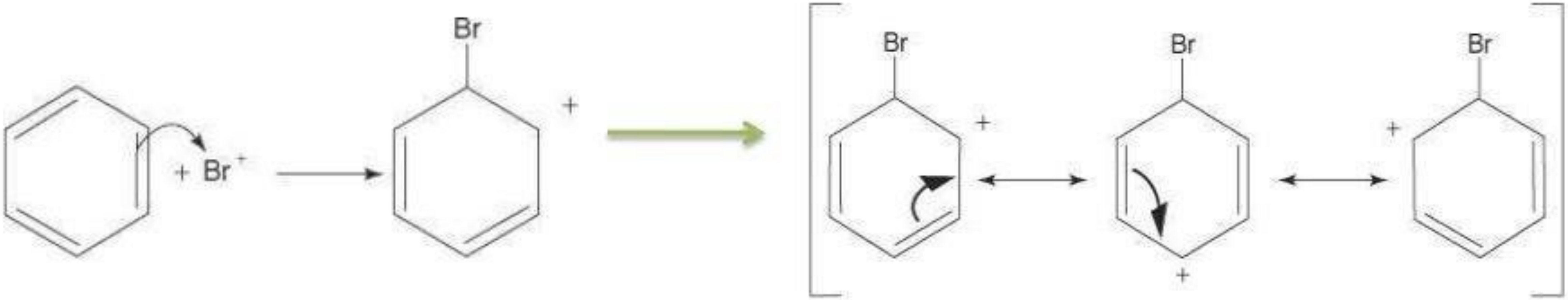
Step 1 : Formation of Cl^+ or Br^+



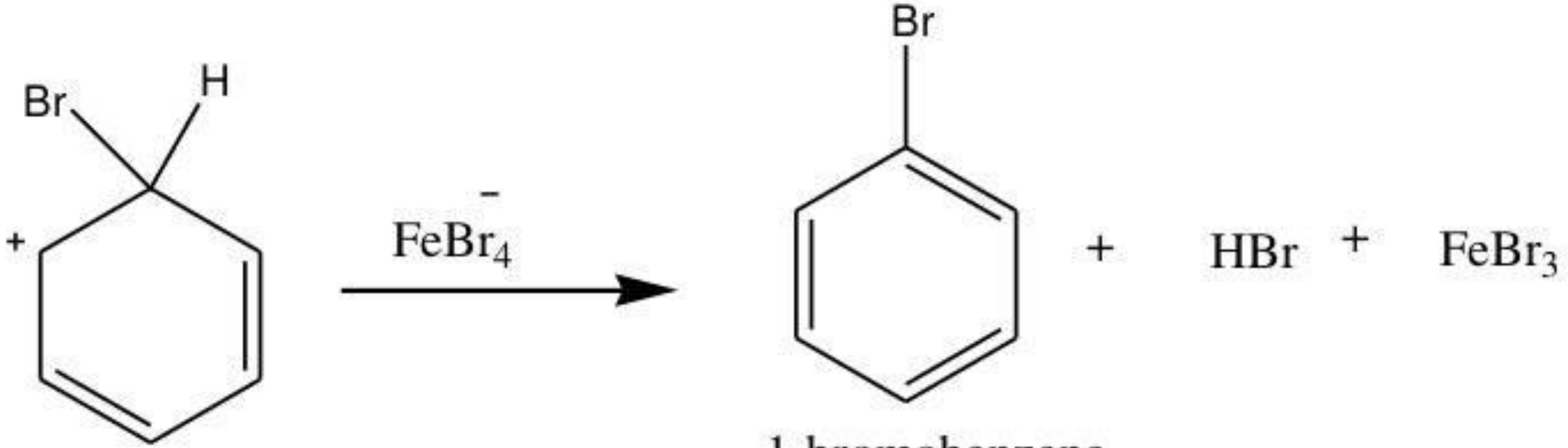
$Br-Br + FeBr_3 \longrightarrow Br-Br^{+}-FeBr_3^{-} \longrightarrow \overset{+}{Br} + FeBr_4^{-}$

Step 2 : Electrophilic substitution

(The electrophile attacks the π electron system of the benzene ring to form a arenium ion)



Step 3 : Loss of proton to reform the aromatic ring



Brominated arenium ion

1-bromobenzene

Function of Lewis acid :

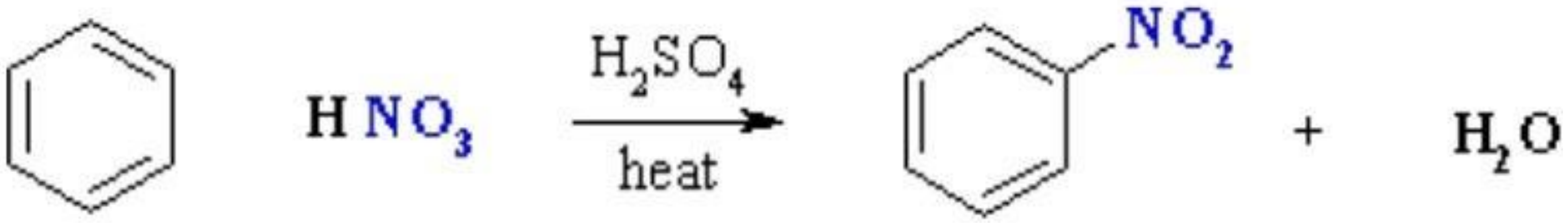
Incerase the polarity of halogen molecules to produce positive halogen ions (Cl^+ or Br^+) = electrophile

AROMATIC NITRATION

Reactants : Benzene and concentrated **HNO_3**

Conditions : Concentrated **H_2SO_4**

Example :



nitrobenzene

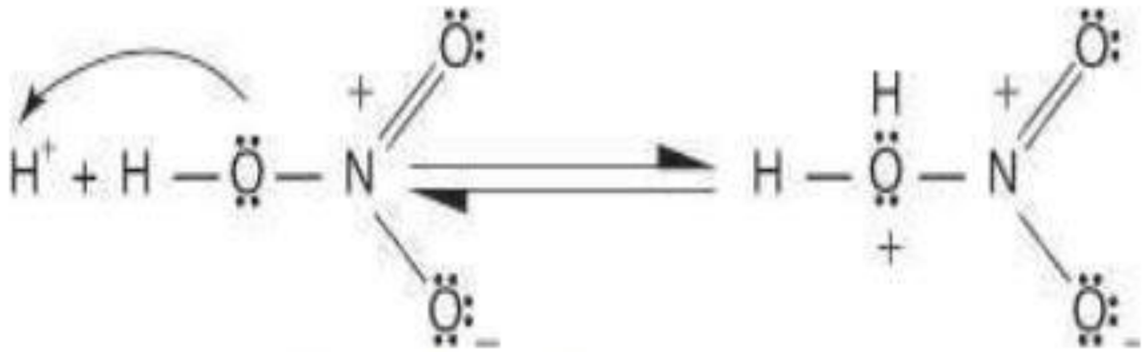
MECHANISM :

Step 1 : Formation of Nitronium ion (NO_2^+)

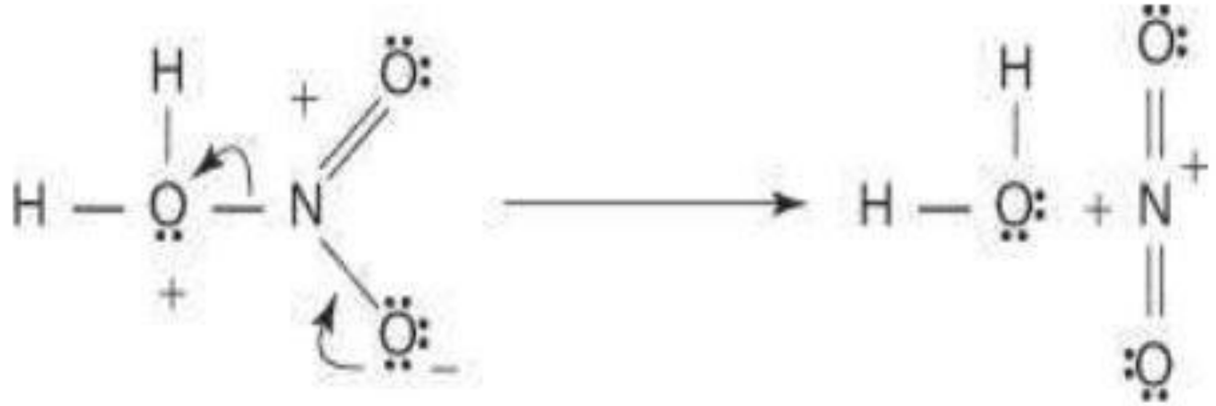
- Sulfuric acid ionizes to produce a proton

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

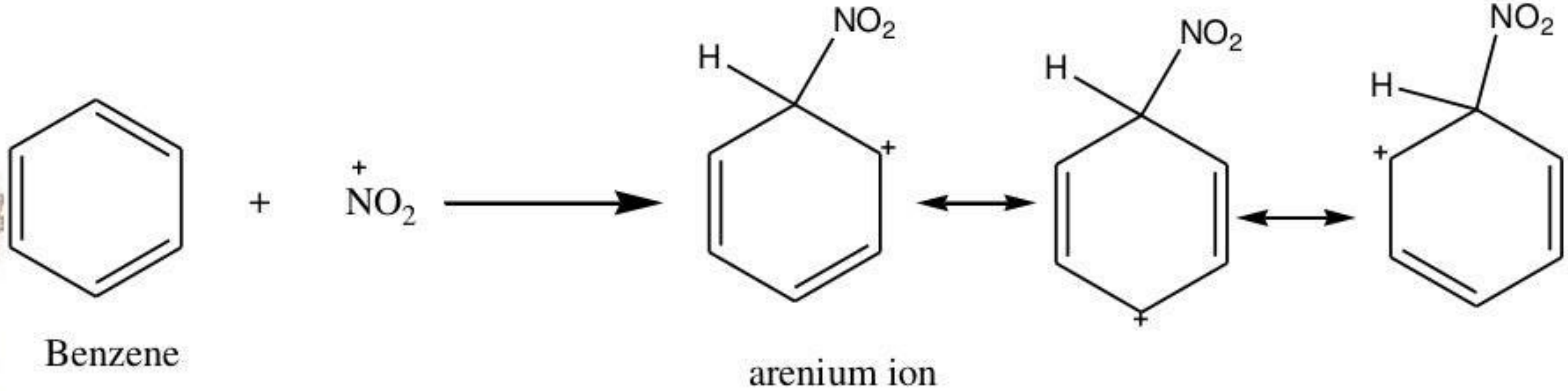
-Nitric acid accepts a proton from a stronger acid (H_2SO_4) and form a protonated nitric acid



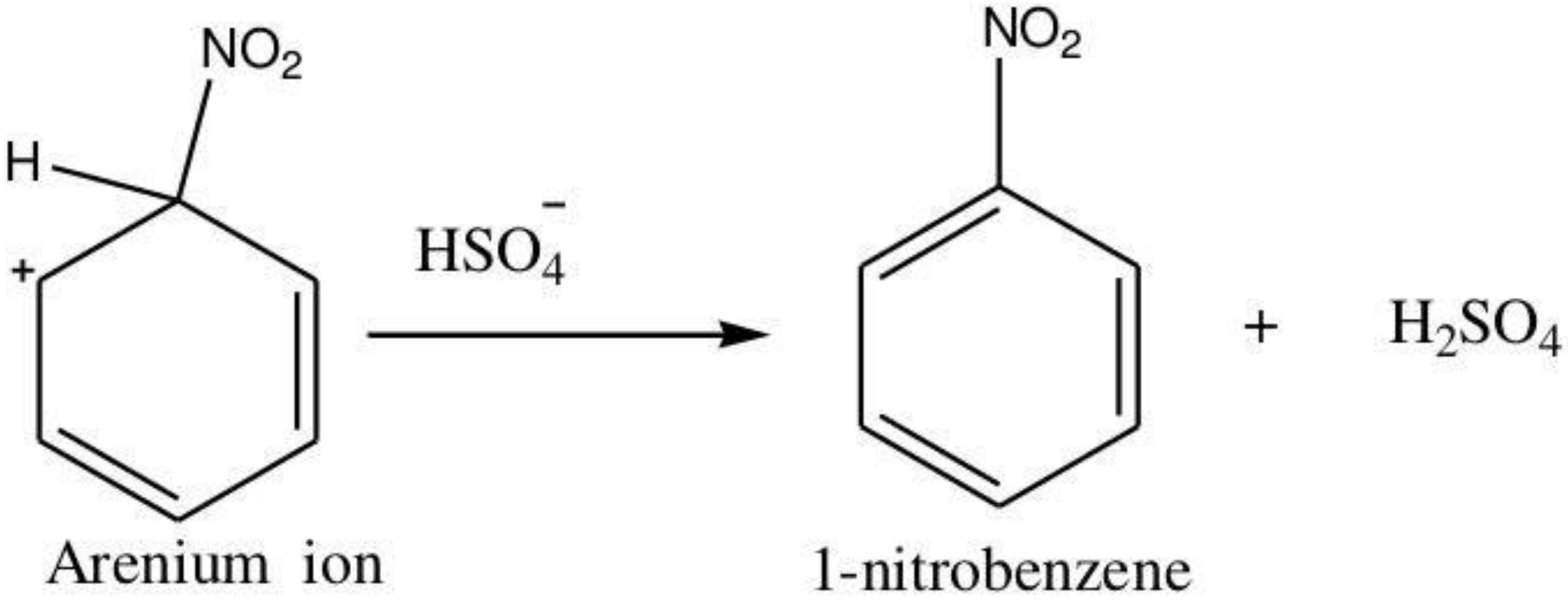
- The protonated nitric acid dissociates to form a nitronium ion ($^+NO_2$)



Step 2 : Electropjilic substitution



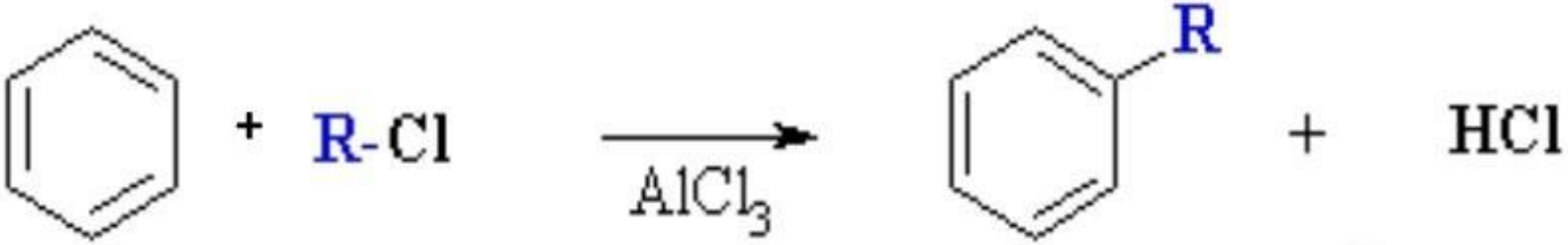
Step 3 : Loss of proton to re-form the aromatic ring



FRIEDEL-CRAFT ALKYLATION

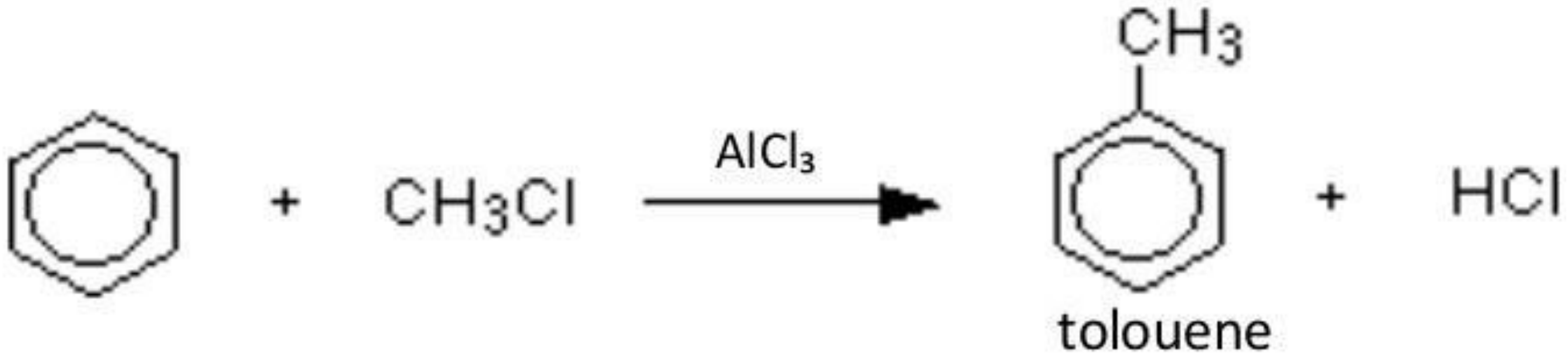
Reactants : Benzene and alkyl halide

Condition : catalyst (Lewis acid like $AlCl_3$)



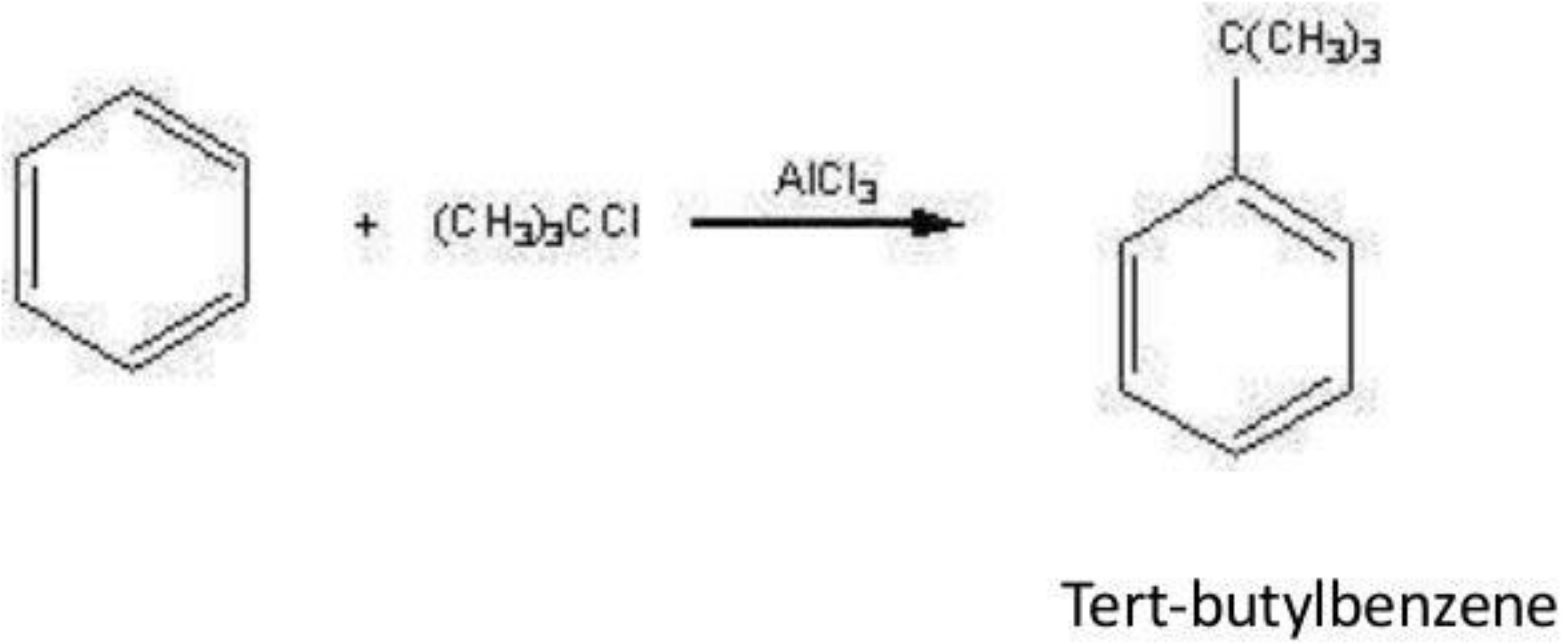
Example :

1)



CH3Cl
AlCl3
CH3
HCl
tolouene

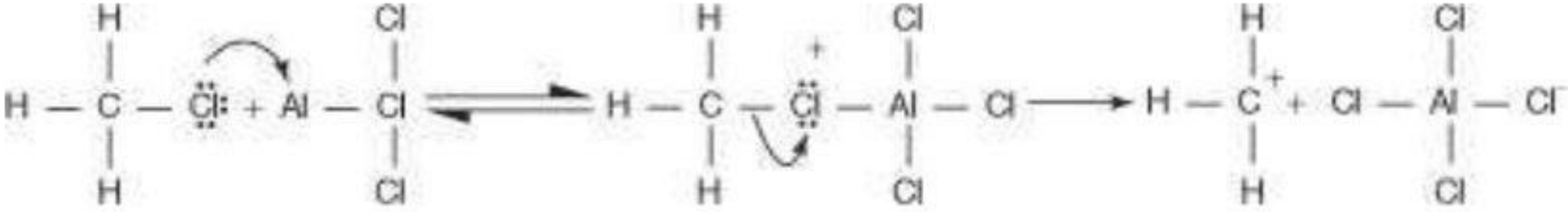
2)



(CH3)3CCl
AlCl3
C(CH3)3
Tert-butylbenzene

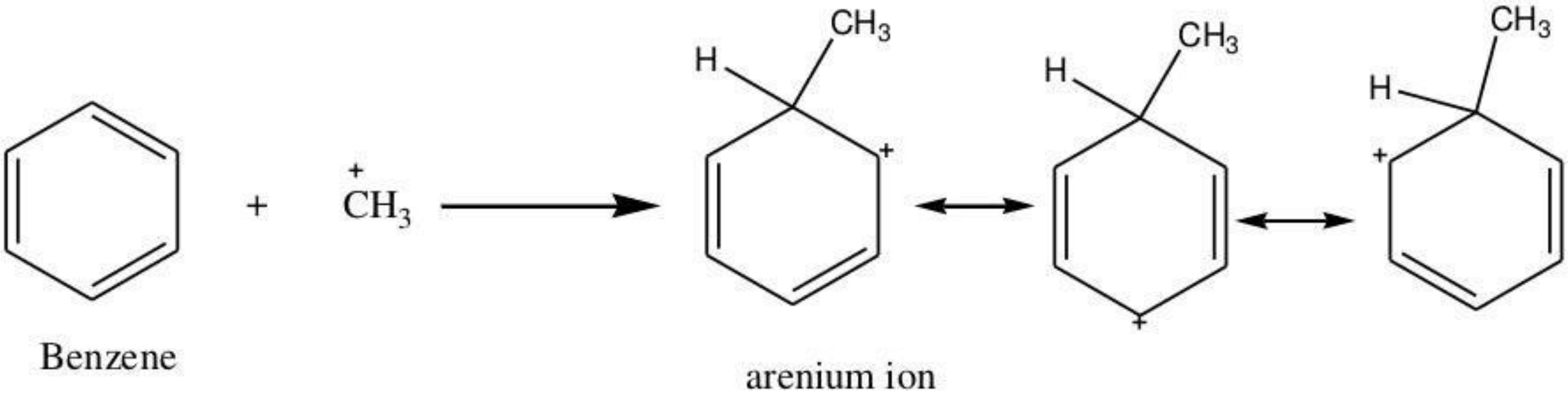
MECHANISM :

Step 1 : Formation of carbocation

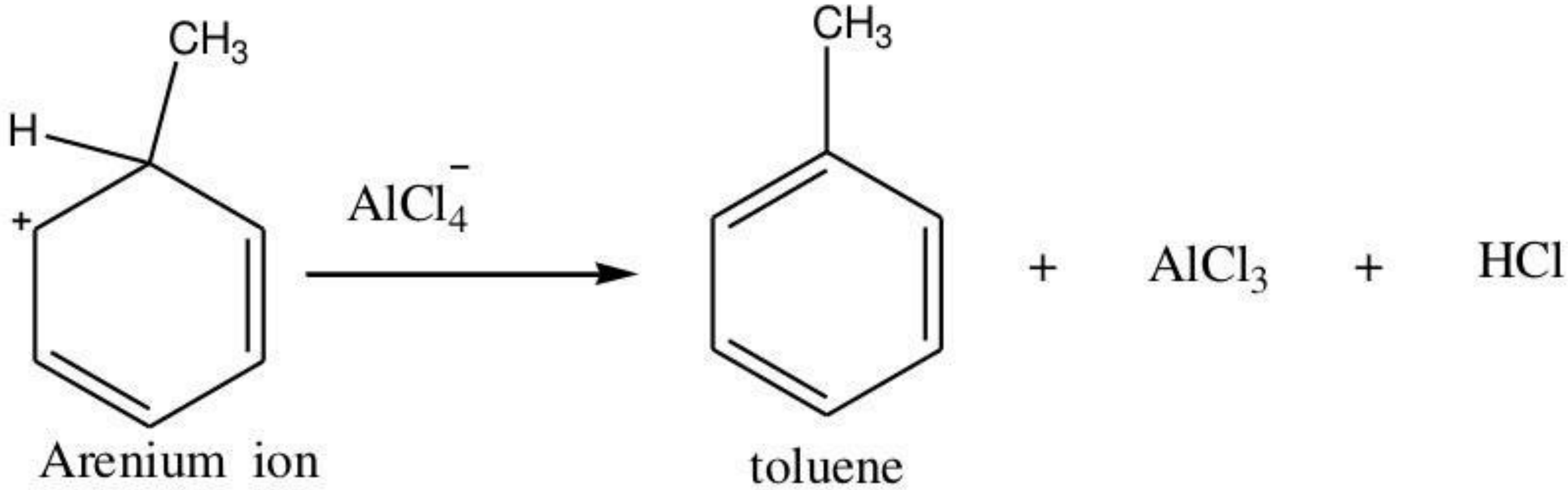


Step 2 : Electrophilic substitution

(electrophile attacks the π electron system of the benzene ring to form an arenium ion)

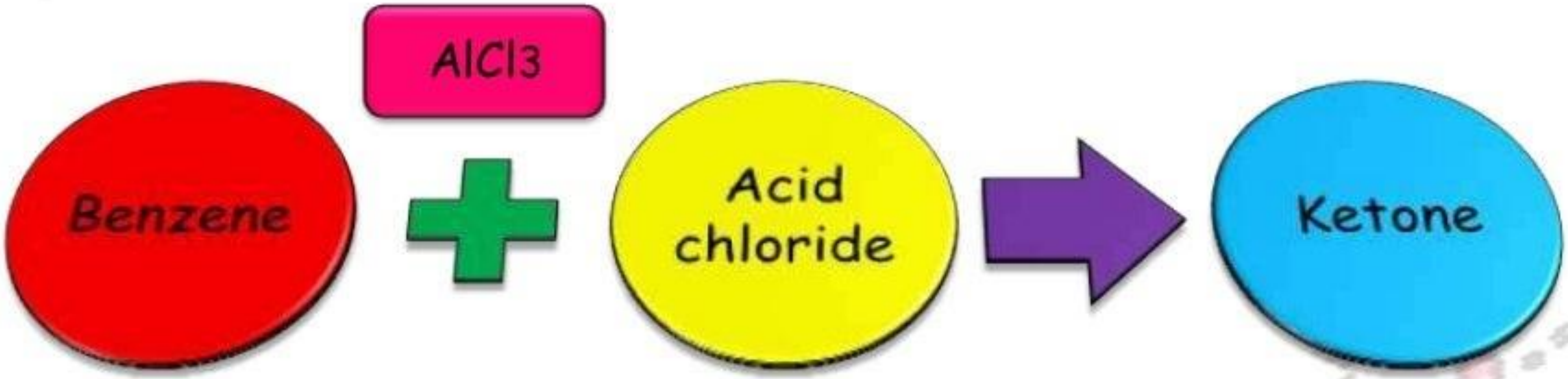


Step 3 : loss of proton to re-form the aromatic ring



Friedel-Craft Acylation

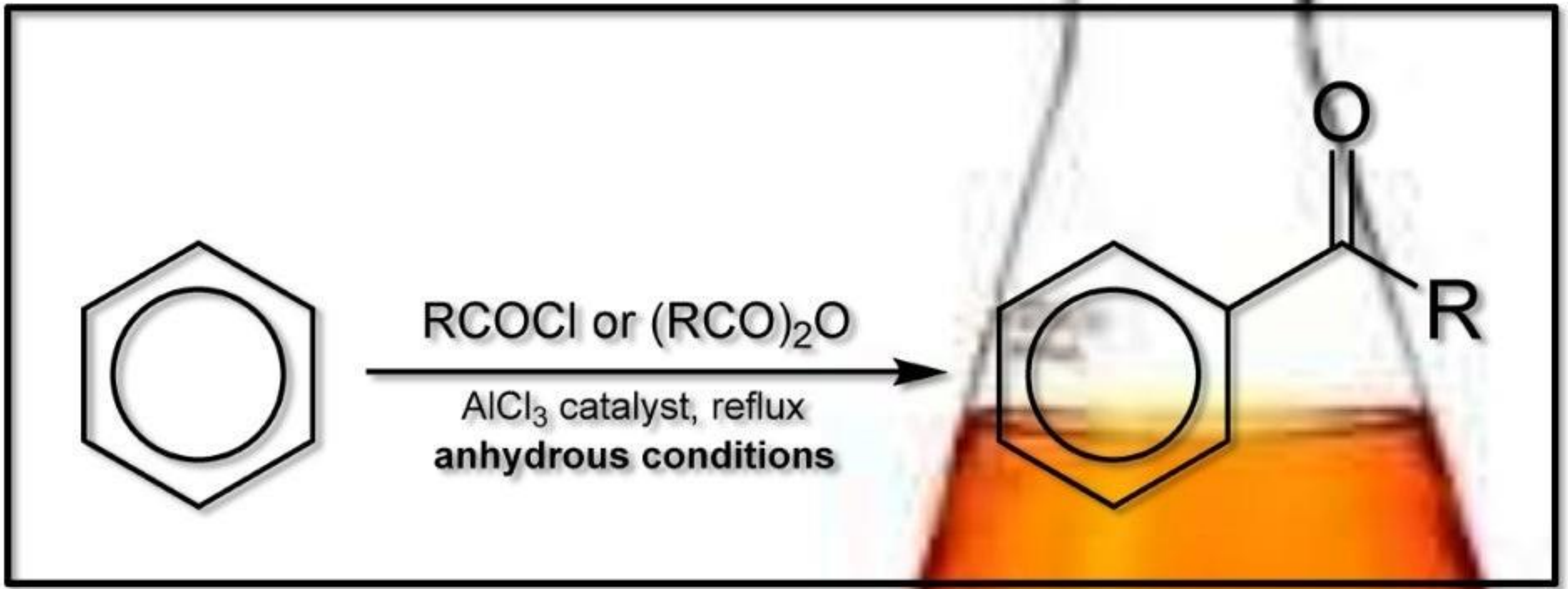
- **Reactancts:** Aromatic rings and acid chloride
- **Product:** Ketone
- **Condition:** Strong Lewis acid



AlCl3

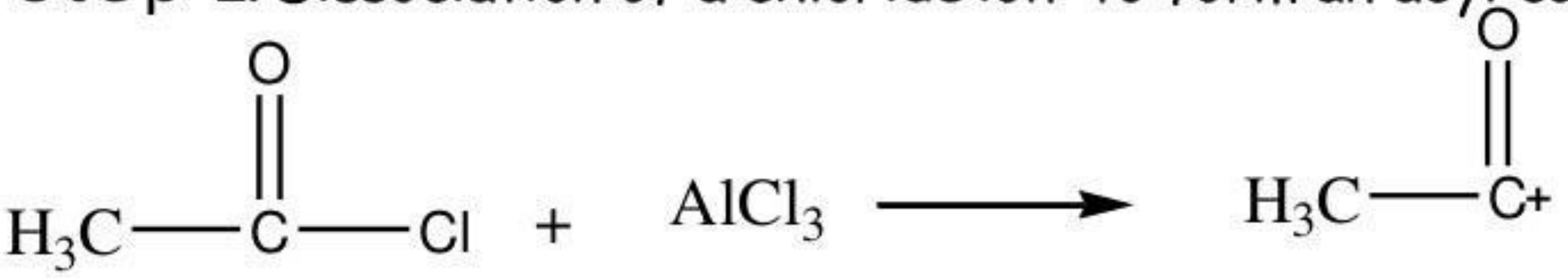
Benzene + Acid chloride → Ketone

Example:

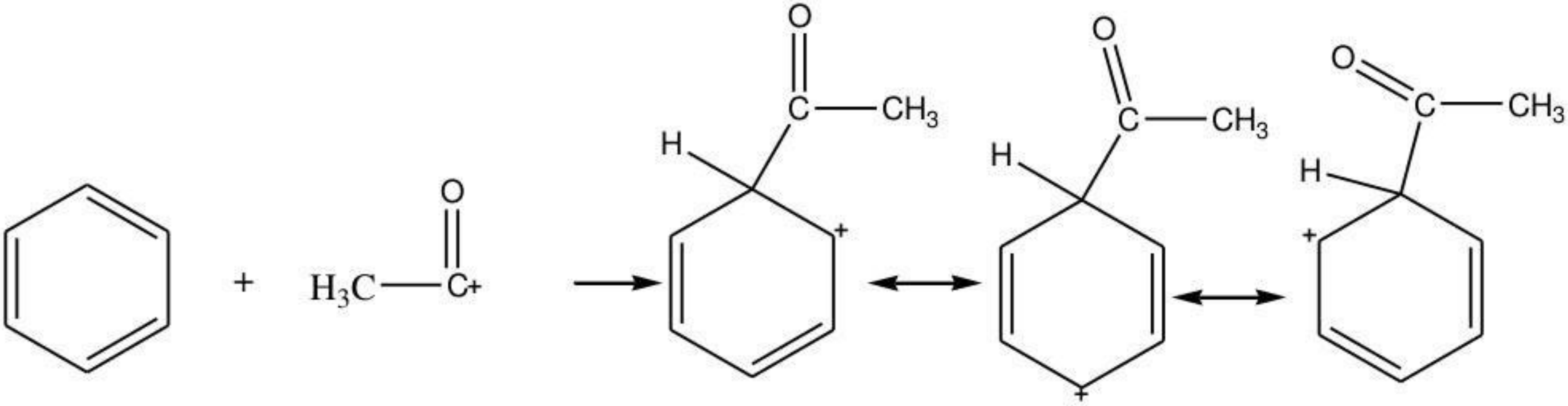

RCOCl or (RCO)2O
AlCl3 catalyst, reflux
anhydrous conditions
O
R

Mechanism

Step 1: Dissociation of a chloride ion to form an acyl cation ("acylium ion")



Step 2: The resulting acylium ion or a related adduct is subject to nucleophilic attack by the arene



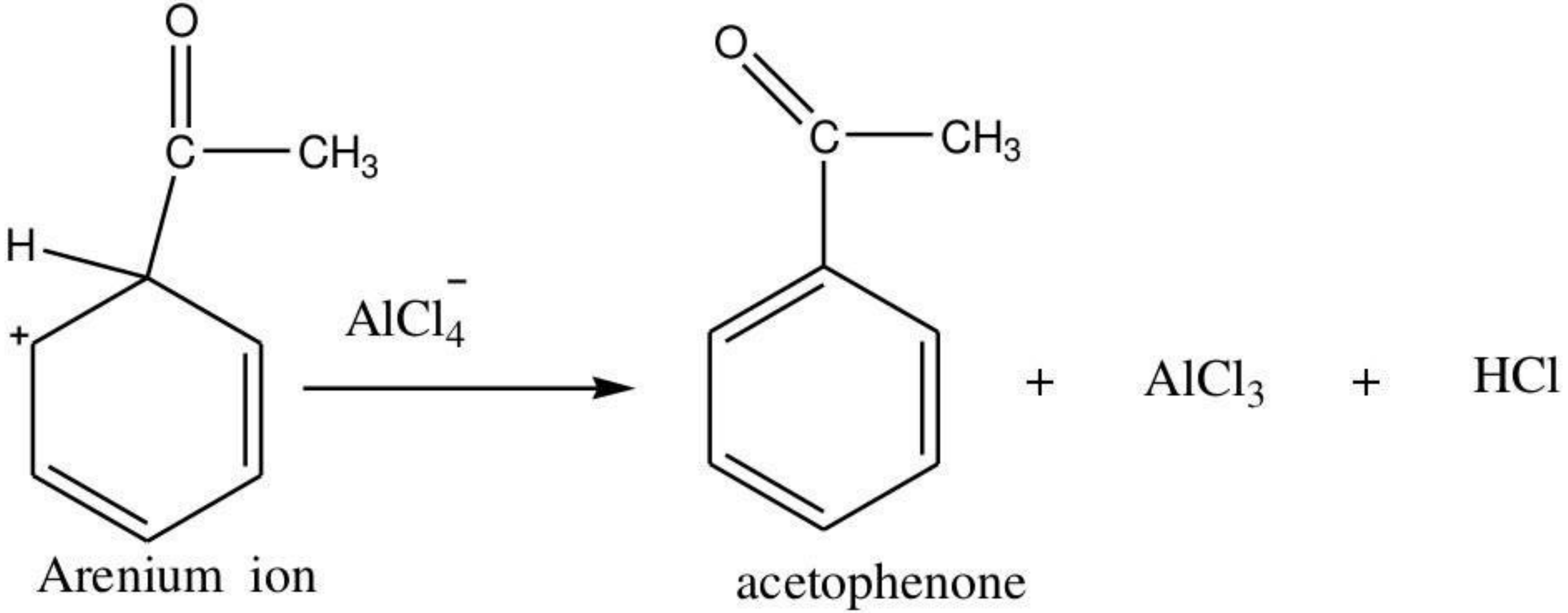
Benzene

arenium ion

Mechanism of Friedal craft acylation

Step 3:

Chloride anion (or $AlCl_4^-$) deprotonates the ring (an "arenium ion") to form HCl, and the $AlCl_3$ catalyst is regenerated

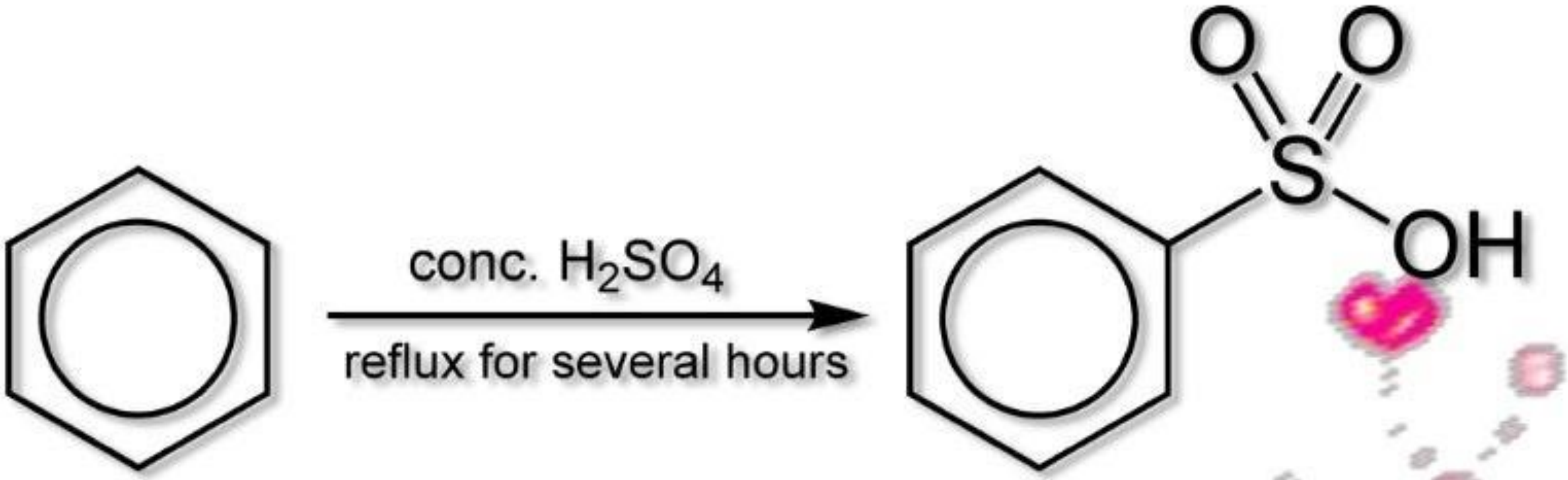


Limitation of friedal craft acylation and alkylation

1. Friedal craft acylation will not carried with strong electron withdrawing group e.g. Nitric acid
2. Friedal craft acylation will not react strong electron rich group. E.g. Ammonia
3. Polysubstitution reaction will not possible.
4. Chlorinated reactant is required for reaction.
5. Catalyst only $AlCl_3$ to produce acylated product.
6. Inability to separate catalyst from the acidified product.
7. Temperature is required to proceed the reaction

Aromatic Sulfonatio

- Organic reaction in which a hydrogen atom on an arene is replaced by a sulfonic acid functional group in an electrophilic aromatic substitution

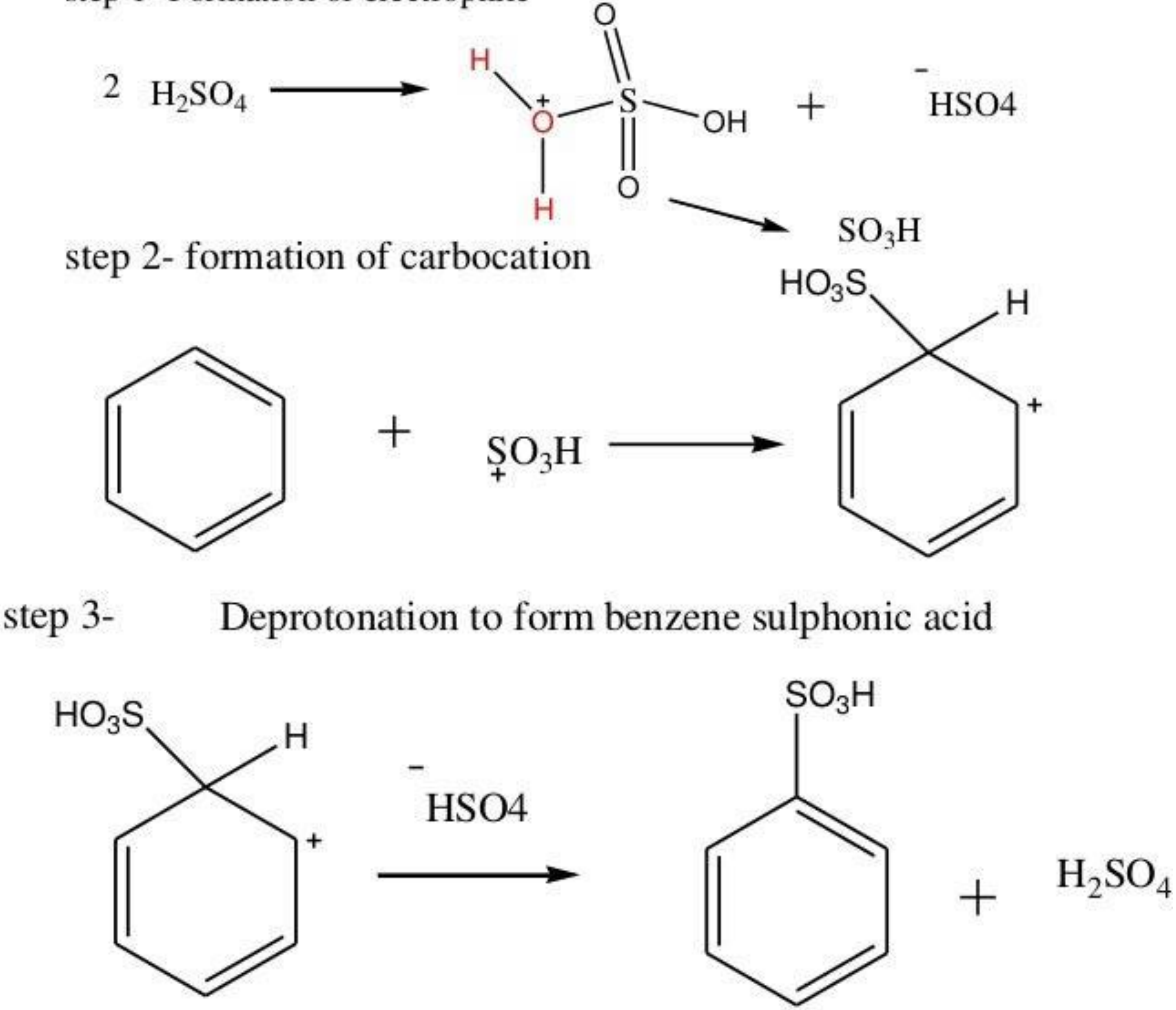


Aromatic Sulfonation

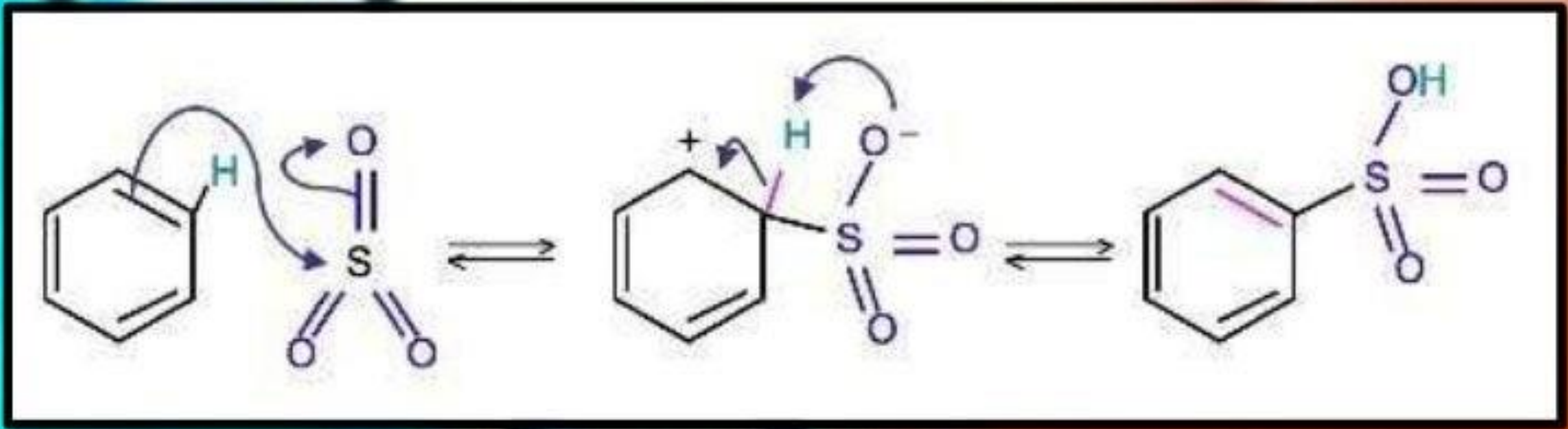
Mechanism:
step 1- Formation of electrophile

step 2- formation of carbocation

step 3- Deprotonation to form benzene sulphonic acid



Mechanism

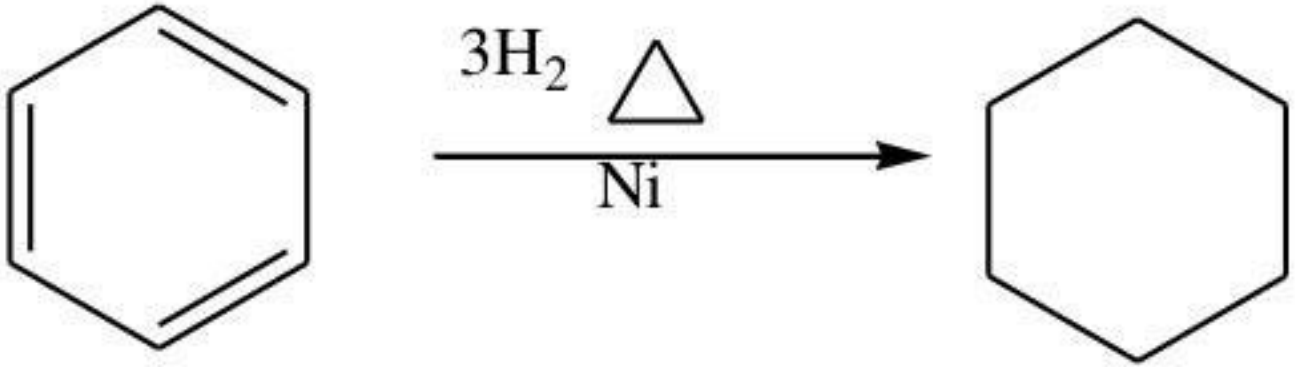


- **Step 1:**
  The p electrons of the aromatic ***C=C*** act as a nucleophile, attacking the electrophilic S, pushing charge out onto an electronegative O atom. This destroys the aromaticity giving the cyclohexadienyl cation intermediate.

- **Step 2:**
  Loss of the proton from the sp^3 C bearing the sulfonyl- group reforms the ***C=C*** and the aromatic system.

- **Step 3**:
  Protonation of the conjugate base of the sulfonic acid by sulfuric acid produces the sulfonic acid.

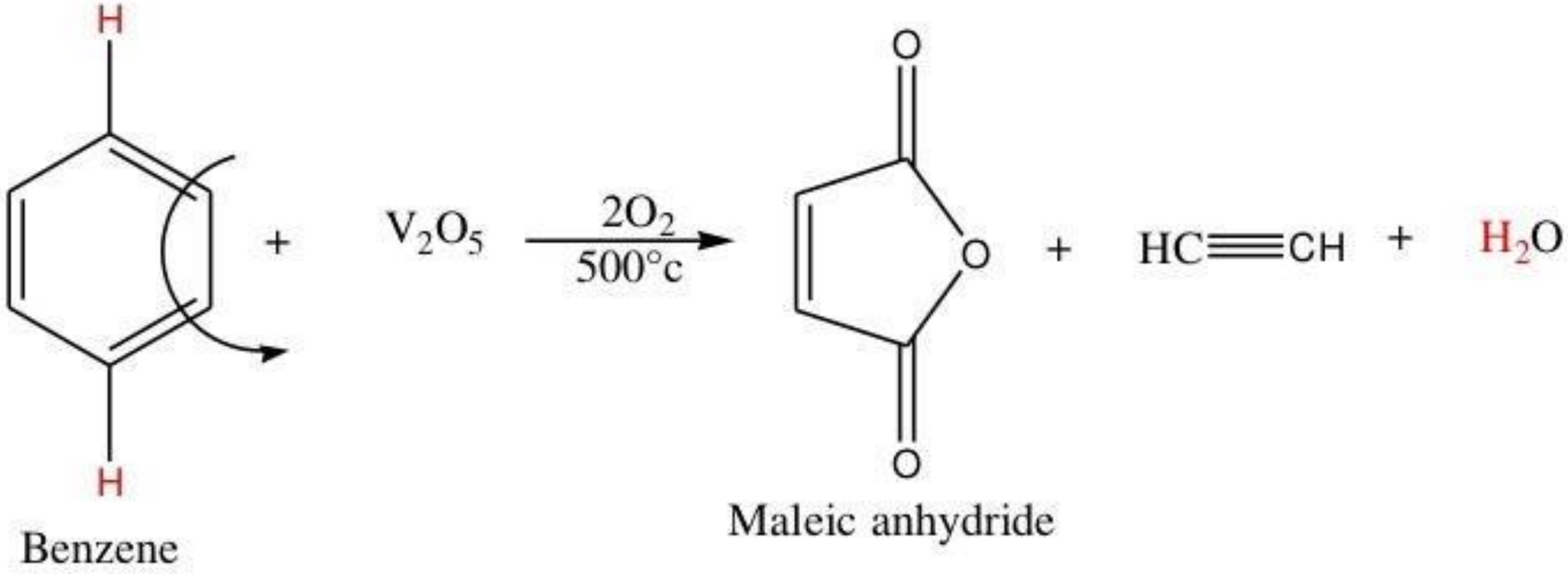
6. Reduction of benzene

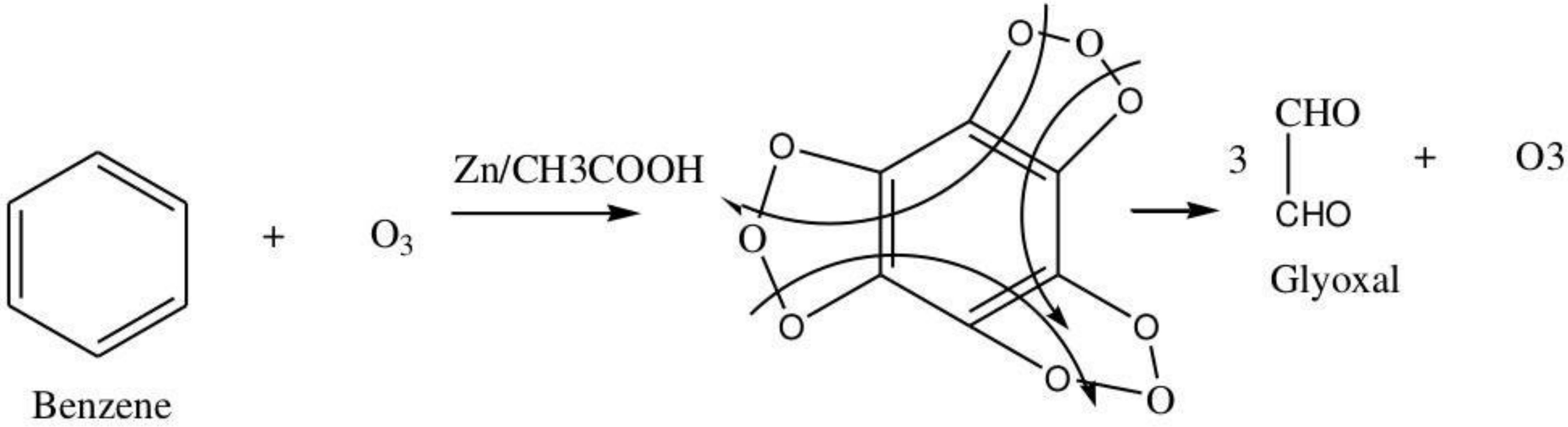


ΔH=-49.8KCal/mole

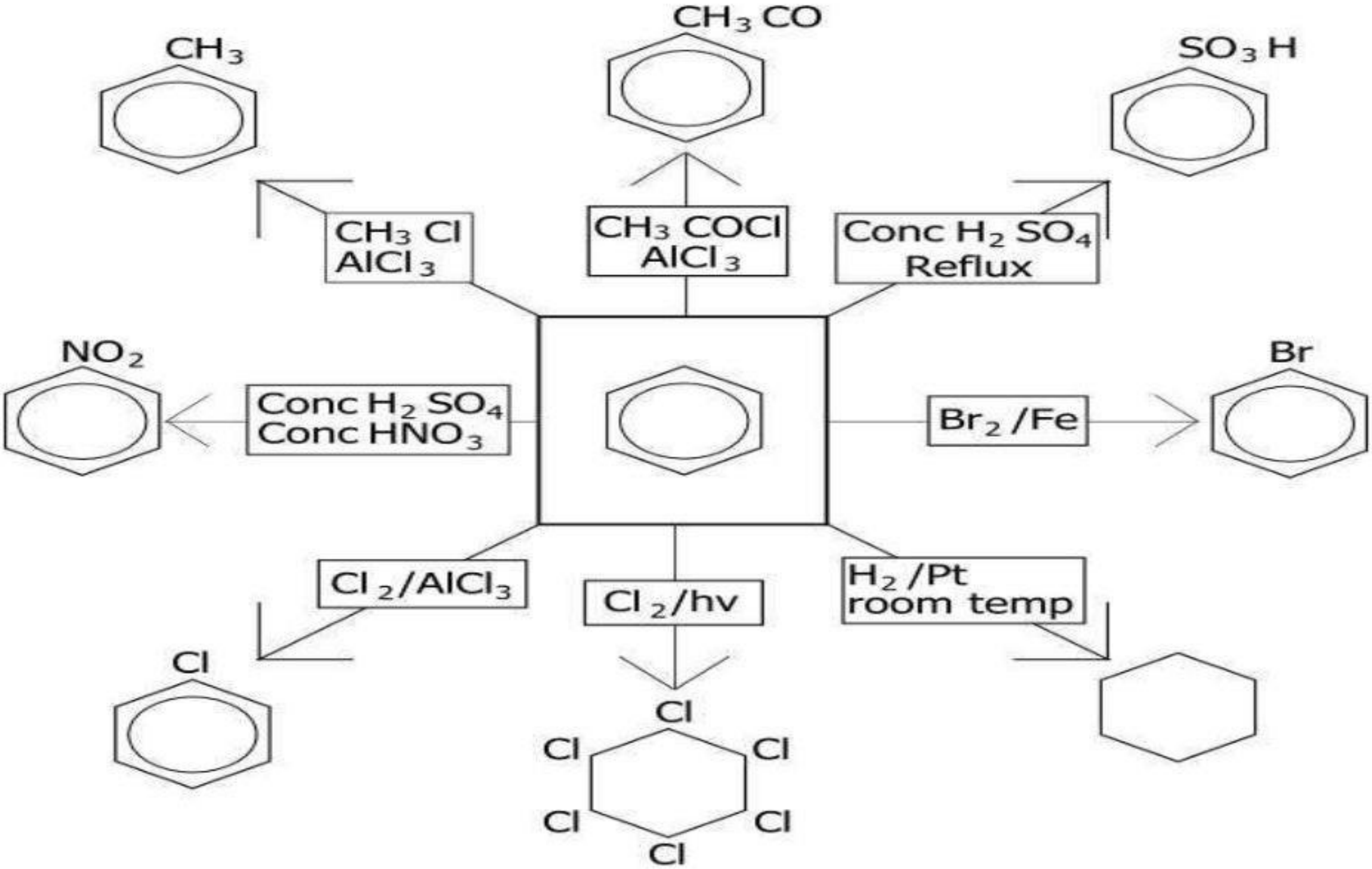
7. Oxidation and ozonolysis

When benzene reacts with Oxygen in presence of vanadium pentoxide to produce succinic anhydride





Summary:



CH_3
CH_3CO
SO_3H
CH_3Cl $AlCl_3$
CH_3COCl $AlCl_3$
Conc H_2SO_4 Reflux
NO_2
Conc H_2SO_4 Conc HNO_3
Br
Br_2/Fe
$Cl_2/AlCl_3$
Cl_2/hv
H_2/Pt room temp
Cl
Cl
Cl
Cl
Cl
Cl
Cl

Substituent Effect in Substituted Aromatic Benzene

1. classification of substituents
2. effect of substituent
3. Directive effect
4. Electrophilic substitution of monosubstituted benzene
5. effect of substituent on orientation and reaction rate of mono substituted benzene

Activating Group & Deactivating Group

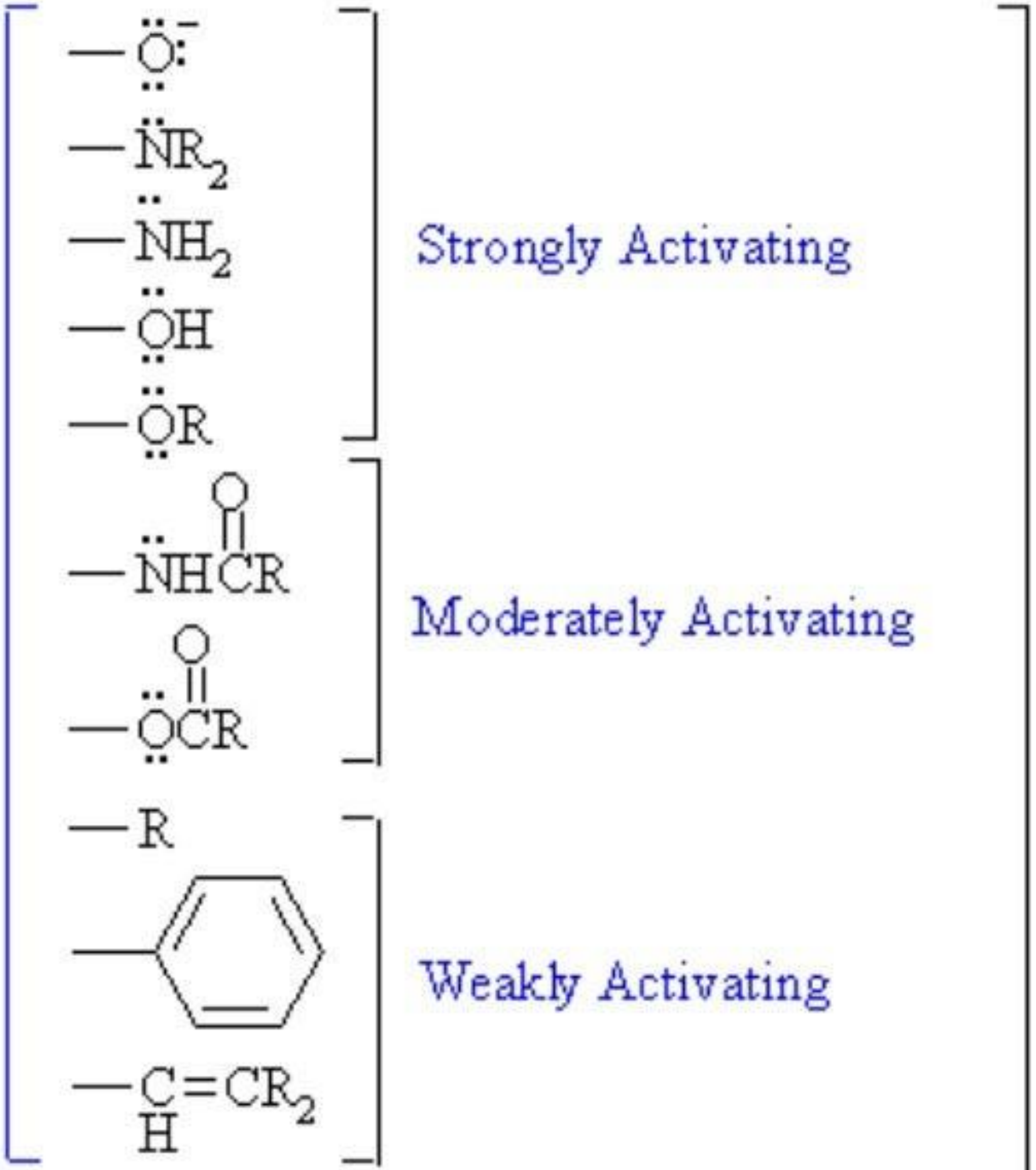
Activating Group:
Substituent that activate the ring, making it more reactive than benzene

Deactivating Group:
Substituent that deactivate ring, making it less reactive than benzene

Most Activating

Activating

EDG



Strongly Activating

Moderately Activating

Weakly Activating

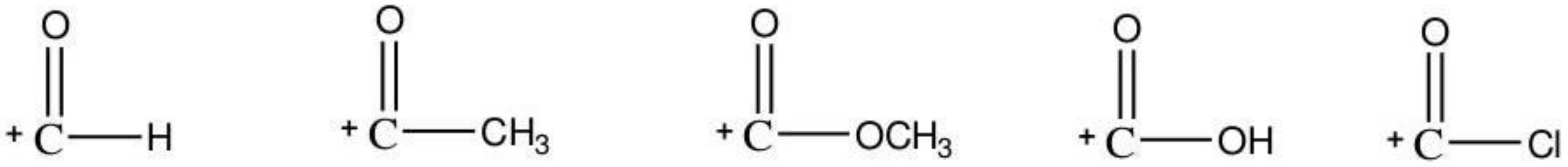
ortho / para directing

Classification of electron withdrawing group

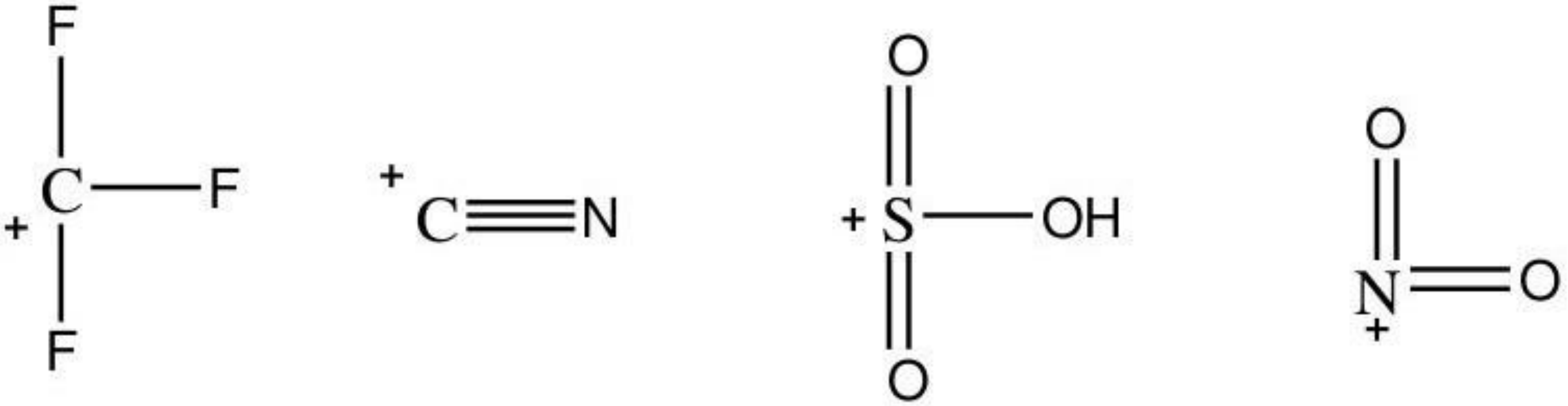
1. Weakly electron withdrawing group:

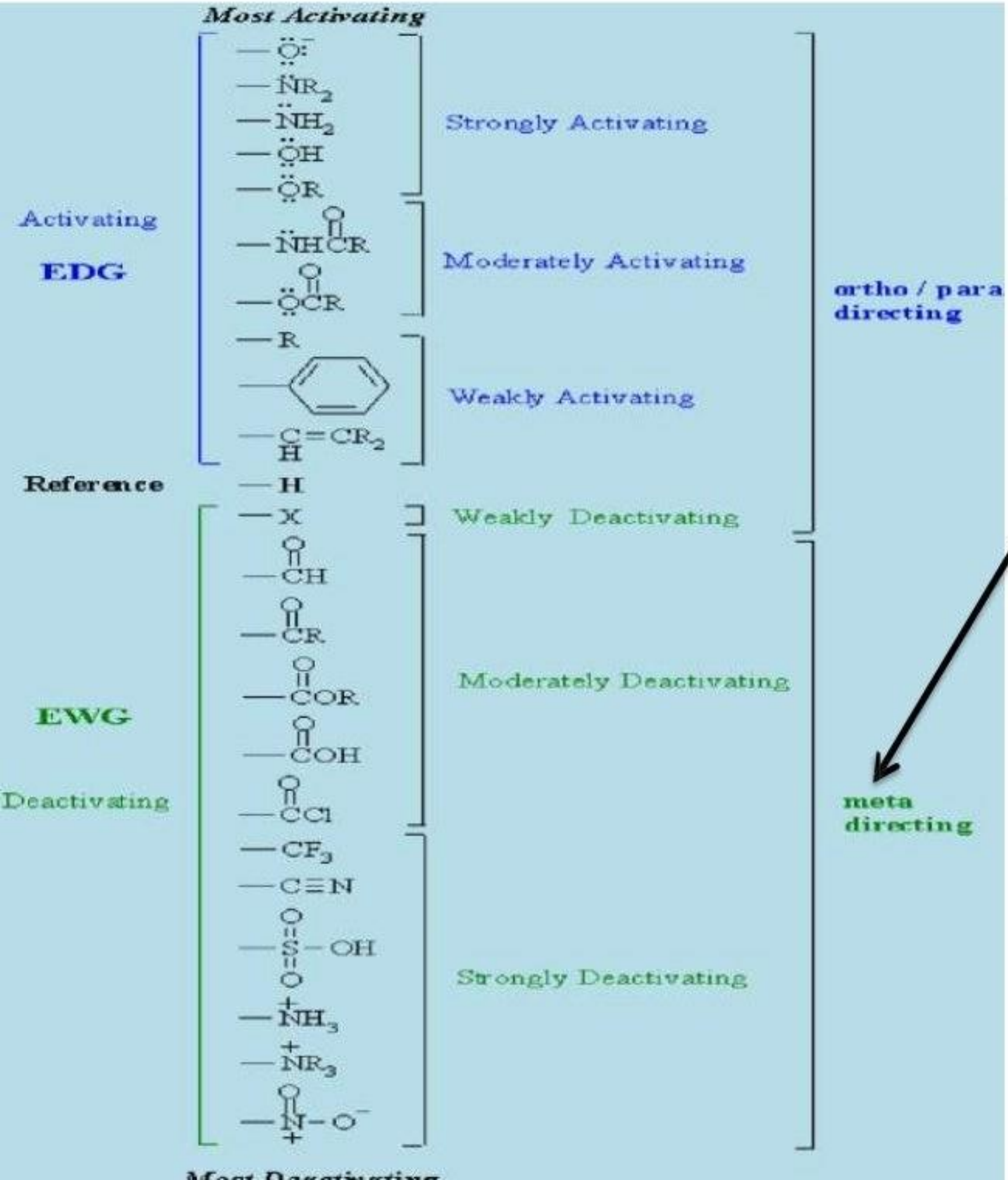
H^{+}, $X^{+} = Cl^{+}$, Br^{+} I^{+}

2. Moderately electron withdrawing group:

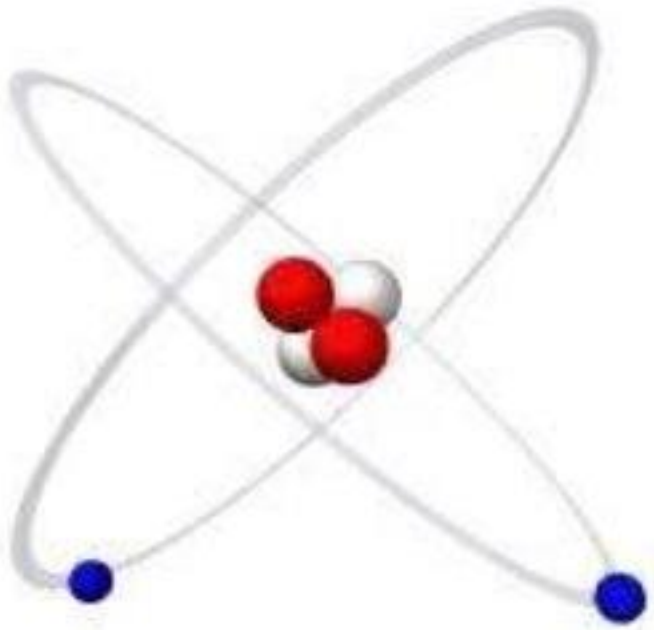


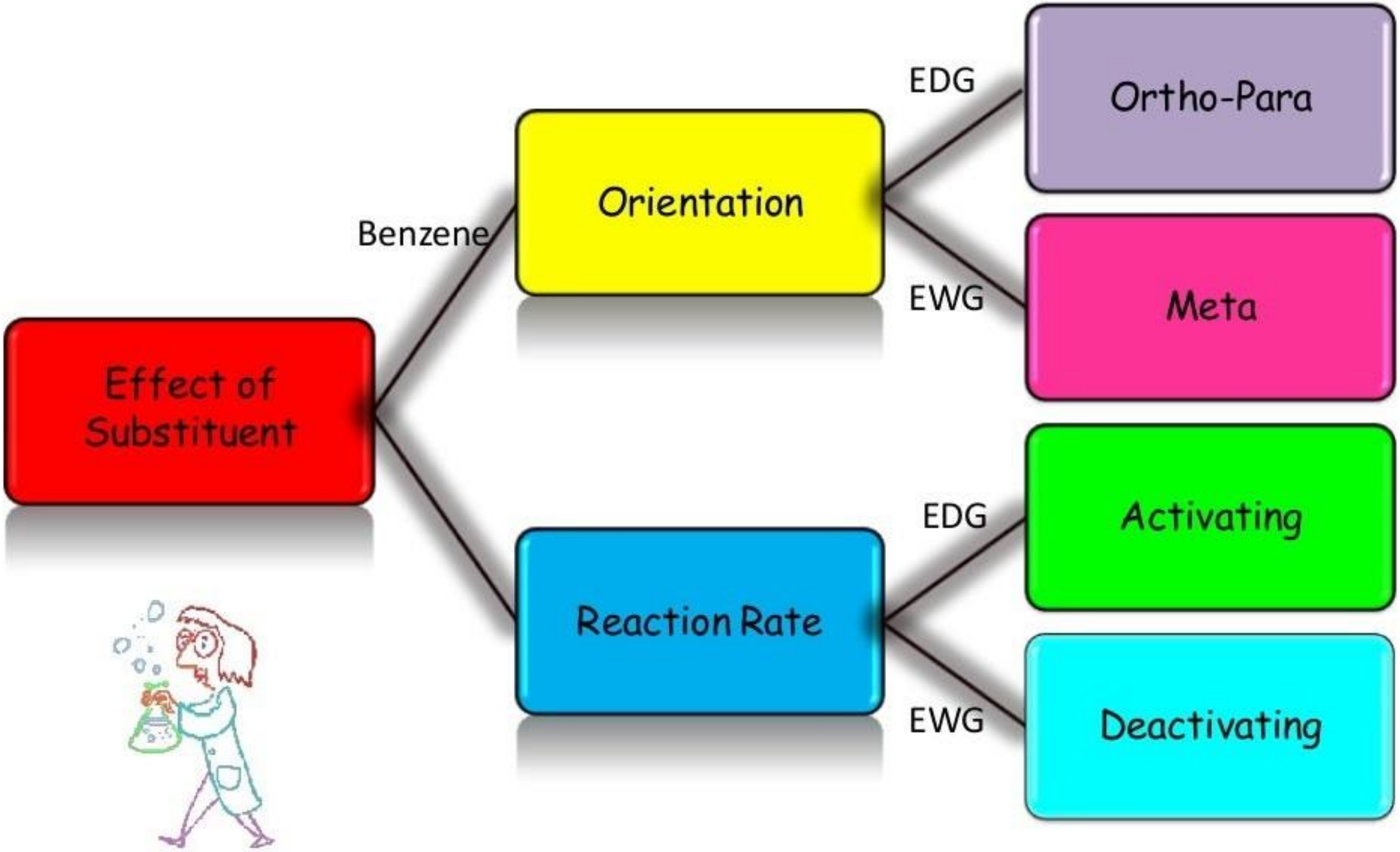
3. Strong electron withdrawing group:





Meta –Directing Deactivator





Effect of Substituent

Benzene

Orientation

EDG

Ortho-Para

EWG

Meta

Reaction Rate

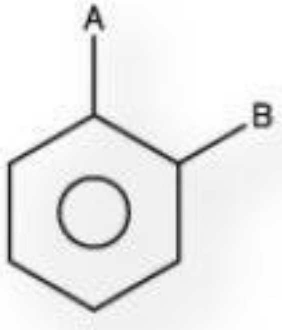
EDG

Activating

EWG

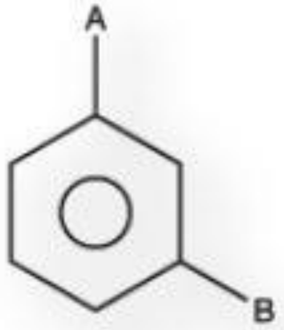
Deactivating

Orientation



1

ortho disubstituted benzene



2

meta disubstituted benzene

3

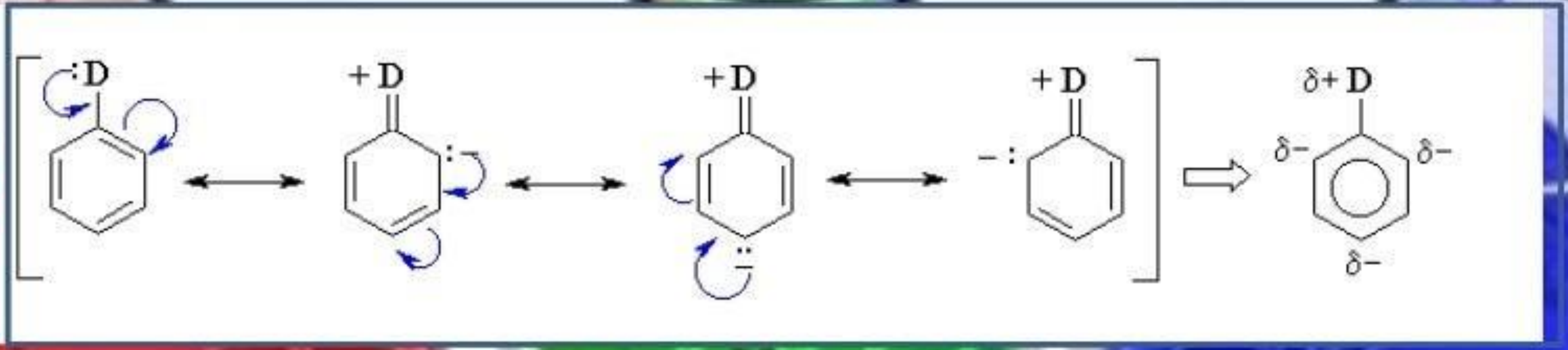
para disubstituted benzene

Ortho-substitution- 2 substituents occupy positions next to each other.

Meta-substitution - Substituent occupy positions 1 and 3

Para-substitution Substituent occupy positions 1 and 4

Directive effect:
A. Ortho-Para Activator



- Electron donating groups (EDG) with lone pairs on the atoms adjacent to the p system activate the aromatic ring by increasing the electron density on the ring through a resonance donating effect.
- The resonance only allows electron density to be positioned at the ortho- and para- positions.
- Hence these sites are more nucleophilic, and the system tends to react with electrophiles at these ortho- and para- sites.

Ortho and Para Director

When electron donating group is attached to benzene ring,

↓

So electron density adds to benzene ring at ortho position.

↓

Negative charge is shifted to Para position due to resonance stabilization effect.

↓

Electron charge again shifted to ortho position.

↓

Hence negative charges are produced at ortho and Para position.

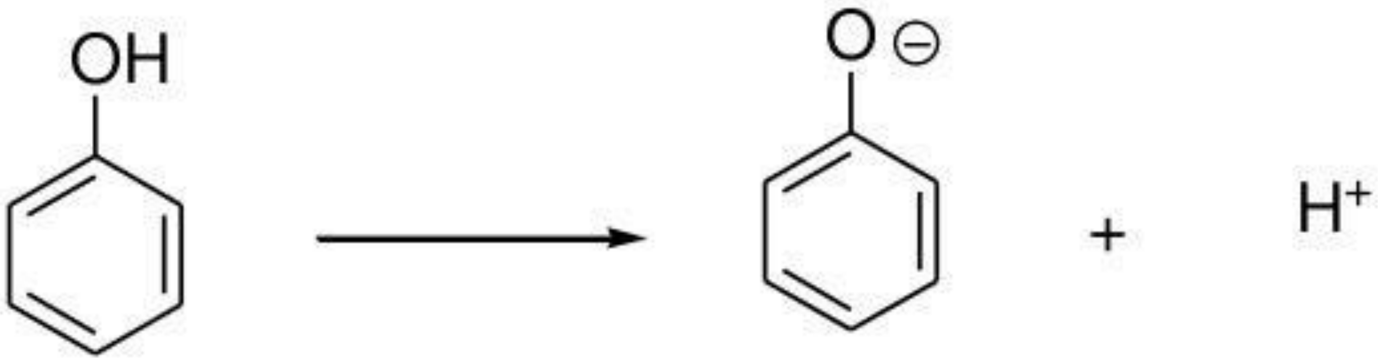
↓

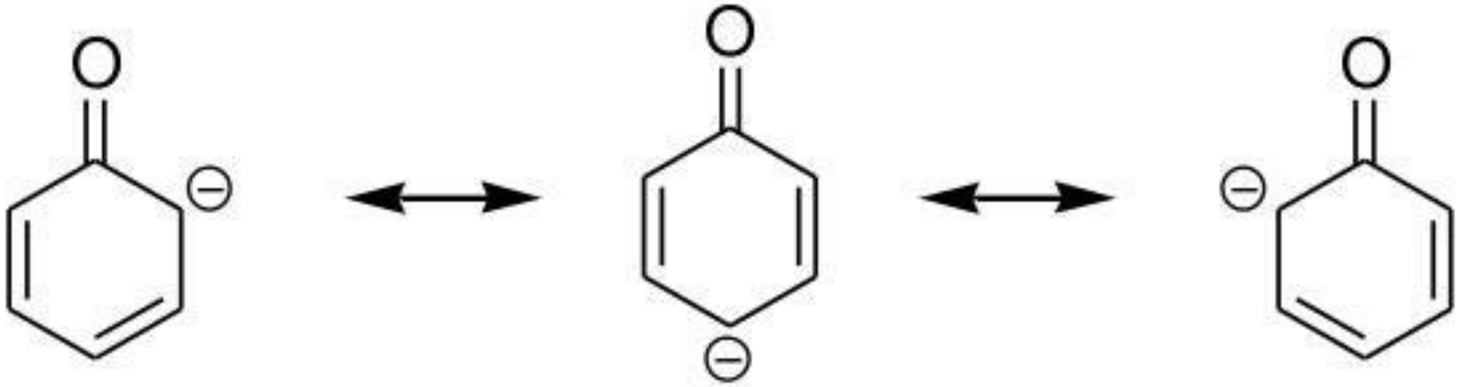
Benzene is become more reactive so elctrophiles are easily attracted to negative position.

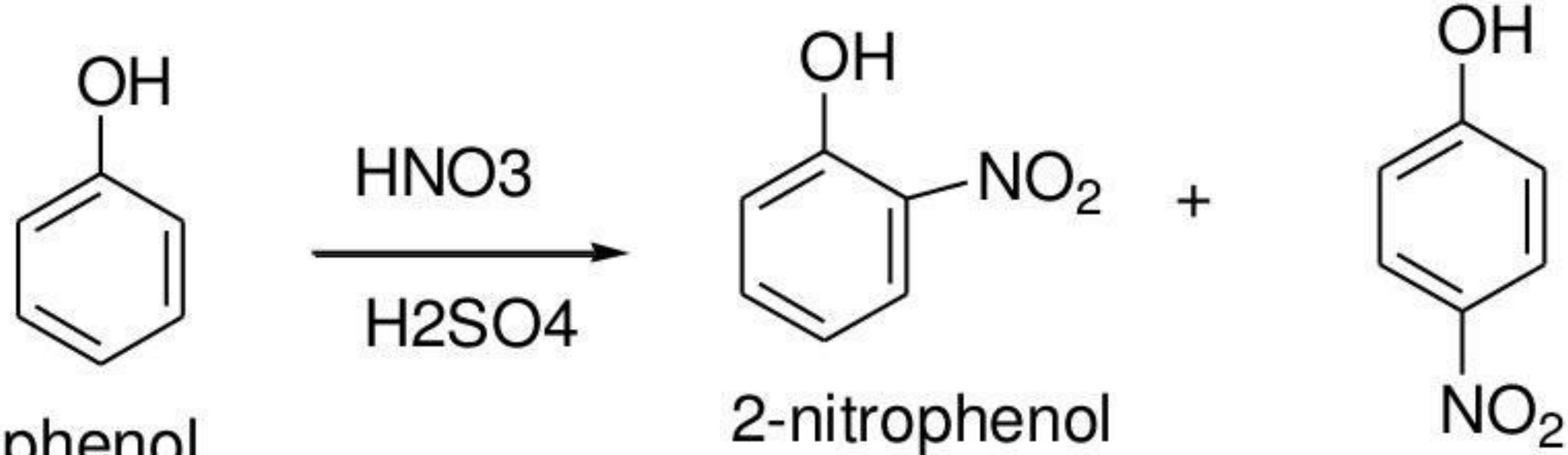
↓

Hence electrophilic substitution reactions carried out at ortho and Para position

Ortho and Para Director-Directive effect







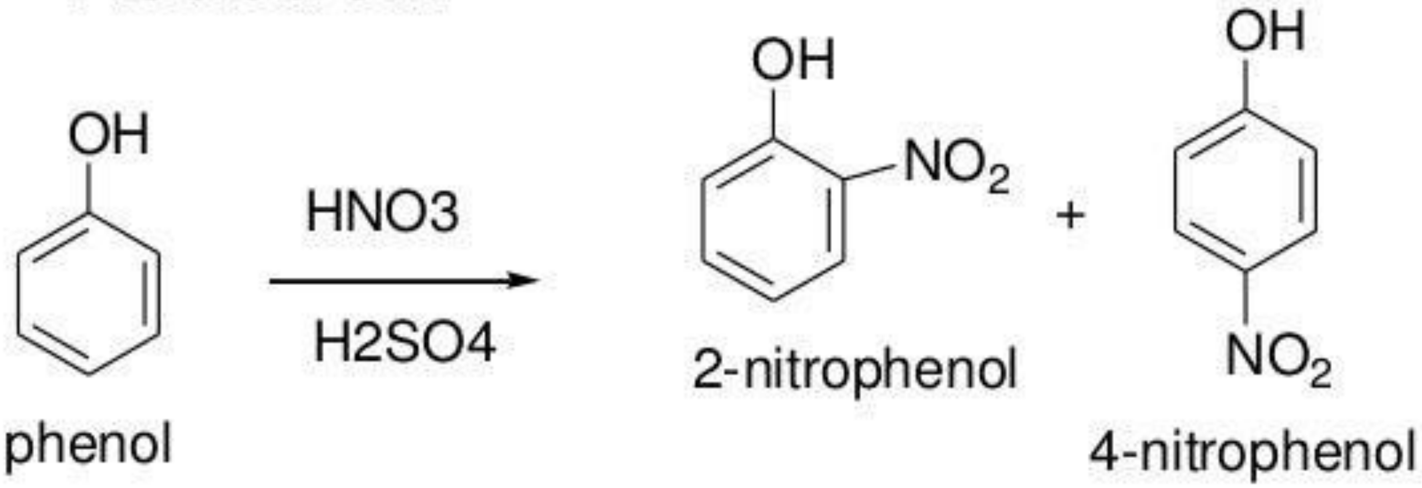
phenol

2-nitrophenol

4-nitrophenol

Mechanism of Ortho–Para directive effect

Reaction



phenol 2-nitrophenol 4-nitrophenol

Mechanism:

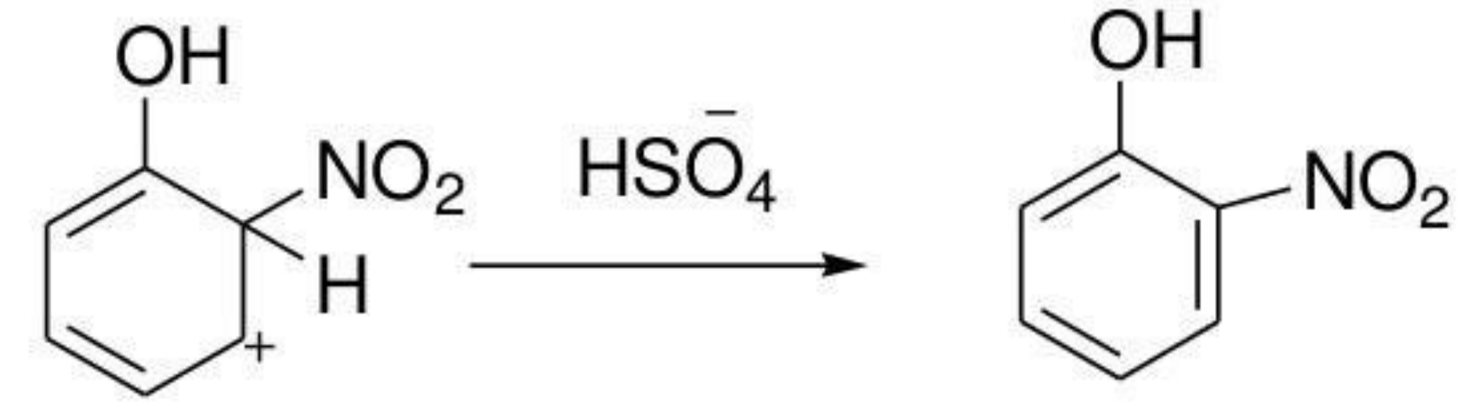
Step-I- Formation of Electrophile

$$2\ HNO_3 + 2\ H_2SO_4 \longrightarrow 2\ \overset{+}{NO_2} + 2\ H_2O + 2\ \overset{-}{HSO_4}$$

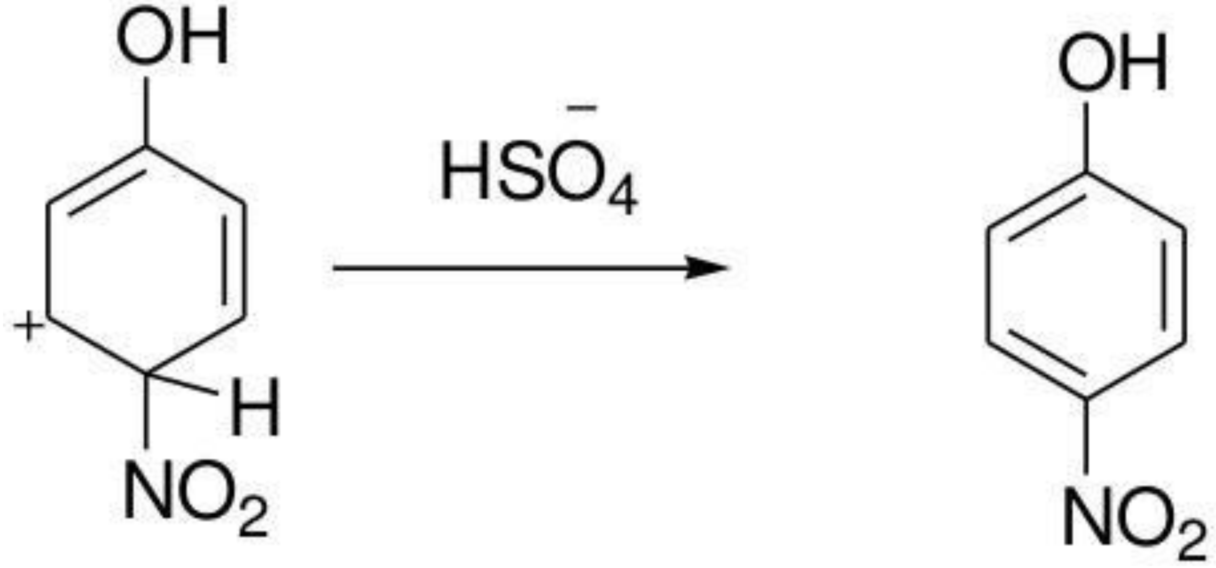
Step-II- Formation of arenium ion

Mechanism of Ortho–para directive effect

Step-III- Loss of proton to produce stable compound



2-nitrophenol



Explanation of *meta*-deactivators

Meta directors slow the reaction by raising the energy of the carbocation intermediate because they have (in one resonance form, shown below) a positively charged atom attached to the ring. Two positively charged atoms so close together is very high in energy (especially unstable).

m- directive effect- m-director

When electron Withdrawing group is attached to benzene ring,

↓

So electron density withdraws from benzene ring to form positive charge at ortho position.

↓

Positive charge is shifted to Para position due to resonance stabilization effect.

↓

Positive again shifted to ortho position.

↓

Hence Positive charges are produced at ortho and Para position.

↓

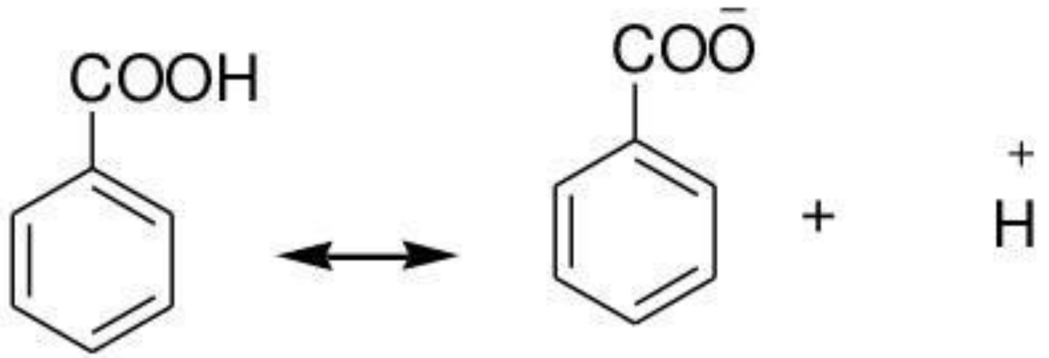
Benzene is become less reactive so elctrophiles not attracted due same charge repulsion

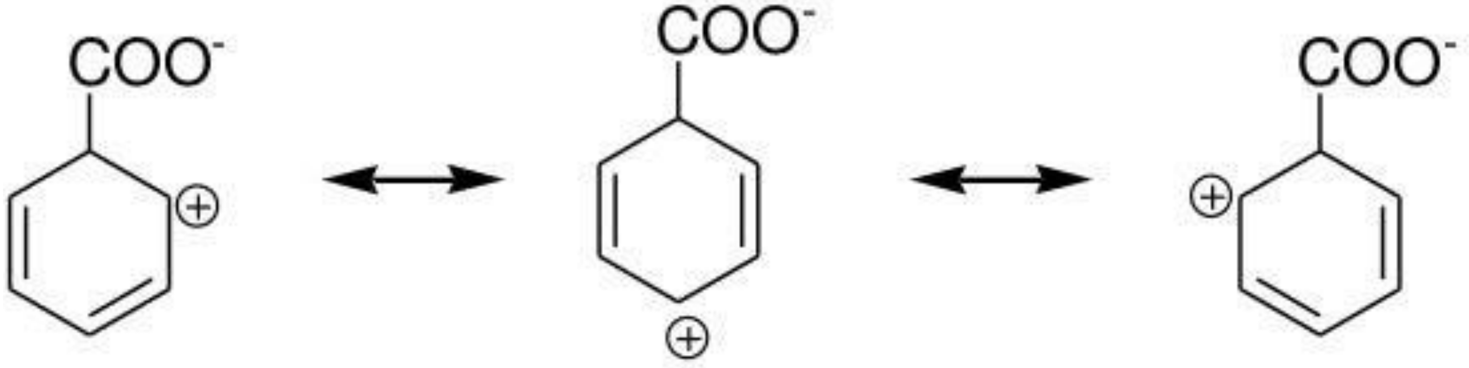
↓

electrophilic substitution reactions Not carried out at ortho and Para position.

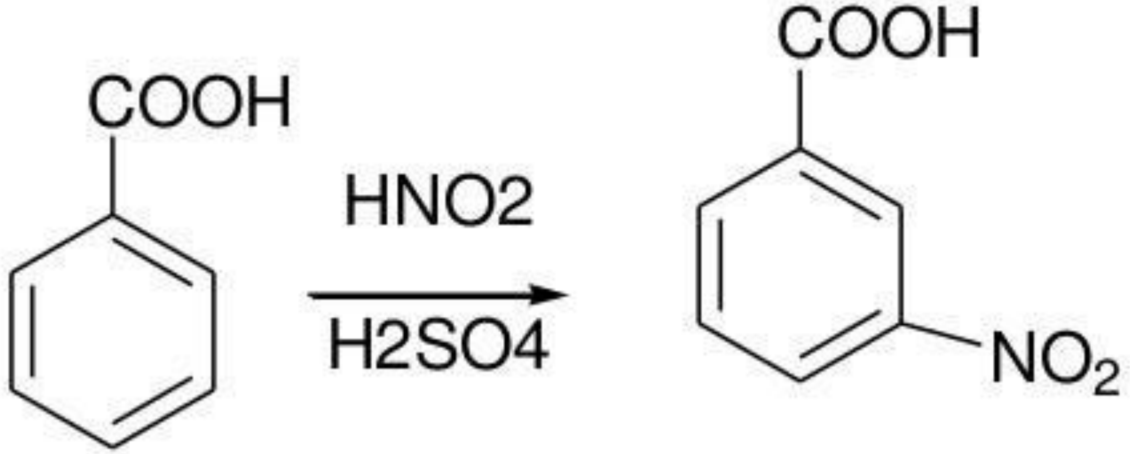
So negative charge arises at meta and electrophiles attracted to meta position proceed electrophilic substitution reaction.

m- directive effect- m-director





Reaction



3-nitrobenzoic acid

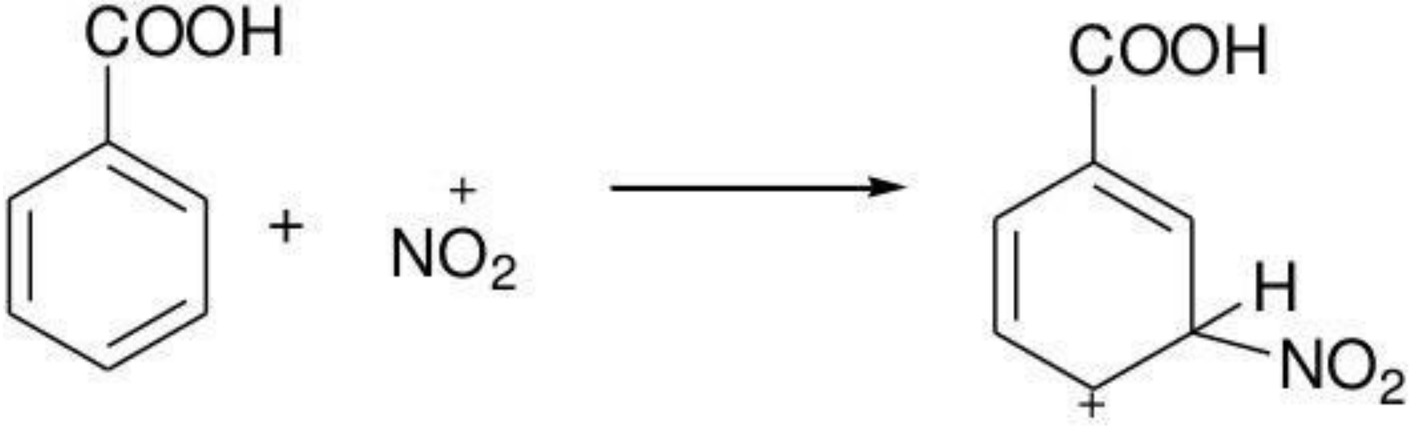
benzoic acid

Mechanism of m-directive effect

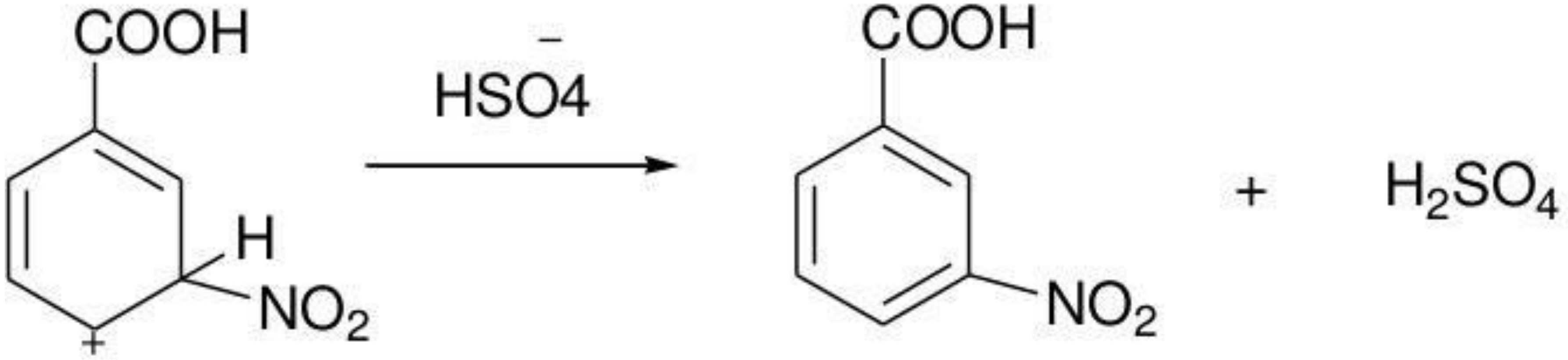
Step-I- Formation of Electrophile

$$HNO_3 + H_2SO_4 \longrightarrow \overset{+}{N}O_2 + H_2O + HS\overset{-}{O}_4$$

Step-II- Formation of arenium ion



Step-III- Deprotonation



Meta-Directing

Deactivator increase

-COR

$-CO_2R$

$-SO_3H$

-CHO

$-CO_2H$

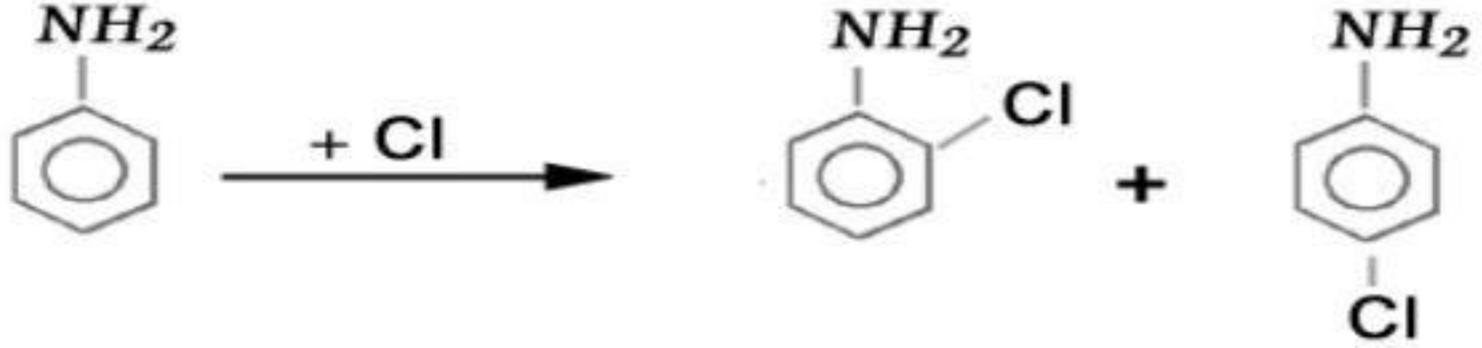
-CN

$-NO_2$

$-NR_2+$

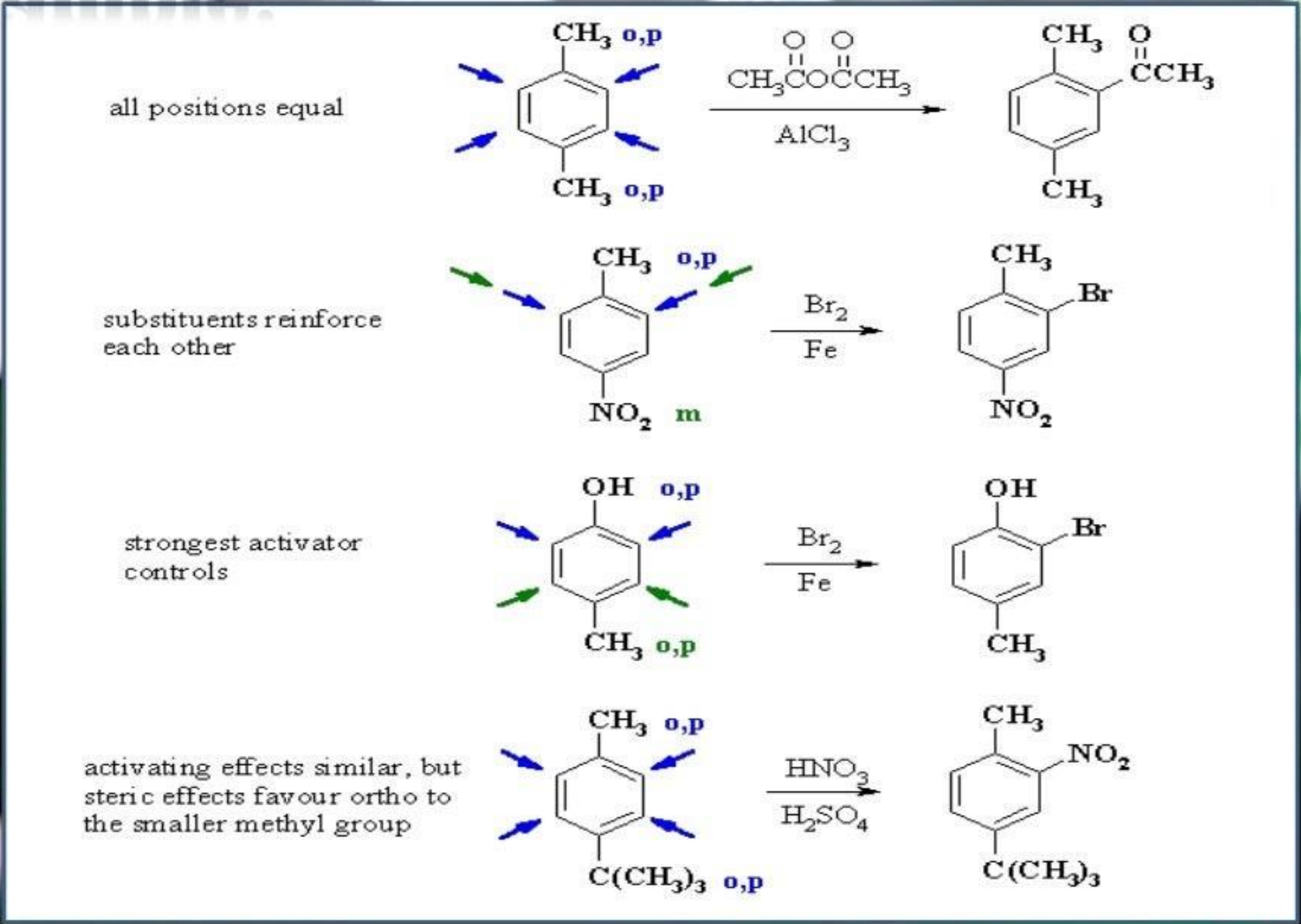
Electrophilic substitution of mono substituted benzene:

1. **Ortho- Para substitution**



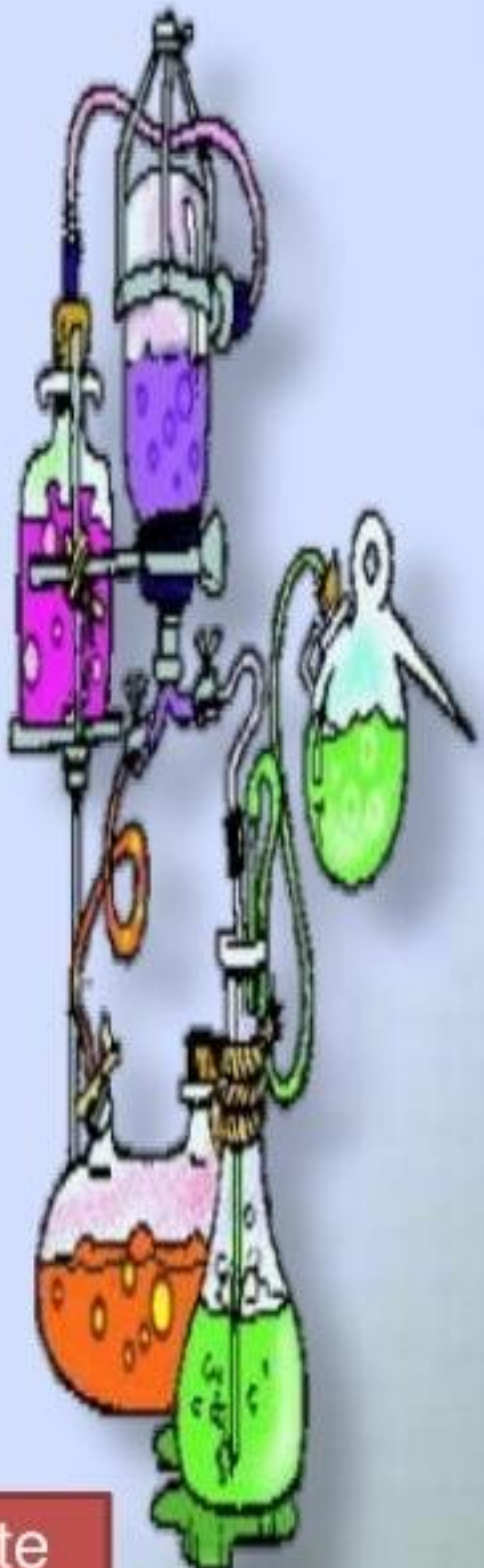
Electrophilic substitution of mono substituted benzene:

1. Ortho- Para substitution



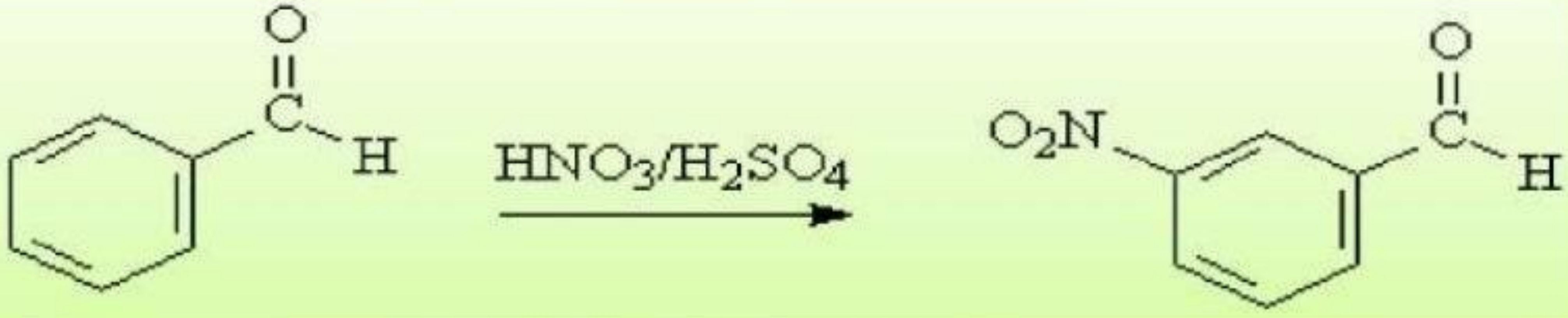
Electrophilic substitution of mono substituted benzene:

2. Meta substitution



SOME EXAMPLES OF "META DIRECTORS“

- the acyl group in benzaldehyde



- the NO$_2$ group in nitrobenzene

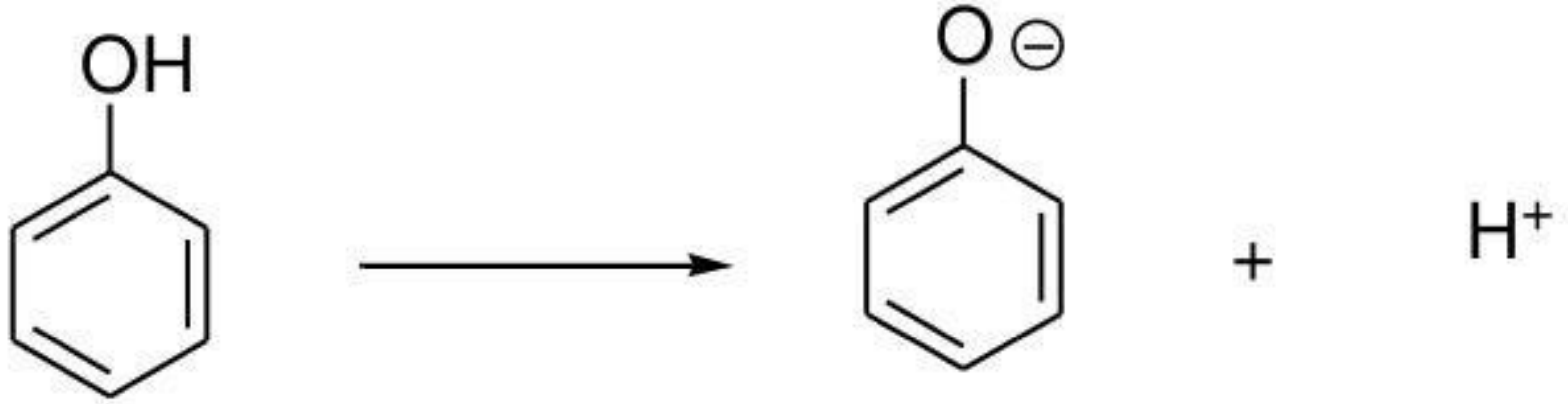
acyl , -CN , -SO$_3$H , CF$_3$, and -NO$_2$ are meta directors and deactivate the ring toward electrophilic aromatic substitution.

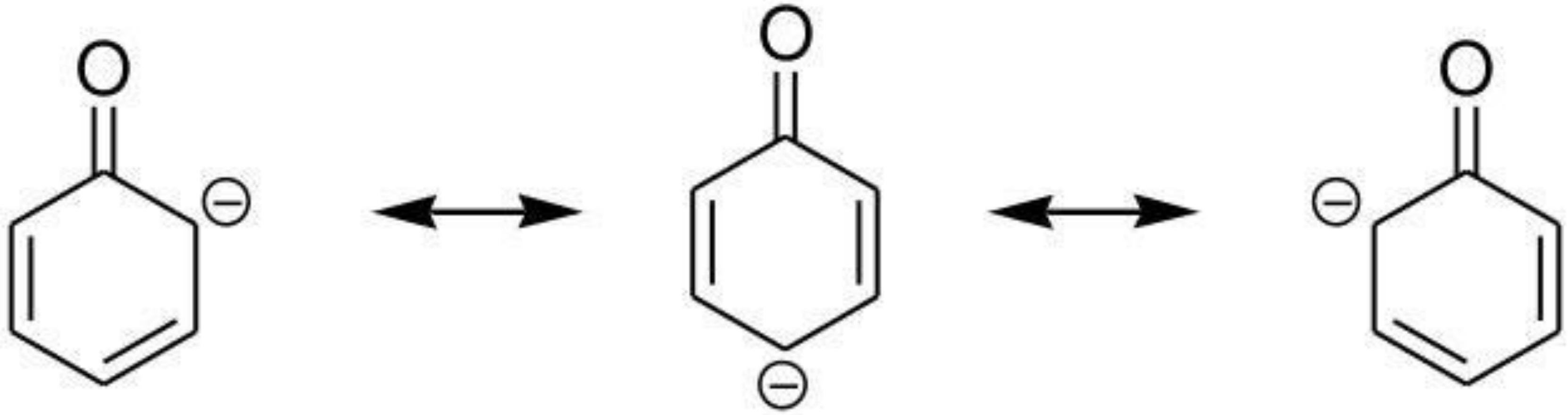
Effect of substituent's on Orientation of benzene

1. Electron donating group attaches to benzene benzene, it adds electron density to benzene to create negative charge at ortho position

↓

Due resonance stabilization it will shifted to para and again ortho position. Hence it acquires **ortho-para orientation**



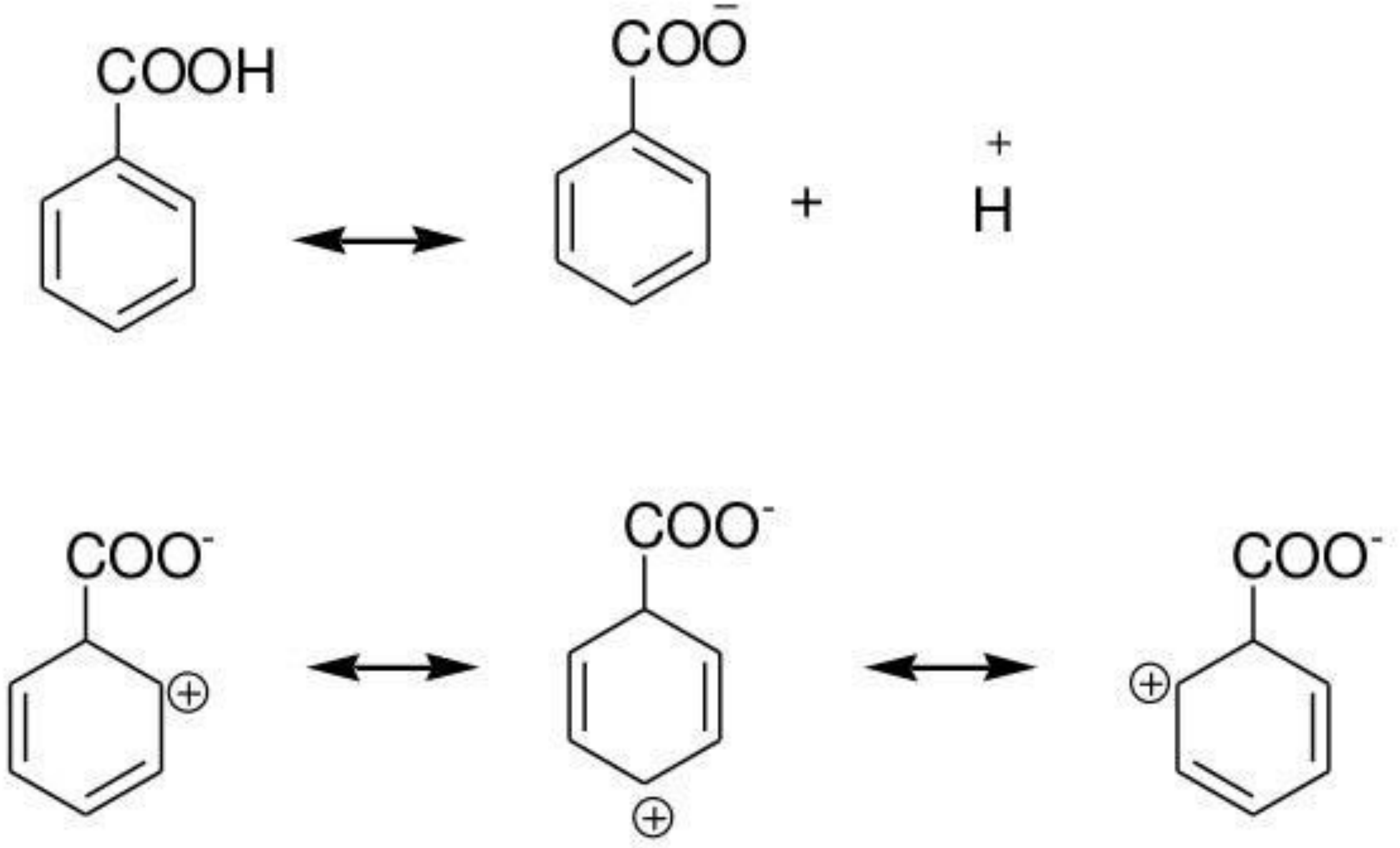


Effect of substituent's on Orientation of benzene

2. Electron Withdrawing group attaches to benzene, it withdraws electron density from benzene to create positive charge at ortho position

↓

Due resonance stabilization positive charge will shifted to para and again ortho position. Hence electrophile directly attracted to meta site, hence it will create **meta orientation**

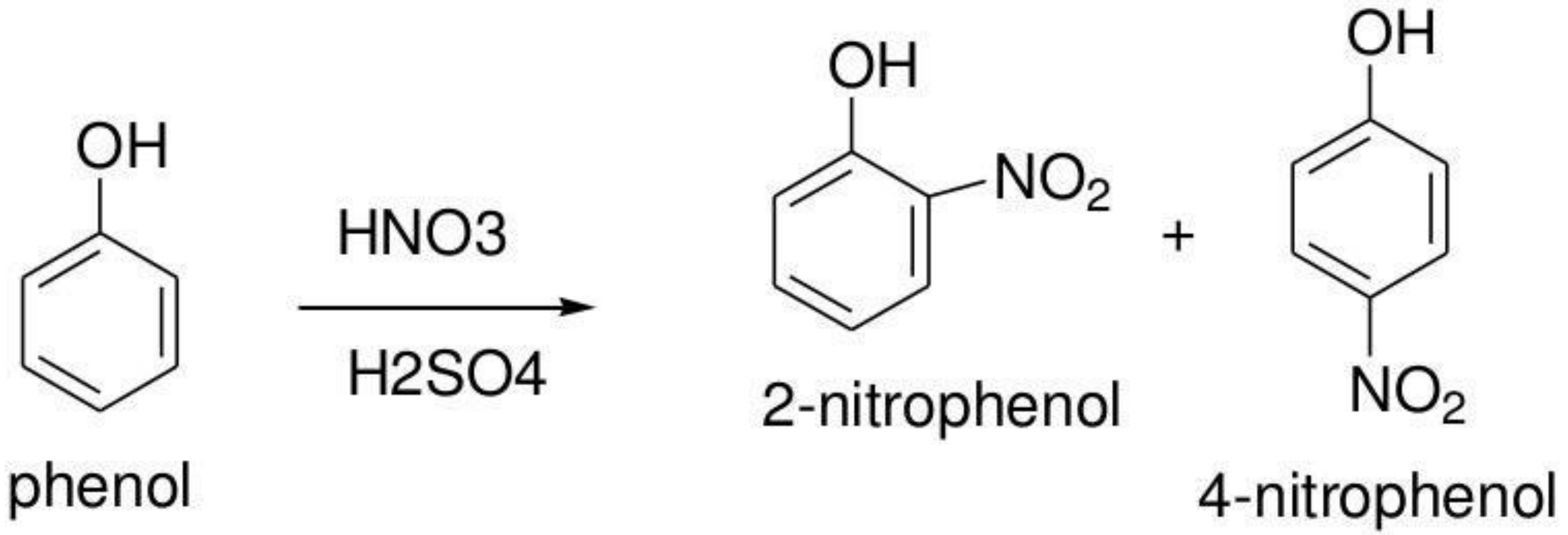


Effect of substituent's on reactivity of benzene

1. Electron donating group increases reactivity of benzene due negative charges are produced at ortho and Para position.

So electrophiles are easily attracted because opposite charge attraction.

Hence electrophilic reaction occurs fast at ortho and Para position



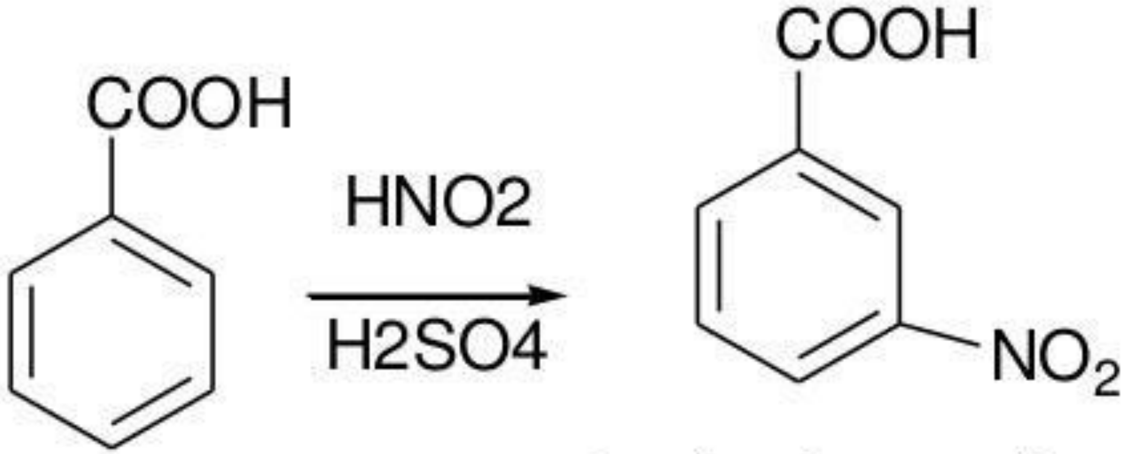
Effect of substituent's on reactivity of benzene

2. Electron Withdrawing group decreases reactivity of benzene due Positive charges are produced at ortho and Para position.

So electrophiles are easily not attracted because same charge repulsion.

Hence electrophilic reaction does not occurs fast at ortho and Para position.

Hence it directs to meta site and it requires ionizing reagent to faster reaction

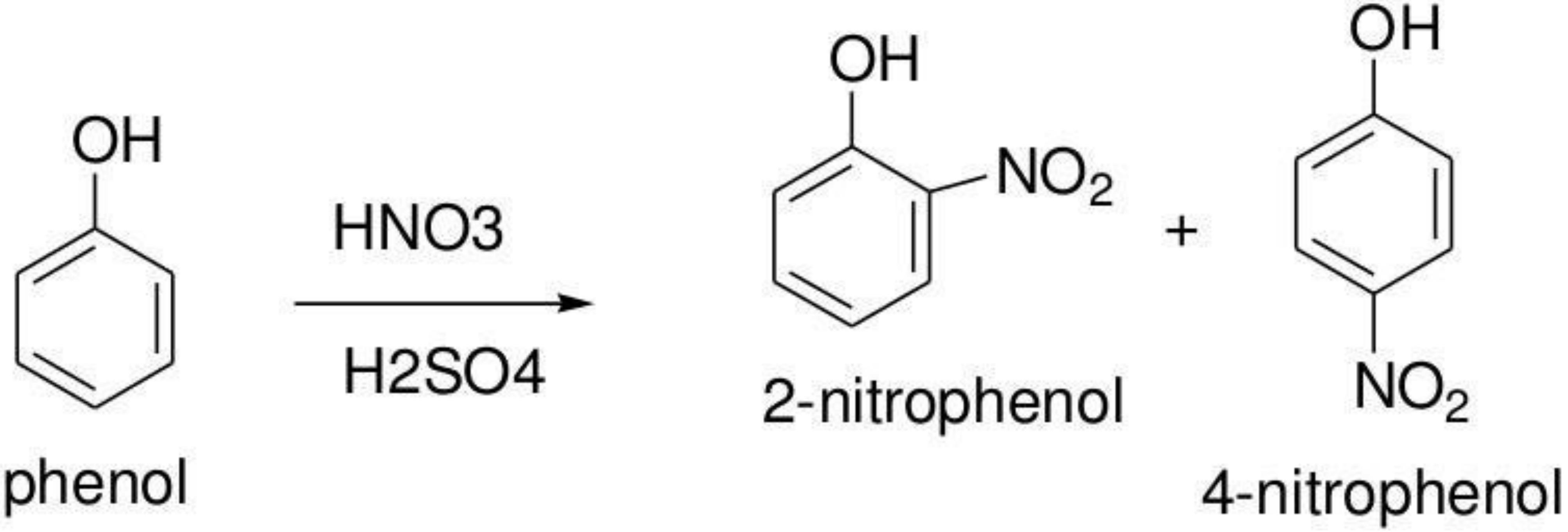


benzoic acid

3-nitrobenzoic acid

Reactions of mono substituted benzene

reaction



phenol

2-nitrophenol

4-nitrophenol

Reactions of mono substituted benzene

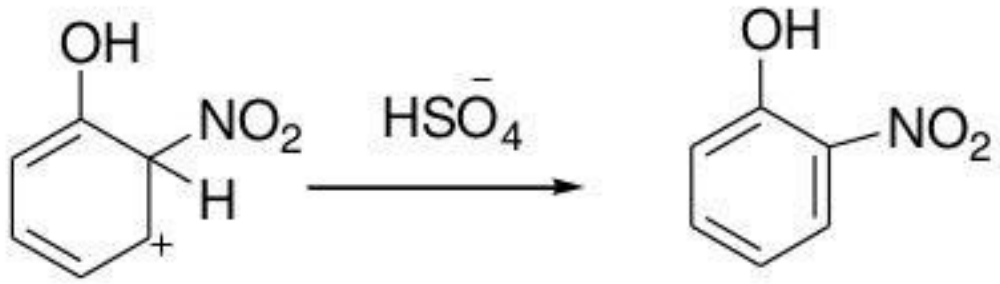
Mechanism

Step-I- Formation of Electrophile

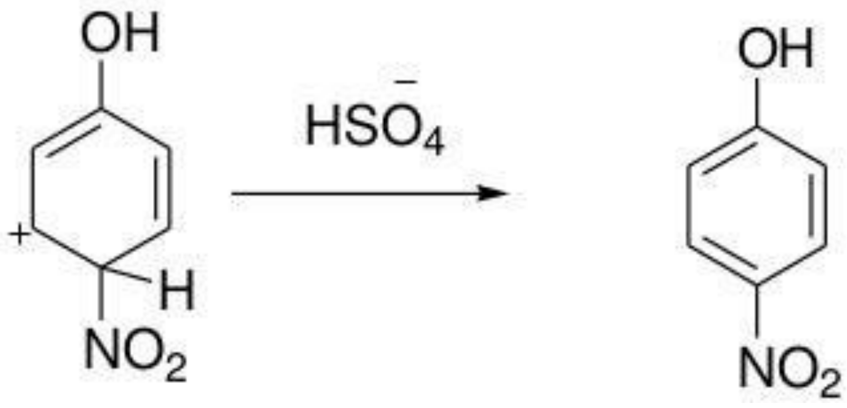
$$2\ HNO_3 + 2\ H_2SO_4 \longrightarrow 2\ \overset{+}{N}O_2 + 2\ H_2O + 2\ HS\overset{-}{O}_4$$

Step-II- Formation of arenium ion

Step-III- Loss of proton to produce stable compound

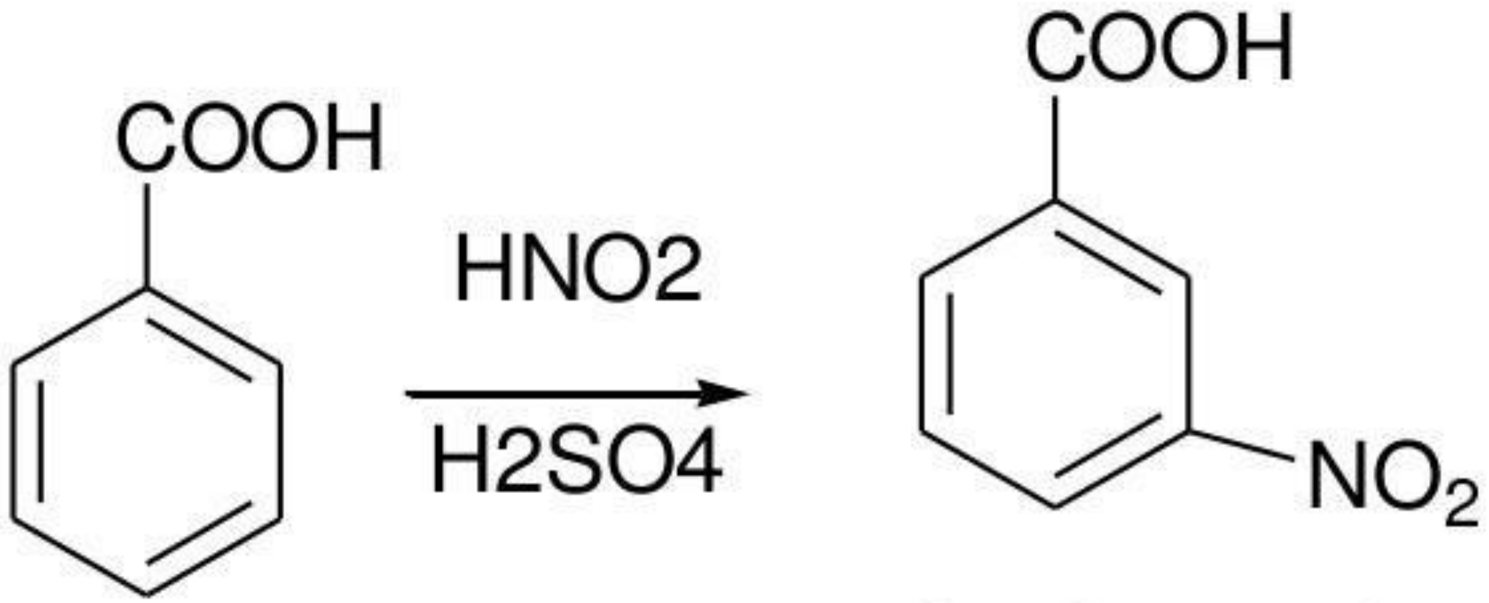


2-nitrophenol



Reactions of mono substituted benzene

reaction



benzoic acid

3-nitrobenzoic acid

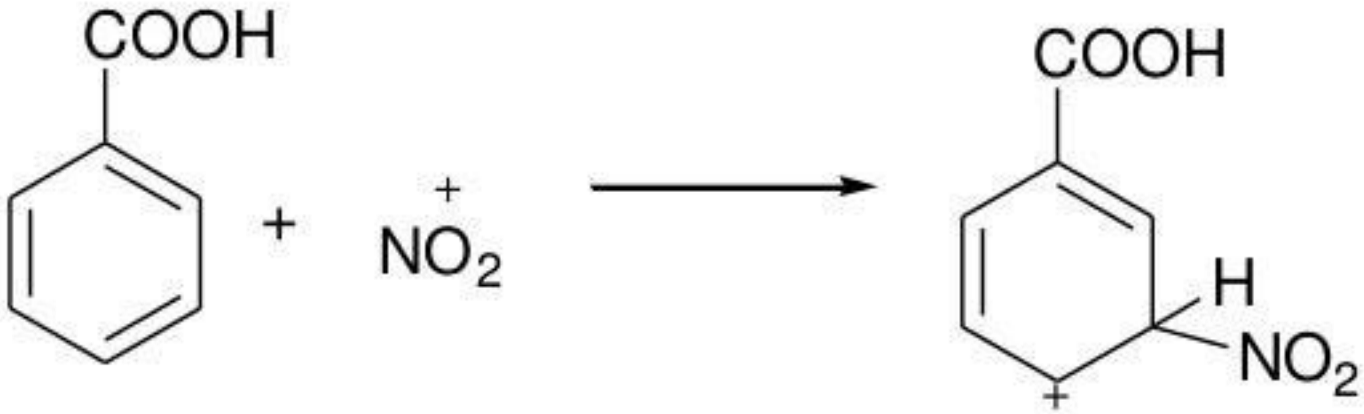
Reactions of mono substituted benzene

Mechanism

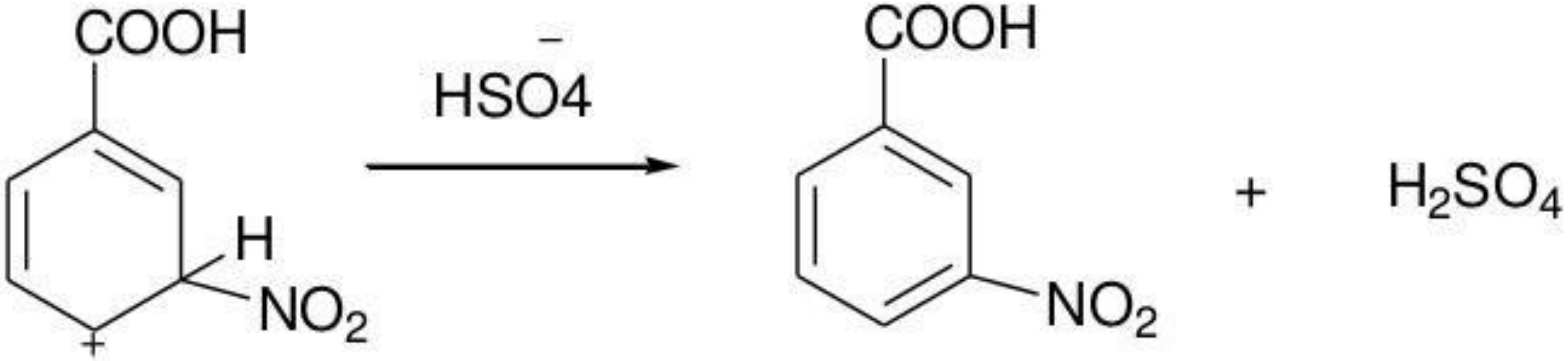
Step-I- Formation of Electrophile

$$HNO_3 + H_2SO_4 \longrightarrow \overset{+}{NO_2} + H_2O + \overset{-}{HSO_4}$$

Step-II- Formation of arenium ion

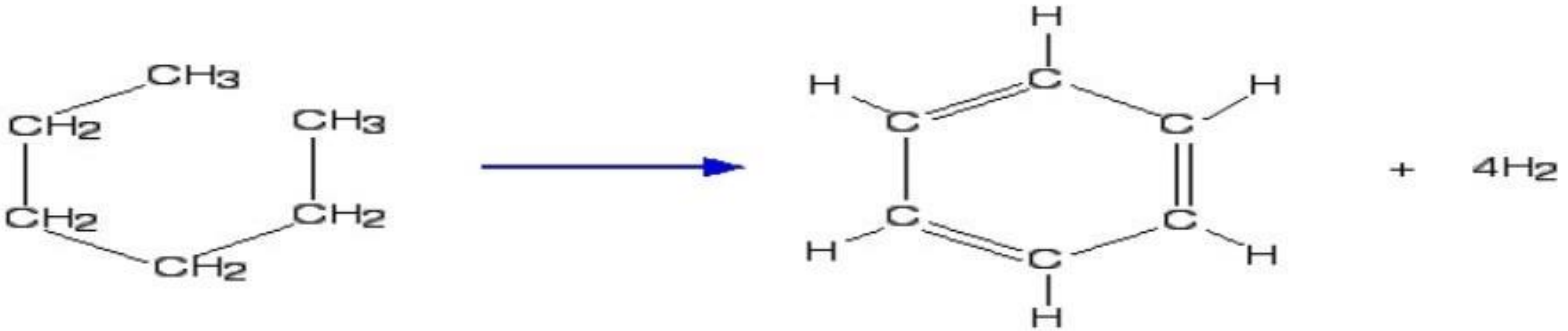


Step-III- Deprotonation



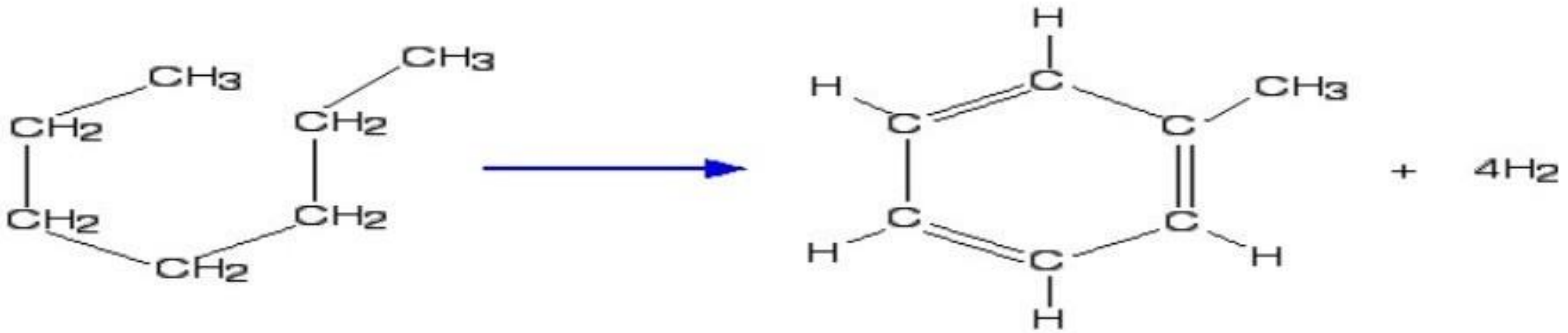
Method of Preparation of **BENZENE**:

Large scale preparation (From Petroleum):



hexane

benzene



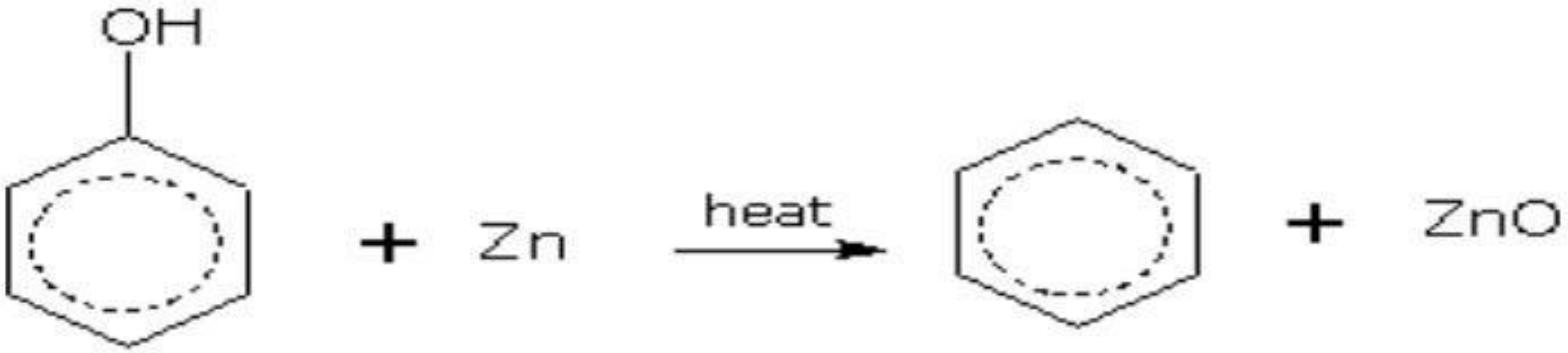
heptane

methylbenzene

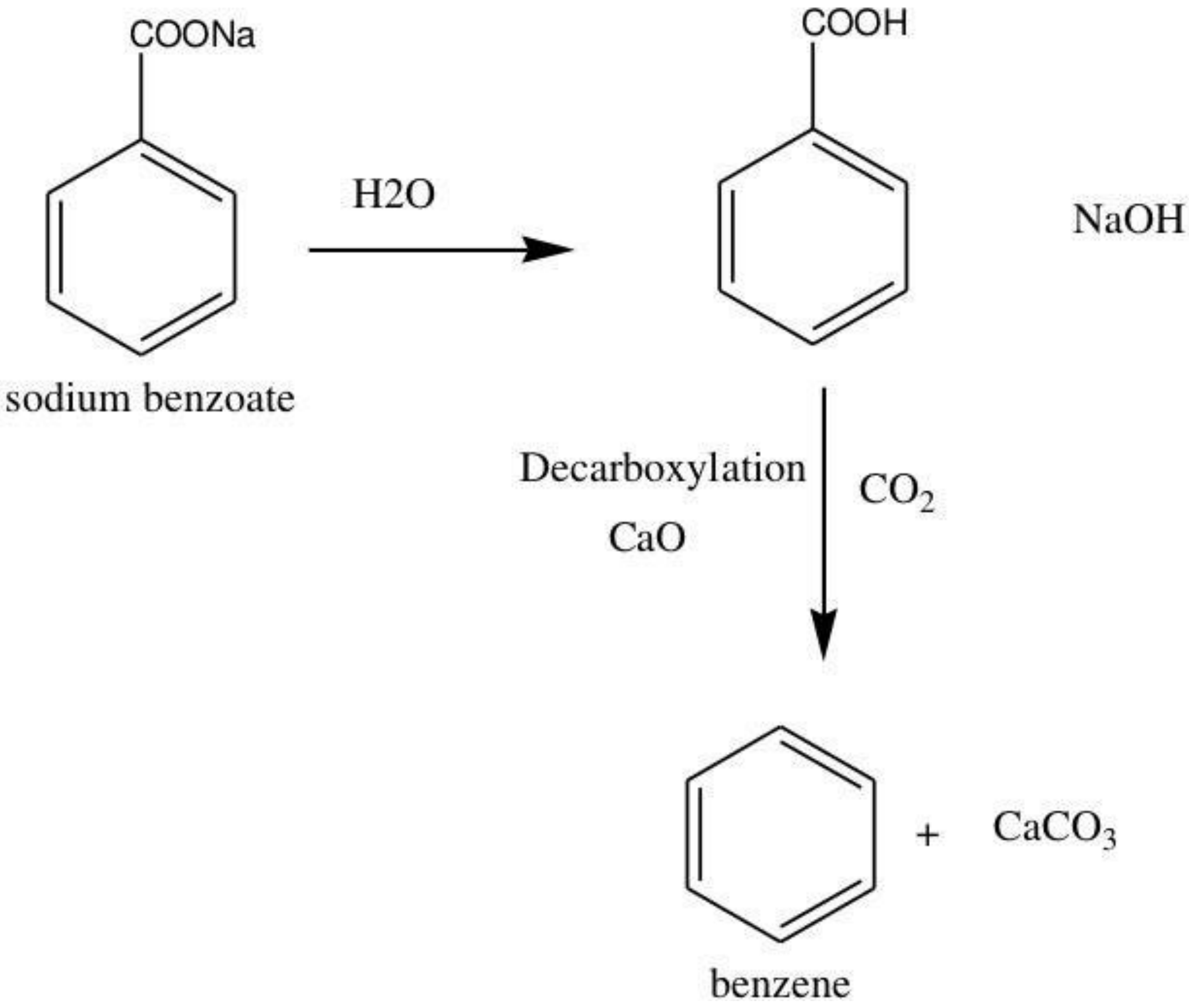
Small scale preparation:

- By passing Acetylene through red hot tube at 500°C

- By heating Phenol with Zincdust

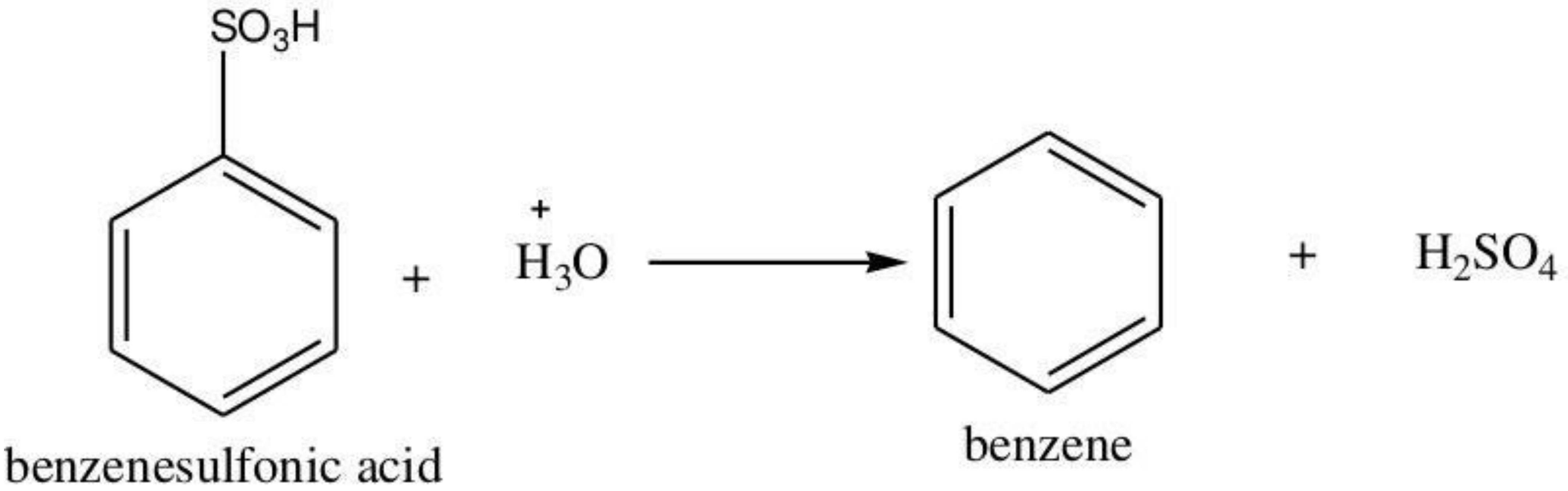


Synthesis of benzene from Sodium benzoate

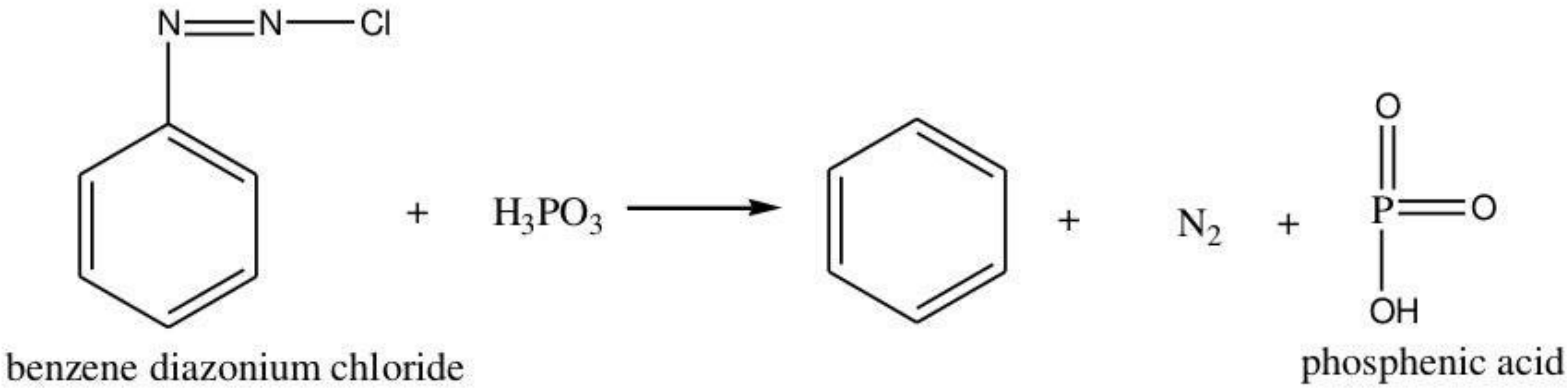


Synthesis of benzene

5. From benzene sulfonic acid

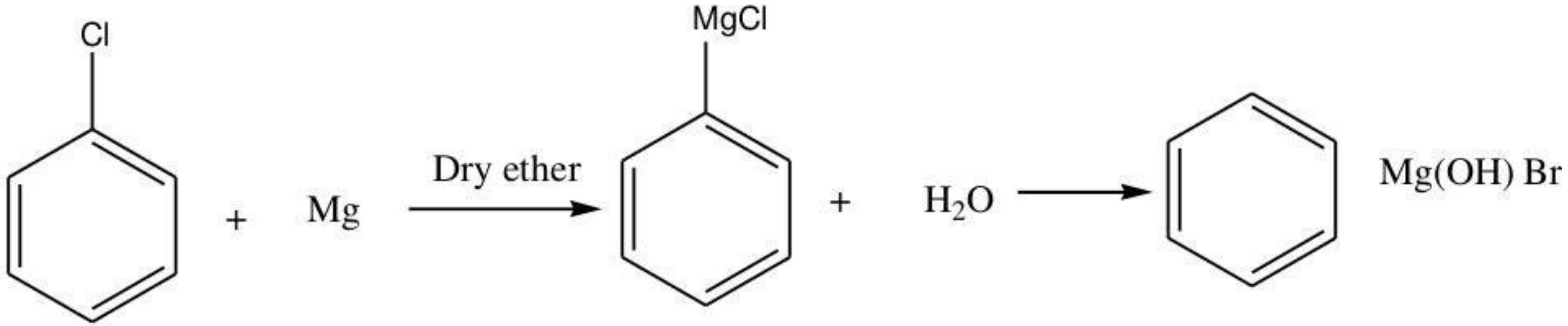


6. From benzene diazonium chloride



Synthesis of Benzene

7. From halo benzene with the help of Grignard reagent

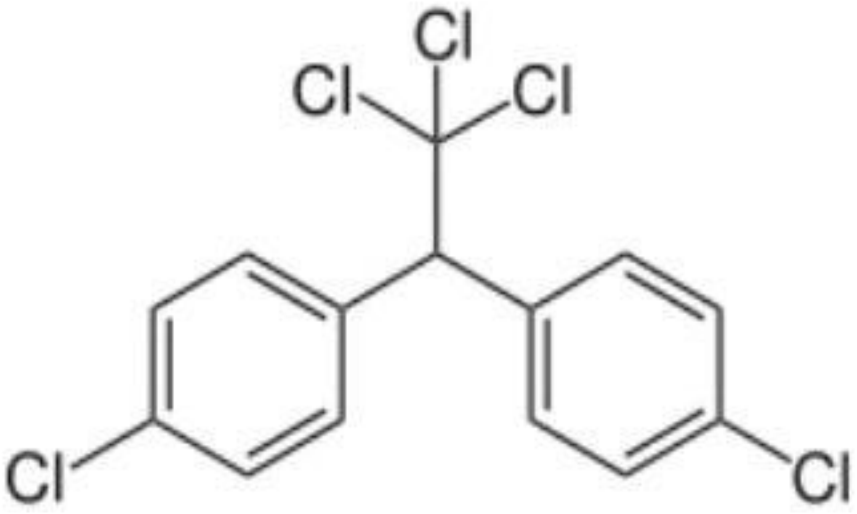


Uses Of benzene:

- Benzene is an important industrial solvent and precursor in the production of drugs, plastics, synthetic rubber, and dyes.
- It is a natural constituent of crude oil, and may be synthesized from other compounds present in petroleum.
- Benzene is widely used in the United States; it ranks in the top 20 chemicals for production volume.
- Some industries use benzene to make other chemicals which are used to make plastics, resins, and nylon and synthetic fibers.
- Benzene is also used to make some types of rubbers, lubricants, dyes, detergents, drugs, and pesticides.
- Natural sources of benzene include volcanoes and forest fires.
- Benzene is also a natural part of crude oil, gasoline, and cigarette smoke.

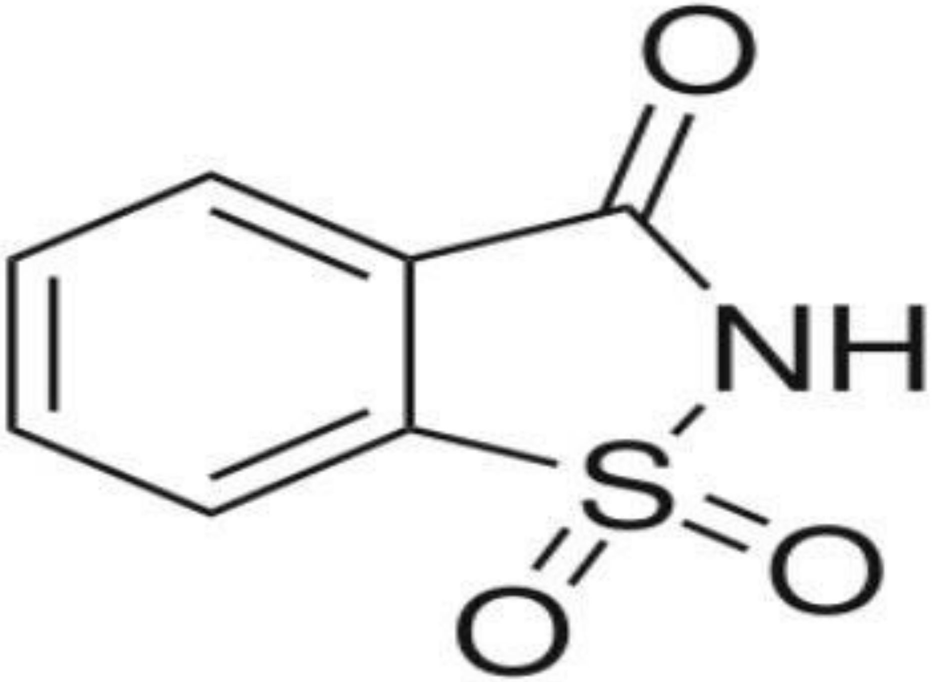
DDT (dichlorodiphenyltrichloroethane)

DDT is a synthetic chemical compound once used widely in the United States and throughout the world as a pesticide (a chemical substance used to kill weeds, insects, rodents, or other pests). It is probably best known for its dual nature: although remarkably effective in destroying certain living things that are harmful to plants and animals, it can also be extremely dangerous to humans and the environment.



Saccharin uses

Sodium **saccharin** (benzoic sulfimide) is an artificial sweetener with effectively no food energy that is about 300–400 times as sweet as sucrose but has a bitter or metallic after taste, especially at high concentrations. It is used to sweeten products such as drinks, candies, cookies, and medicines

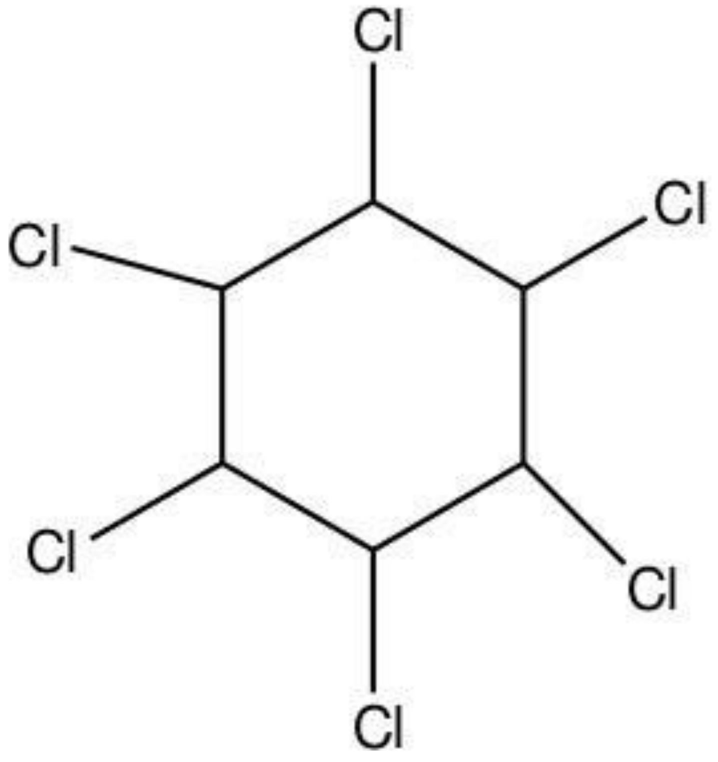


Uses of chloramines

1. **Drinking water disinfection**
2. **Swimming pool disinfection**
3. **Chloramines** can be **used** to improve odor and flavor of the water when **chlorine** is **used** as a disinfectant. **Chloramines** are also **used** for the disinfection of drinking water and waste water and to resist biofouling in cooling water systems.

Uses of benzene hexachloride (BHC),

Benzene hexachloride (BHC), any of several stereoisomers of 1,2,3,4,5,6-hexachlorocyclohexane formed by the light-induced addition of chlorine to benzene. One of these isomers is an insecticide called lindane, or Gammexane.



THANK YOU